The surface chemistry of metal oxide nanocrystals
from theory to applications

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Many people start their acknowledgements, not by acknowledging but by commenting on how the acknowledgement was written. I am no different. Sitting here in the far Switzerland — Yes, I already wrote this almost a year ago — I am thinking of all the clichés to avoid. However I realize, clichés are not that bad. Off we go.

It is conventional to follow up the first paragraph with thanking your promoter. For this thesis, it is a bit of a tedious affair since I have a tendency to collect these illustrious beings. First, I started my master thesis under the tutelage of Isabel Van Driessche. Isabel, you are my guiding light, always ready to support me, to share laughter, succes or setback. I cherish not only our scientific but also our personal conversations. Therefore, I daresay, if Chemistry had a mother, it would be you. Alas, however amazing you are, at the end of my masterthesis, we had to admit that the combined intelligence of all the SCriPTS members was nothing compared to the mind of Zeger Hens and we made the strategic decision of forging an alliance with this nanocrystal god. Zeger, I learned a great deal from you, paper writing amongst others. I could also enter your office in total chaos and leave it with a structured head. But what is even more impressive, you don’t show the slightest hint of arrogance and you manage to keep mens sana in corpore sano. Finally, and this has been described by certain people as the best career move I ever made; I embraced NMR and concomittantly captured José Martins as my last promotor. José, thank you for letting the most clumsy chemist play with your super-expensive NMR machines called Hercules and Nestor. I appreciate your encouragement and guidance and yes, the Claridge is my new bible. To my three tutors, I apologize for bursting into your office with the next crazy idea which in the end didn’t
work or was miscalculated. I also apologize for the obvious millions that we missed since we could not patent the esterification due to my enthusiastic abstract writing. I realize these acknowledgements are becoming amends so let’s change direction. I want to thank all the jury members for their constructive comments. Especially prof. Willem provided an exhaustive, 27–pages report which greatly improved this book.

Before I thank my colleagues, I must start by praising the technical staff. Without their help, there would be no chemicals, conferences, exchange visits, reimbursements or organization whatsoever. Bart often produced custom–made tools for the lab and Pierre is simply invaluable in his organizational skills. The list of people that keep the department going is long and here I would like to express my gratitude to them all.

I want to thank all my colleagues throughout the years and initially I tried to put every relevant name in here. However, I soon realized that I was bound to fail and many people would not see their names, contrary to expectations. This would have created the next social drama. As I have created already enough of those, I shall try a different strategy. I want to thank all present and previous colleagues of SCriPTS — don’t ask me what it stands for, but if you do, my answer would be it is time to change that name. A special thanks needs to go to Katrien De Keukeleere (mind how I spelled that name correctly as this woman is a VIP) since we are such close friends and managed to work on the same subject without any major disturbance in our relationship. We shared laughter, we sniffed each other, we dance together and we help each other to perform better scientifically. Basically, we are the perfect couple — or so it is whispered throughout the halls of the S3 sanctuary... I would like to thank Jonas and Mieke for putting up with me in their office and for occasional good advice such as “use a towel to dry your hair”. Hannes is thanked for joining and reinforcing our YBCO team, Jonathan Watté for always ordering our chemicals and Matthias for relieving me of the chore ‘rubbish’. I would also like to express my gratitude to my thesis slaves/students: Sofie, Sebastiaan, Evert and Olivier. Sofie even earns a special sentence since she basically provided me with an extra chapter for this book. Thank you very much Sofie!

Collecting promoters, I also infiltrated other research groups. I am grateful to the PCN group (present and previous colleagues) for the interesting discussions and also the various social events. Especially Yolanda con-
tribute directly to this thesis so a special thanks is justified. Also Emile has to be thanked since he grants me more attention than his girlfriend. Séraphine, thank you very much! Kim, thanks for the NMR discussions! Jorick, Willem, Mickaël and Dorian, you are all very nice to work with and I enjoyed our collaborations very much. The last (UGent) research group that I need to thank is NMRSTR (previous and present colleagues). Freya, I should thank you on my bare knees since your encouraged me to learn NMR and also actually taught me NMR. Furthermore, you contributed directly to several chapters in this book. Dieter, Niels and Tim helped me out more than once when the machine was misbehaving. Davy, your intellectual input was also invaluable and you spent quite some time educating me, thank you!

Finally, I am grateful to many people in both S3 and S4. The first one that springs to mind is Els De Canck from COMOC and this train of thought leads me to the interesting conversations with prof. Van Der Voort. Sophie Lingier is also a dear friend and colleague. I am not going to list everybody that I like in both departments since this list is too long (and automatically puts people in the “don’t like” category, which is not my intention). However, I am compelled to thank Quantum Sofie because she always smiles so nicely (and was one of the few women that managed to confuse me when I was a student). Jan Goeman is greatly thanked for GC analysis and I am grateful to Prof. De Smedt for being able to use the zetasizer and Bart Lukas for training. But now we have our own zetasizer which is amazing, thank you Zeger and Isabel!

I would also want to thank my advisors, colleagues and friends abroad, both in Zürich and in Barcelona and Germany. Special thanks goes to Pablo who supported Katrien and me and is a very open and trustworthy person. There are also many people I liked in Zürich but beyond any doubt, Maria made the biggest impression on me. She is an intelligent, hard-working, funny and independent women that broadened my view on the scientific community. We too, would be a great couple! I could say the same of Nick but he would probably be scandalized. Nevertheless, Nick represents many qualities that I can only describe as good and true. I must not forget the Niederberger group and to thank Alessandro for his trust and belief in me. I hope we will collaborate further for quite some time. Finally, I am very happy about the collaboration with BASF and Deutsche Nanoschicht and
I would like to thank Michael, Thorsten and Max for putting their faith in Isabel and our research group.

A warm thank you to my good and diligent students from first bachelor to turn me away from my research, it is always a joy to teach enthusiastic people. What about the other, uninterested fraction of students? I simply scared the hell out them and never saw them again.

Then I wanted to thank some friends since there can be no work without a break. I would have liked to start with my chemistry friends by saying they are more than colleagues but than I know several people from the above list that will be grievously offended (and rightly so). Anyway, Debbie, Wannes, Mys, Sophie, Queen Isabelle, Pieter, Pelson, you guys were there when it was needed. Especially I need to thank Wannes and Sam for supporting me when times were difficult. Hurray to the cocktail parties with Heleen and Birgit. And get me that wedding party! Kevin and Jelle, do something and you will earn my gratitude. Although we don’t see each other often, I have not forgotten my old friends from high school. New friends that I made which will most likely stick: Stijn, Laurens, Miek, Sofie, Kirian, Tess and Pieter. Thank you for the skiing holiday of my life and everything after that. Thomas, Inse and Tim, you are special ones so let’s keep our special friendship! Finally, my FWO colleagues from ESOF with whom I had a wonderful time in Kopenhagen and especially Sofie and Harry, I consider now dearest friends.

Thanks to my family, both close and further, in particular Tantann, Boske, Elisa — my lovely sister who is also a bit of a teenager so she will probably hate this comment, which is exactly why I include it — and Joachim. Meetje, bedankt voor het lekkere eten dat je telkens hebt gekookt voor mij en de vele babbels! And even if we are not really bound by law, I would also like to thank my — hopefully — future family in law, who have made me feel more welcome than I could have hoped. Moreover, Lisette and Koen were essential in creating the cover of this book.

In particular, I would like to thank my parents for supporting me since I was born, through all the stages of my life and university studies, for letting me go on Erasmus and for all the effort they put in me. They are very hard workers and taught me to work just as hard. “Mama’s moeten veel doen voor de kindjes”, dixit 6 year old Jonathan. Although I will never again
admit this, I am growing to resemble my parents and I will probably die with the looks of my father and the personality of my mother.

Just like in the authorship of papers, the most important places are the first and the last. Maarten, you probably expected here a long and emotional paragraph but since I already feel emotional writing this first sentence, I will limit myself. Thank you for your support in everything that comes to mind. Let’s tackle every future challenge together! Ik zie je graag.

Gent, maart 2016
Jonathan De Roo
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<tr>
<td>Am</td>
<td>Octylamine</td>
</tr>
<tr>
<td>APC</td>
<td>Artificial Pinning Center</td>
</tr>
<tr>
<td>BnOH</td>
<td>Benzyl alcohol</td>
</tr>
<tr>
<td>BnOBn</td>
<td>Dibenzyl ether</td>
</tr>
<tr>
<td>CBC</td>
<td>Covalent Bond Classification</td>
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<tr>
<td>CSD</td>
<td>Chemical Solution Deposition</td>
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<tr>
<td>DDAc</td>
<td>Dodecanoic Acid</td>
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<tr>
<td>DOSY</td>
<td>Diffusion Ordered Spectroscopy</td>
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<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>EDXRF</td>
<td>Energy Dispersed X-ray Fluorescence</td>
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<tr>
<td>FID</td>
<td>Free Induction Decay</td>
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<tr>
<td>FT–IR</td>
<td>Fourier Transform – Infrared</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>GC–MS</td>
<td>Gas Chromatography – Mass Spectrometry</td>
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<tr>
<td>GC–FID</td>
<td>Gas Chromatography – Flame Ionization Detection</td>
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<tr>
<td>Gly</td>
<td>Glycine</td>
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<tr>
<td>Gln</td>
<td>Glutamine</td>
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<tr>
<td>HAADF–STEM</td>
<td>High Angle Annular Dark Field – Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HATR</td>
<td>Horizontal Attenuated Total Reflectance</td>
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<tr>
<td>HOAc</td>
<td>Oleic acid</td>
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<tr>
<td>HMBC</td>
<td>Heteronuclear Multiple Bond Correlation</td>
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<td>HRMAS</td>
<td>High Resolution Magic Angle Spinning</td>
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<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
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<tr>
<td>HSQC</td>
<td>Heteronuclear Single Quantum Coherence</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>HTS</td>
<td>High Temperature Superconductors</td>
</tr>
<tr>
<td>ITC</td>
<td>Isothermal Titration Calorimetry</td>
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<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>LAO</td>
<td>LaAlO$_3$</td>
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<td>LTS</td>
<td>Low Temperature Superconductors</td>
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<tr>
<td>MONC</td>
<td>Metal Oxide Nanocrystal</td>
</tr>
<tr>
<td>Met</td>
<td>Methionine</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystal</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>NOESY</td>
<td>Nuclear Overhauser Effect Spectroscopy</td>
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<tr>
<td>OAm</td>
<td>Oleylamine</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>ODE</td>
<td>Octadecene</td>
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<td>RE</td>
<td>Rare Earth</td>
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<td>T</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>TFA</td>
<td>Trifluoroacetic acid</td>
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<tr>
<td>TFSA</td>
<td>Trifluorosulphuric acid</td>
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<tr>
<td>TGA</td>
<td>ThermoGravimetric Analysis</td>
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<td>Thr</td>
<td>Threonine</td>
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<td>TOCSY</td>
<td>Total Correlation Spectroscopy</td>
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<td>TTS</td>
<td>Transition State</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>Y</td>
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<tr>
<td>YBCO</td>
<td>YBa$_2$Cu$<em>3$O$</em>{7-\delta}$</td>
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<td>Z</td>
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<tr>
<td>ZQ</td>
<td>Zero Quantum</td>
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Nederlandse samenvatting
–Summary in Dutch–

Vraagt u zich soms af hoe we in duurzame energie zullen voorzien voor 9 miljard mensen in 2050? Ik wel. Er zijn verschillende oplossingen voor dit probleem en supergeleiding is daar één van. Supergeleiders geleiden electriciteit zonder weerstand te bieden aan de stroom en hun superieure eigenschappen laten toe om innovatieve applicaties te ontwikkelen die ofwel energie besparen of energie opwekken. Deze doctoraatsthesis had als oorspronkelijk doel om de transporteigenschappen van de supergeleider YBa$_2$Cu$_3$O$_{7-d}$ (YBCO) te verbeteren door de inclusie van metaal oxide nanokristallen in het keramische materiaal. Dit onderzoek is echter geëvolueerd naar een fundamentele studie over het oppervlak van metaal oxide nanokristallen, wat aanleiding gegeven heeft tot diepgaande inzichten en finaal, doorbraken in zowel supergeleiding als katalyse. De hier ontwikkelde concepten betreffen voornamelijk oppervlaktechemie en vormen een brug tussen de synthese van nanomaterialen en hun toepassingen, een aspect dat in de internationale literatuur vaak ontbreekt.

Ons onderzoek begint met een gepubliceerde synthese van HfO$_2$ nanokristallen, uitgaande van HfCl$_4$ en benzyl alcohol. Het solvothermale (autoclave) proces van Buha et al. is reproduceerbaar maar de auteurs leverden geen bewijs voor het veronderstelde benzyl chloride eliminatie mechanisme. Integendeel, met behulp van gas chromatografie gekoppeld met massa spectrometrie en nucleaire magnetische resonantie (NMR) metingen hebben wij duidelijk de vorming van dibenzyl ether kunnen aantonen. Dit wijst niet alleen op een ether eliminatie als oxide vormingsmechanisme maar ook dat HCl — wat vrijkomt bij de liganduitwisseling van hafnium chloride met benzyl alcohol — de Williamson ether synthese katalyseert. De nanokristallen zijn licht anisotroop, iets wat werd opgemerkt via transmissie elektronen
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microscopie en de variërende piekbreedte van de verschillende reflecties in het X-stralen diffractogram. Interessant genoeg gaat de reactie veel sneller door met microgolfverwarming, vergeleken met conventionele verwarming. Hoewel de microgolfsynthese meer monodisperse en kleinere deeltjes oplevert, behouden de nanokristallen voor de rest hun vorm en monokline kristalstructuur. Aggregaten van de nanokristallen zijn ladingsgestabiliseerd in water en het iso-elektrisch punt werd bepaald op pH = 8. Om de nanokristallen te de-aggregeren, is een post-synthetische oppervlaktemodificatie nodig met dodecaanzuur en oleylamine.

Ten tweede ontrafelen we de oppervlaktemodificatie van HfO$_2$ en ZrO$_2$ nanokristallen. Initieel hebben de nanokristallen een positieve zetapotentiaal in ethanol en X-straal fluorescentie metingen tonen ook chloride aan, het anion dat de positive lading van het proton compenseert. Wanneer de nanokristallen neergeslagen en terug gedispergeerd worden in chloroform, is een carbonzuur onvoldoende om de waterstof chloride van het oppervlak te verdrijven, tenzij ook oleylamine toegevoegd wordt. Hoewel onverwacht op het eerste zicht is het oleylamine slechts zwak gebonden aan het oppervlak en kan het verwijderd worden met een eenvoudige opzuiveringsprocedure, samen met resten van chloride. Uiteindelijk is er dan een zuiver oppervlak met enkel het carbonzuur en een ligand densiteit van ongeveer 3 liganden per vierkante nanometer oppervlak. Dergelijke carbonzuren vertonen hetzelfde dynamische gedrag als metal chalcogeniden, gestabiliseerd met carboxylaten. Echter, via een titratie met gedeutereerd oliezuur, hebben we aangetoond dat de negatieve lading van het carboxylaat anion niet gebalanceerd wordt door een overmaat metaalkationen maar door protonen die geadsorbeerd zijn op de zuurstofatomen aan het oppervlak van het nanokristal. Carbonzuren kunnen dus dissociëren op het oppervlak van metaaloxide nanokristallen (zie Figuur 1) en dit is een cruciaal verschil met de andere chalcogeniden. Verder vervult oleylamine niet de rol van surfactant maar eerder die van base. Oleylamine reageert met waterstof chloride en laat zo een lege adsorptieplek achter waarop het carbonzuur kan dissociëren. Dit wordt bevestigd aangezien ook andere basen zoals triethylamine kunnen gebruikt worden.

De interessante verschillen tussen de andere chalcogeniden en de oxide nanokristallen blijken een invloed te hebben op de uitwisselingseigenschappen van het carboxylaat anion. Inderdaad, octylamine, een L-type ligand, stelt

oliezuur vrij van HfO$_2$ nanokristallen (zie Figuur 2) terwijl cadmium oleaat wordt verwijderd van CdSe nanokristallen. De uitwisselingsreactie is exotherm — en dus gehinderd door hoge temperatuur — door de vorming van een zuur/base paar in het geval van oxide nanokristallen of een metaal complex in het geval van CdSe nanokristallen. Een dergelijke waarneming is interessant aangezien dit betekent dat de ligand binding gedurende een nanokristal synthese compleet anders zal zijn dan de ligand binding gedurende de opwerking bij kamertemperatuur. Bijkomend bewijs voor de vorming van het ionenpaar wordt gegeven door het infrarood spectrum en door het feit dat de evenwichtsconstante van de uitwisselingsreactie alleen constant is bij verschillende amine concentraties als er rekening wordt gehouden met de ionenpaar vorming. Tenslotte vertoont oliezuur ook autoadsorptie aan het oxide oppervlak en niet aan het CdSe oppervlak (zie Figuur 2). We redeneren dat dit bijzondere verschijnsel te wijten is aan de dissociatieve adsorptie van de carbonzuren. Het nanokristal oppervlak heeft dus een even grote hoeveelheid anionische als kationische X-type liganden, een bindingsmotief dat we de naam NC(X)$_2$ geven. Aangezien een X-type ligand omschreven wordt als een ligand dat in zijn neutrale vorm 1 elektron doneert aan de nanokristal–ligand binding, kunnen we zeggen dat inderdaad zowel kationen als anionen aan die beschrijving kunnen voldoen. Dit staat in constrast met de literatuur waar enkel anionische liganden als X-type worden beschouwd. Belangrijk hierbij is dat de waarneming van het NC(X)$_2$ type bindingsmotief een nieuwe klasse van nanokristallen naar voren schuift — stoichiometrisch met een ladingsneutrale combinatie van
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Figuur 2: A. L–type alkylamines zijn in staat om carbonzuren — NC(X)₂ — te verwijderen van het metaal oxide oppervlak. B. Auto–adsorptie van carbonzuren op het oppervlak van hafnium oxide nanokristallen.


De volgende stap is het gebruik van zwak coördinerende liganden, zoals amines of alcoholen, om sterk gebonden carbonzuur chemisch om te zetten naar niet coördinerende amides of esters. Daarmee wordt de carbonzuur/amine of carbonzuur/alcohol uitwisseling gestimuleerd. Aangezien de reactie kinetisch tegengehouden wordt bij kamertemperatuur maar wel doorgaat bij 130 °C, is dit systeem ook handig om de ligandschil te tunen. Een dergelijke gemengde ligandschil biedt voordelen zoals verbeterde oplosbaarheid in dichlorobenzeen. Verder wordt ook continue ester vorming geobserveerd wanneer de ligandschil vernieuwd wordt met carbonzuur. Aangezien de gebonden fractie niet verandert tijdens het proces en er ook geen ester gevormd wordt in de afwezigheid van nanokristallen, kunnen we dit een katalytisch proces noemen. We relateren de katalytische activiteit aan het dissociatieve NC(X)₂ bindingsmotief van de carbonzuren op hetoxide oppervlak want er wordt ook geen ester gevormd met CdSe nanokristallen. Het potentiële van deze deeltjes wordt verder onderbouwd door te tonen dat ook
transesterificatie doorgaat bij dezelfde temperatuur. Deze bevindingen to-
nen dat, naast een subtiële maar krachtige oppervlakte-ontwikkeling, deze
chemisch gedreven ligand uitwisseling ook het coloidale stabiliteit / kataly-
tische activiteit raadsel oplost. Liganden zijn normaal nodig om te zorgen
voor coloidale stabiliteit maar tevens belemmeren ze de toegang tot het
oppervlak. Door reagentia te gebruiken als ligand, kunnen we dit probleem
vermijden. Gezien het uitgebreide scala aan metaal oxide nanokristallen
de en de ongelimiteerde mogelijkheden om hun samenstelling en oppervlak-
terminatie te wijzigen, stellen we hier chemisch gedreven liganduitwisseling
aan metaal oxide nanokristallen voor als een nieuwe route naar goedkope,
duurzame en veelzijdige katalysatoren.

Tenslotte, om de oxide nanokristallen te introduceren in de methanol geba-
seerde YBCO precursor oplossing, is het nodig om de hydrofobe vetzuren uit
te wisselen voor kleine polaire liganden. Er is helaas geen geschikte proced-
dure beschikbaar in de literatuur die tegemoet komt aan de vereisten voor de
supergeleidende composieten. Daarom presenteren we hier een nieuwe, veel-
zijdige methode, gebaseerd op aminozuren en trifluoroazijnzuur. Na ligand-
uitwisseling kunnen de nanokristallen worden neergeslagen en vervolgens
opnieuw gedispergeerd in verschillende polaire solventen. We verhelderen
ook het mechanisme van de liganduitwisseling door gebruik te maken van
$^1\text{H NMR}$ en infraard metingen. We tonen dat trifluoroazijnzuur noodzakel-
lijk is om het vetzuur te protoneren, waarin het positief geladen aminozuur
adsorbeert op het oppervlak, het nanokristal elektrostatisch stabiliserend.
Daarenboven is er ook een kleine sterische bijdrage tot de coloidale sta-
bilisatie vanwege het resterende carbonzuur aan het oppervlak. Hoewel de
gebonden toestand van de meeste aminozuren niet detecteerbaar is in NMR,
tonen we het bestaan van deze onzichtbare toestand aan door competitieve
titraties. Glycine wordt toegevoegd aan de suspensie, gestabiliseerd met
glutamine, en we observeren een duidelijke toename in observeerbaar glu-
tamine, voldoende bewijs voor het bestaan van de onzichtbare toestand.
Meer nog, methyl eenheden hebben een hogere interne mobiliteit en een
gebonden methyl wordt geobserveerd in het $^1\text{H NMR}$ spectrum van methi-
onine gestabiliseerde nanokristallen, ook al is deze eenheid dicht gesitueerd
bij het oppervlak. De oxide nanokristallen zijn stabiel in de YBCO precuur-
sor in hoge concentratie en blijven zo maanden lang. Helaas leidt directe
depositie van de nanocomposiet-precursor tot minder kwalitatieve YBCO
lagen. Enkel de afzetting van een dun laagje zuivere YBCO, waarna het
nanocomposiet wordt afgezet, zorgt voor de vorming van een kwalitatieve supergeleidende coating. De nanokristallen reageren tot barium zirkonaat of barium hafnaat en lijken te groeien in de laag. Dit is echter nog maar het eerste bewijs van het mogelijk gebruik van voorgevormde nanokristallen in YBCO nanocomposieten en optimalisatie van zowel de processen als de nanokristalparameters is mogelijk en noodzakelijk.

In conclusie, we hebben metaal oxide nanokristallen gesynthetiseerd via een snel microgolf geassisteerd proces. We hebben zowel het mechanisme van de oxide vorming als van de oppervlaktemodificatie opgehelderd. Verder hebben we ook nieuwe, fundamentele inzichten aangeboden betreffende de nanokristal oppervlaktechemie en we hebben nieuwe mogelijkheden gede- monstreerd voor ligand uitwisseling, zowel in apolaire als in polaire solven- ten. Tenslotte waren we in staat om de oxide nanokristallen te introduceren as artificiële pinning centra in YBCO dunne filmen en we hebben uitstekende kritische stroomdichtheden behaald van $4.6 \, \text{MA/cm}^2$ in eigen veld.
Do you ever wonder how we are going to provide sustainable energy for nine billion people in 2050? I do. Among several solutions for this problem, superconductivity has its place. Superconductors transport electricity without resistance and their superior properties allow the construction of innovative energy harvesting or energy saving machines and devices. This thesis was initially set out to improve the properties of the superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) by the distribution of metal oxide nanocrystals (NCs) in the ceramic material. However, this research evolved towards a fundamental study on the surface chemistry of metal oxide NCs, leading to an in-depth understanding and finally, breakthroughs, both in superconductivity as well as in catalysis. The concepts developed in this thesis form a bridge between synthesis of nanomaterials and their applications, something sorely needed.

Our research commenced with a published synthesis of HfO$_2$ NCs, from HfCl$_4$ and benzyl alcohol. The solvothermal (autoclave) process of Buha et al. is reproducible but no proof is found for the claimed benzyl chloride elimination mechanism. In contrast, GC–MS (Gas Chromatography coupled with Mass Spectrometry) and NMR (Nuclear Magnetic Resonance) analyses show large amounts of dibenzyl ether. This not only points towards an ether elimination oxide formation mechanism but also indicates that HCl — released by ligand exchange with benzyl alcohol — catalyzes a Williamson ether synthesis. The NCs are slightly anisotropic, not unlike rice, as indicated by High Resolution TEM (Transmission Electron Microscopy) and the different peak widths of different reflections in XRD (X–ray Diffraction). Interestingly, the reaction is considerably faster with microwave heating, compared to conventional heating. Although the microwave synthesis also yields more monodisperse and smaller particles, the NCs retain the same shape and monoclinic crystal structure. Aggregates
of the NCs are charge stabilized in water and the iso–electric point was
determined at pH = 8. In order to obtain non–agglomerated NCs, a post–
synthetic surface modification was successfully performed with dodecanoic
acid and oleylamine. The synthesis performs equally well for ZrO\textsubscript{2} NCs.

Secondly, we elucidate the surface modification mechanism of HfO\textsubscript{2} and
ZrO\textsubscript{2} NCs. Initially, the NC aggregates feature a positive zeta potential
in ethanol and XRF (X–ray Fluorescence) measurements reveal also the
chloride counterions. When the NCs are precipitated and dispersed in chlo-
roform, a mere carboxylic acid is unable to replace the initially present
hydrogen chloride without the presence of oleylamine. However puzzling
at first, oleylamine is only weakly entangled in the ligand shell and can be
removed by simple purification together with undesired traces of chloride,
leaving a clean surface of only carboxylic acids on the surface, with a ligand
density of about 3 nm\textsuperscript{-2}. Those carboxylic acids feature the same dynamical
behavior in solution as metal chalcogenide NCs stabilized with carboxylates.
However, careful monitoring of the acidic protons while adding deuterated
oleic acid to a HfO\textsubscript{2} NC suspension, establishes that the negative charge
of the carboxylate is not balanced by an excess of cations but by protons
which are adsorbed on different surface adsorption sites than the carboxy-
lates. Carboxylic acids can thus dissociate on the surface of the metal oxide
NCs (see Figure 3) and this is a crucial difference with respect to the other
chalcoenides. Furthermore, oleylamine is not a surfactant but a base and
reacts with hydrogen chloride, leaving a free adsorption spot for the car-
boxylic acid to dissociate on. This is confirmed by the use of other bases
such as triethylamine.

The interesting differences between other chalcogenide NCs and oxide NCs
raise the question whether this also changes the exchange characteristics of
the carboxylate anion. Indeed, octylamine, an L–type ligand, releases oleic
acid from HfO\textsubscript{2} NCs (see Figure 4) while cadmium oleate is released from
CdSe NCs. The ligand exchange reaction is rendered exothermic — and
thus impeded at high temperatures — by the formation of an acid/base
pair in case of oxide NCs or a metal complex in case of CdSe NCs. Such an
observation is interesting as this means that ligand binding during NC syn-
theses might be completely different from ligand binding during the room
temperature work–up. More evidence for the ion pair is found in the IR
(infrared) spectrum and by the fact that the equilibrium quotient of the ex-
Figure 3: The amine captures a proton of the carboxylic acid. Subsequently the carboxylate exchanges for the chloride. The chloride is paired with the ammonium compound as a salt and remains in the ligand shell. In a second step the NCs are purified with polar solvents and the salt leaches out of the ligand shell. The final result is a dissociated carboxylic acid on the oxide NC surface.

change reaction is only constant for different amine concentrations if the ion pair formation is accounted for. Finally, oleic acid features self-adsorption at the oxide but not at the CdSe NC surface (see Figure 4). We argue that the peculiar exchange characteristics of carboxylic acids, bound to metal oxide NCs, result from their dissociative adsorption. The NC surface thus contains equal amounts of anionic and cationic X-type ligands, a binding motif we label as NC(X)_2. As X-type ligands are defined as ligands that, in their neutral form, donate one electron to the NC–ligand bond, both anionic and cationic species fit that description, although in literature X-type ligands are often seen as anionic ligands. Importantly, acknowledging the occurrence of NC(X)_2 type binding brings about a new class of NC–ligand systems — stoichiometric NCs with an overall charge neutral combination of X-type ligands — in addition to cation rich NCs with anionic X-type ligands and stoichiometric NCs with neutral Z- or L-type ligands. As the same exchange characteristics were found for ZrO_2 NCs, synthesized with a different precursor, we infer that this new binding motif will be most relevant to understand the surface chemistry of metal oxide NCs in general.

Going one step further, employing weakly binding ligands such as amines or alcohols, allows to chemically convert tightly bound carboxylic acids in non–coordinating amides or esters and thus promote acid/amine or acid/alcohol ligand exchange. As the reaction is impeded at room temperature, but advances at 130 °C, this allows for a convenient tuning of the NC ligand shell. Such mixed ligand shells offer for example increased solubility in
solvents such as dichlorobenzene. Furthermore, sustained ester formation is observed when the ligand shell is continuously replenished with carboxylic acids. Because the fraction of bound ligand does not change during this process while there is no ester formation observed in the absence of oxide NCs, this is a catalytic process. We relate the catalytic activity to the dissociative NC(X)₂ binding of carboxylic acids to oxide NCs because no ester formation is catalyzed by carboxylate capped CdSe NCs. We further underscore the catalytic potential by showing that HfO₂ NCs also catalyze transesterifications at the same temperature as esterification. These findings show that apart from a powerful yet subtle surface engineering tool, chemically driven ligand exchange bypasses the colloidal stability / catalytic activity conundrum in colloidal nanocatalysis. Ligands are needed to impart colloidal stability, but they also block catalytically active surface sites. By using the reagents as ligands, this trade-off is circumvented. Given the extensive range of metal oxides that can be synthesized as nanocrystals and the almost unlimited possibilities to tune their composition and surface ligands, chemically driven ligand exchange on metal oxide nanocrystals may offer a new route towards low-cost, durable and versatile catalytic processes.

Finally, to introduce the oxide NCs in the methanol based YBCO precursor solution, ligand exchange of the hydrophobic fatty acids for small polar ligands is necessary. There is no suitable ligand exchange strategy in the literature and therefore we present a new, versatile method, based on amino
acids and trifluoroacetic acid. After ligand exchange the NC are precipitated and redispersed in various polar media. We elucidate the mechanism of the ligand exchange by means of $^1$H NMR and IR analysis and show that trifluoroacetic acid is necessary to protonate the original carboxylic acid ligand, after which a positively charged amino acid adsorbs on the surface, electrostatically stabilizing the surface. In addition there is a small steric contribution to the colloidal stabilization due to some remaining carboxylic acid on the NC surface. Although the bound state of most amino acids is undetectable in NMR, we prove the existence of this dark state by competitive titration experiments. Glycine is added to a HfO$_2$ NC suspension, stabilized with glutamine, and we observe a clear increase in the amount of detected glutamine, clear evidence for the dark state. In addition, methyl moieties have a higher internal mobility and a bound methyl resonance is observed in the $^1$H NMR spectrum of methionine stabilized NC, even though it is located relatively close to the surface in a small, tightly bound ligand. The oxide NCs are stable in the YBCO precursor in high concentration, for months. Unfortunately, direct depositon of the nanocomposite precursor leads to poor YBCO layers. Only the application of a thin seed layer of pristine YBCO, onto which the nanocomposite layer was deposited, led to the growth of a high quality superconducting coating. The NCs react to form barium zirconate or barium hafnate and seem to grow in size. As this is only the first proof of concept regarding the use of preformed NC in YBCO nanocomposites, optimization of the processing and NC parameters is still possible.

In conclusion, we synthesized metal oxide NCs in a fast and convenient microwave assisted process. We elucidate the oxide formation mechanism and the surface modification mechanism. Furthermore, we offered new fundamental insights, regarding NC surface chemistry and demonstrated new possibilities for ligand exchange in both apolar and polar media. Finally, we were able to introduce the oxide NCs as artificial pinning centers in YBCO thin films and achieved high critical current densities of 4.6 MA/cm$^2$ in self field.
1 Introduction

1.1 Problem definition

Do you ever wonder how we are going to provide sustainable energy for nine billion people in 2050? I do. Among several solutions for this problem, superconductivity has its place. Superconductors are — as we will learn — extraordinary conductors, transporting electricity without resistance. Their superior properties allow the construction of innovative energy harvesting or energy saving machines and devices. It is for that reason that I entered the field of superconductivity. However, the current superconductors suffer from poor performance in high magnetic fields, hampering the implementation of these materials in sustainable applications.

This thesis was set out to improve the properties of the superconductor \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) by the creation of \textit{ex situ} pinning forces. In that respect, a homogeneous distribution of metal oxide nanocrystals in the ceramic material, and the formation of nanocomposite coatings is imperative. A major milestone was the stabilization of nanocrystals in solution, and soon it became evident that fundamental insights in the surface chemistry of nanocrystals were essential to obtain stable precursor solutions. Therefore, this work evolved more to a fundamental study of the surface chemistry of
metal oxide nanocrystals. Furthermore, our augmented understanding of
the nanocrystal surface allowed us to recognize their potential for biodiesel
production, another domain of rethinking energy. Biodiesel is a possibly
sustainable idea but at the moment only high purity, edible oils can be pro-
cessed into biodiesel. In a world where rain forests are cut down to make
place for farmland, this might not be the most efficient or moral solution. In
addition, the non-reusability of current biodiesel catalysts is an issue, and
the quest for reusable catalysts is nowadays an important topic in catalysis
research.

1.2 State of the art

The study of inorganic nanocrystals (NCs) is a major topic in materials
chemistry as they show significant differences with their bulk counterpart.
First, all NCs exhibit an enormous surface area, an attractive feature for
catalysis,\textsuperscript{1,2} gas adsorption\textsuperscript{3} or batteries.\textsuperscript{4,5} In addition, electrons in a NC
behave like particles in a box and if the box becomes very small, the elec-
tronic states show quantization and, e.g., the color of light, emitted by
semiconductor NCs, can be tuned by adjusting the diameter of the NCs.
Furthermore, metastable crystal phases may be kinetically favored during
NC nucleation and growth.

Unfortunately, NCs have a tendency to aggregate in order to minimize the
surface free energy, reducing their utility. There are several stabilization
mechanisms but most often, NCs are capped with a layer of organic surfac-
tants to prevent agglomeration and impart colloidal stability by steric hin-
drance. Such ‘colloidal nanocrystals’ are therefore hybrid objects of which
the physical and chemical properties are determined by both core and sur-
face. Controlling the latter has proven indispensable for all NC applications,
ranging from thermoelectrics\textsuperscript{6} and thin film electronics\textsuperscript{7,8} to electrochromic
applications.\textsuperscript{9}

1.2.1 Superconducting nanocomposites and oxide NCs

Composites combine different materials with distinct physical or chemical
properties to achieve a new material with different or improved properties.
The use of NCs to fabricate inorganic–organic or all inorganic nanocom-
posites is compelling as colloidal NCs can be finely distributed in a precur-
sor solution. High Temperature Superconductors (HTS, superconductivity
above 30 K), especially, rely on nanoscale inclusions to improve the amount
of current they can carry.
Ever since the discovery of HTS, huge efforts have been dedicated to develop useful conductors for, e.g., power applications.\textsuperscript{10,11} Firstly, YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO), the most commonly researched HTS, is brittle, precluding wire pulling. Nowadays, YBCO is therefore deposited as a thin film on a metallic, flexible substrate. The latter transfers its excellent mechanical properties to the thin YBCO layer. Secondly, the current density of YBCO decreases dramatically in high magnetic fields, which is problematic for many applications.\textsuperscript{12} To improve the electrical properties of YBCO, nanoscale, non–superconducting defects — so called artificial pinning centers (APCs) — are to be included in the YBCO matrix.

The practical realization of the layered architecture and the inclusion of APCs depends on the type of deposition techniques. Vacuum methods, such as pulsed laser deposition, yield high quality YBCO films but struggle with upscaling and cost issues. Chemical solution deposition (CSD) is appealing as affordable, long length HTS tapes can be produced.\textsuperscript{10,13,14} For this, a precursor solution, containing yttrium, barium and copper salts is deposited on a substrate, pyrolysed and converted to YBCO. In particular, methanol–based solutions containing trifluoroacetate salts have been reported to yield epitaxial layers with high critical current densities ($J_C = 2–4 \text{ MA/cm}^2$).\textsuperscript{15,16}

In this work, we will therefore focus on CSD with trifluoroacetate precursor solutions. Currently, APCs in YBCO are attained by the spontaneous segregation of nanoscale, secondary phases during the growth process. The precursors for the APCs are simply added to the YBCO precursor solution. YBCO layers have been improved by Au, Y$_2$O$_3$, BaZrO$_3$, BaCeO$_3$ and Ba$_2$YTaO$_6$ nanoparticles.\textsuperscript{12,17,18} However, the spontaneous segregation of secondary phases lacks control over the size, the size distribution and the stoichiometry of the particles.

In this work, we propose a new approach, in which preformed nanocrystals are added to the YBCO precursor solution. To our knowledge, the only attempt to use preformed NCs was reported by Martinez–Julián et al. who employed preformed Au nanoparticles.\textsuperscript{19} In that case however, the NCs were pushed to the top of the layer and no effective artificial pinning centers were formed. Ideally, double metal oxide NCs, such as BaZrO$_3$, should be used as APCs because they are chemically inert towards YBCO and are proven to be efficient APCs, albeit formed via spontaneous segregation during the YBCO growth process.\textsuperscript{12} However, the formation of double metal oxide NCs remains troublesome\textsuperscript{20,21} and we will focus here on single metal oxide NCs such as HfO$_2$ and ZrO$_2$. For efficient vortex pinning, 3–5 nm NCs are required and we aim at synthesizing crystalline NCs since amorphous
materials are expected to be more prone to react with the YBCO matrix.

1.2.2 Nanocrystal synthesis strategies

Although physical methods of NC preparation exist, solution–based approaches stand out because they yield a wide range of NCs with control over size, size–dispersion and shape. Aqueous methods are able to quickly deliver monodisperse colloids but the particles are often very large (> 100 nm) and amorphous.\textsuperscript{22,23} To obtain crystalline material, a heat treatment is necessary which unfortunately also induces agglomeration. In addition, the final nanoparticle properties are very sensitive to the precise reaction conditions.

The so–called ‘hot injection’ or ‘heating up’ approaches are typically surfactant–assisted, nonaqueous methods and use large quantities of surfactants to control nucleation, growth and colloidal stability. The resulting particles are often exceptionally monodisperse and no other method delivers the same kind of control and colloidal stability.\textsuperscript{24–28} However, syntheses are sensitive to variations in heating rate, precursor addition rate, etc., and the surfactants might decompose at the high temperatures.\textsuperscript{29} Generally, many of these synthesis recipes have been developed by combining trial, error and chemical intuition, and in depth mechanistic investigations are necessary to fully understand the chemistry behind the recipes. Such investigations are far from trivial as impurities in reagent batches can dictate the outcome of a synthesis.\textsuperscript{30,31}

Surfactant–free nonaqueous methods are quite the opposite, both in setup as in final outcome. Especially useful for metal oxide NCs, they rely on chemically robust, autoclave procedures with high yields.\textsuperscript{32} Benzyl alcohol, tert–butylalcohol and benzylamine are the most popular solvents as oxide formation can proceed through controlled chemical reactions, based on $S_N1$ and $S_N2$ substitutions. A vast range of metal oxide NCs can be prepared at moderate temperature (200 °C) but this method offers less control over size and shape of the NCs. However, the most important drawback is NC agglomeration.\textsuperscript{32}

Fortunately, it was already shown that a post–synthetic surface modification in nonpolar solvents can provide colloidal stability by steric hindrance. Aggregate–free suspensions of ZrO$_2$\textsuperscript{33,34} and Fe$_3$O$_4$\textsuperscript{35} NCs were obtained with fatty acids whereas the surface modification of ITO\textsuperscript{34} (indium tin oxide) proved successful with long–chain primary amines. Although this approach is certainly beneficial because only minimal amounts of surfactant are required to obtain a stable, aggregate–free dispersion of NCs, a rational
basis for and fundamental understanding of the surface functionalization is lacking.

1.2.3 Surface Chemistry models

In order to understand surface functionalization, it proves useful to have a rigorous framework for thoughts. Inspired by the Covalent Bond Classification (CBC), Jonathan S. Owen and coworkers were the first to classify NC–ligand interaction, see Figure 1.1.\textsuperscript{37,38} L–type ligands are lewis bases, donating two electrons to the NC, a typical example being oleylamine. In apolar solvents (here defined as solvents with a dielectric constant, $\epsilon < 5$), L–type ligands coordinate to the surface metal ions of stoichiometric NCs to yield overall charge–neutral objects.\textsuperscript{39}

![Figure 1.1: L–type ligands as Lewis bases and Z–type ligands as Lewis acids. X–type ligands are anionic moieties that terminate the crystal lattice.](image)

Z–type ligands, having an empty orbital, are neutral electron–pair acceptors (e.g., metal carboxylates) and bind to the surface anions of stoichiometric NCs.\textsuperscript{37} The most well known NC model system is CdSe and those NCs are covered with a layer of cadmium carboxylate, see Figure 1.2. Interestingly, one could also look at Figure 1.2 and conclude that the nanocrystal is cation–rich at the surface and is covered with a layer of carboxylate ligands. The latter are categorized as X–type ligands, which were initially introduced as anionic moieties that terminate the crystal lattice.\textsuperscript{37} However, in this thesis, we will consider the more rigorous definition of X–type ligands being radicals in their neutral form, see Chapter 4.

There are many techniques in place to characterize the NC surface such as infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and Isothermal Titration Calorimetry (ITC). However, none of these allow to directly observe the organic ligand or in fact, tell bound ligands from free organic residuals. In contrast, $^1$H NMR grants insights in the chemical nature of the ligand, its dynamic behaviour in solution and the solvodynamic radius of the ligand. Even thermodynamic data
Stoichiometric CdSe NCs are covered with a layer of Z–type cadmium carboxylate ligands. Equally correct, would be to regard the nanocrystal as cation–rich with anionic X–type ligands to terminate the crystal lattice.

Figure 1.2: Stoichiometric CdSe NCs are covered with a layer of Z–type cadmium carboxylate ligands. Equally correct, would be to regard the nanocrystal as cation–rich with anionic X–type ligands to terminate the crystal lattice.

can be extracted from temperature dependent spectra. Therefore, $^1$H NMR will be our main tool in the elucidation of the NC–ligand interaction.

1.2.4 Colloidal nanocatalysis

Nowadays, 90% of all chemicals are produced with the aid of catalysts. Catalysts facilitate chemical reactions at lower temperatures or can even synthesize new, previously inaccessible, products. As such, there is a strong demand for catalysts to reduce energy consumption and to create innovative products. In general, there are two classes of catalysts: heterogeneous and homogeneous catalysts. Heterogeneous catalysts are porous powders which can be easily separated from the reaction mixture while homogeneous catalysts are molecular compounds which are either highly active or vastly selective but difficult to reuse.

In the field of acid/base catalyzed reactions, the homogeneous catalyst always outruns the solid but features neutralization and corrosion problems. Although different in the nature of their respective issues, both disciplines might benefit from colloidal nanocrystals as they combine the advantages of homogeneous and heterogeneous catalysts and constitute model systems to obtain insight in catalytic processes. While deemed promising, colloidal nanocatalysis is often problematic since surface–adsorbed ligands, needed for colloidal stability, prevent reagents from reaching catalytically active surface sites. Hence the general preference for heterogeneous approaches using supported, ligand–stripped nanocrystals over colloidal nanocataly-
sis.\textsuperscript{42–44} However, this inadvertently reduces again the surface area. In contrast, the surface area of colloidal nanocrystals can easily be increased by decreasing the NC diameter. Another approach is to select catalytically active ligands,\textsuperscript{45;46} or ligands that enhance the catalytic activity of the NCs but in this approach the catalytic properties are lost upon desorption of the original ligand. Therefore, there is still ample room for improvement in this young field.

1.3 Outline

In this thesis, we aim to synthesize < 5 nm HfO\textsubscript{2} and ZrO\textsubscript{2} nanocrystals for the application as artificial pinning centers in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} superconductors. We will focus on a fundamental understanding of both reaction mechanisms and surface chemistry. This knowledge will allow us to move rationally towards a ligand exchange strategy to stabilize the oxide NCs in methanol and thus in the superconducting precursor solution. Finally, we show how the oxide nanocrystals can contribute to either improved superconductors or even catalysis.

Chapter 2 compares a conventional HfO\textsubscript{2} nanocrystal synthesis in an autoclave with the same reaction under microwave heating. We show that the reaction is much faster under microwave heating and that the nanocrystals are smaller, with a better size dispersion. The reaction mechanism is investigated and finally, the nanocrystal surface was functionalized with dodecanoic acid, resulting in a stable suspension in chloroform.

Chapter 3 investigates in detail the surface modification from chapter 2. As-synthesized nanocrystals are charge-stabilized by protons, with chloride acting as the counterion. We find that the addition of amines provides the basic environment in which carboxylic acids can dissociate and replace chloride. This results in stable, aggregate-free dispersions of HfO\textsubscript{2} nanocrystals, sterically stabilized by carboxylate ligands. Moreover, the charge on the carboxylate ligands is balanced by co-adsorbed protons.

In chapter 4, we take the observation that the surface of the oxide nanocrystals is covered by dissociated carboxylic acids and formalize this new ligand binding in theory. We propose that both proton and carboxylate moieties must be regarded as X-type ligands yielding a combined NC(X)\textsubscript{2} binding motif that allows for self-adsorption and exchange for L-type ligands. Both processes are incompatible with an NC(MX\textsubscript{2}) binding motif of carboxylic acids as reported for sulphide/selenide NCs but we show that they effectively take place at the HfO\textsubscript{2} NC surface.
Chapter 5 elaborates on ligand exchange methods via true chemical reactions. Amide and ester formation reaction are used to tune the ligand shell composition. However, if more reagents are provided to the mixture, we observe a catalytic process. Both esterification and transesterification reactions are possible with the metal oxide nanocrystals as catalyst. We relate this catalytic activity to the dissociative NC(X)\(_2\) binding of carboxylic acids to oxide NCs. This bifunctional catalyst might be of use in biodiesel production.

Chapter 6 shows the transfer of the nanocrystals form nonpolar to polar solutions and finally, the superconductor precursor solution. The transfer is realized by the exchange of the native ligands for amino acids. The exchange reaction is again investigated in full detail, revealing that also the acid, trifluoroacetic acid, is involved in the stabilization process. Finally, a superconductor with superior properties is produced with these nanocrystals.
References


Introduction


[37] Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals:
Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *Journal of the American Chemical Society* 2013, 135, 18536–18548.


Microwave synthesis of metal oxide nanocrystals\textsuperscript{1}

La Chimie crée son objet. Cette faculté créatrice, semblable à l’art lui-même, la distingue essentiellement des sciences naturelles et historiques.

– Marcelin Berthelot

2.1 Introduction

Metal oxide nanocrystals (MONCs) constitute an important class of nanomaterials regarding their potential in medicine,\textsuperscript{1} (photo)catalysis,\textsuperscript{2,3} gas sensing,\textsuperscript{4} magnetic applications,\textsuperscript{5} solar cells,\textsuperscript{6} transparent electrodes,\textsuperscript{7} lithium ion batteries,\textsuperscript{8,9} and electrochromic applications.\textsuperscript{10} Their suitability for a specific application depends on their properties, such as chemical nature, size, shape, size dispersion, crystallinity, colloidal stability and surface composition, and their eventual industrial implementation requires fast and

\textsuperscript{1}Adapted from: De Roo, J.; De Keukeleere, K.; Feys, J.; Lommens, P.; Hens, Z.; Van Driessche, I. Fast, microwave-assisted synthesis of monodisperse HfO\textsubscript{2} nanoparticles. Journal of Nanoparticle Research \textbf{2013}, \textit{15}, 1778
robust syntheses with a high yield, cheap precursors and low energy input. Many research activities have therefore been dedicated to the development of various synthetic strategies, where solution–based approaches stand out since they can be applied to prepare a wide range of MONCs with often, an exceptional control over size, size–dispersion and shape.

2.1.1 Nanocrystal synthesis strategies – state of the art

Using solution–based approaches in aqueous media, it proved possible to synthesize monodisperse colloids in short reaction times, but the particles were often very large (> 100 nm) and amorphous. The subsequent, necessary crystallization step induced undesired agglomeration. In addition, the final properties of the nanoparticles were found to be very sensitive to the precise reaction conditions (e.g., pH, temperature, etc.). In surfactant–assisted nonaqueous methods — typically carried out in a hot injection or heating up setup — large quantities of ligands are used to control nucleation, (anisotropic) growth and colloidal stability, often leading to very monodisperse MONCs. In general, these syntheses proceed at high temperatures (> 300 °C) to quickly decompose the metal precursor and obtain crystalline products. Successful syntheses require a rigorous control of heating rate, precursor addition rate, etc., whereas further complications may result from structural changes of the surfactants at the high temperatures used or from impurities in surfactants, which can be more decisive to the outcome of a synthesis than the surfactant itself.

On the other hand, surfactant–free nonaqueous methods are based on chemically robust procedures with high yields. The metal precursors — typically cheap metal salts — are simply mixed with a benign solvent such as benzyl alcohol or benzyl amine, and heated for several days in an autoclave. The reduced hydrolysis and condensation rates result in crystalline particles even at moderate temperatures of 200 °C and lower. The slow autoclave process is objectionable but it was shown that these reactions can be accelerated considerably by using microwave heating, while still retrieving products with excellent crystallinity. With this surfactant–free approach, a vast range of (binary or doped) MONCs can be prepared but it offers less control over size and shape of the NCs. Moreover, the resulting MONCs suffer from agglomeration and lack of redispersibility.

2.1.2 Hafnium oxide

Hafnium oxide in particular is a material with a number of technologically attractive properties such as
- a high melting point (2758 °C)
- a high dielectric constant (≈ 30)
- a high chemical stability
- a wide band gap (6 eV)
- a high neutron absorption cross section

HfO₂ was proposed to replace SiO₂ as a gate dielectric and HfO₂ thin layers are highly promising as high-κ dielectric layers, heat-resistant and highly reflective, protective optical coatings or sensors. Amorphous nanoparticles of HfO₂ were used for Extreme Ultraviolet patterning to develop inorganic photoresists. Hafnia (HfO₂) nanoparticles were embedded in either an inorganic or organic matrix to increase the dielectric constant. Hafnium based nanoparticles were also grown in GdBa₂Cu₃O₇₋δ coated conductors to improve the critical current of the superconductor. Although HfO₂ nanostructures were considered for their intrinsic luminescent properties, it was shown more recently that HfO₂ nanocrystals are actually an excellent host for luminescent rare earths (RE) ions. Finally, HfO₂ nanoparticles are appealing for biomedical applications (e.g., radiotherapy) because of the negligible cytotoxicity and high X-ray absorption cross section.

In this work, we envisage the synthesis of sub 10 nm monodisperse HfO₂ NCs to incorporate them in an inorganic matrix of solution grown YBa₂Cu₃O₇₋δ superconductors to increase the critical current (see Chapter 6). However, the application window is wider since also thermoelectric materials benefit from the inclusion of nanoscale impurities, which are scattering phonons. Due to the high chemical stability and the high melting point, hafnia is an ideal candidate for these kind of nanocomposites. In order to incorporate the nanoparticles, they need to be colloidally stable in the precursor solution of the inorganic matrix. In case of High Temperature Superconductors (HTS) these solutions are mostly water or methanol based.

Hafnium oxide nanoparticles have already been synthesized with a variety of methods, such as surfactant based, hydrothermal, microwave assisted hydrothermal, ultrasonically assisted hydrothermal, solvothermal, precipitation and sonochemical synthesis. However, most of these methods are unfavorable because of a long reaction time, a broad size distribution, the agglomerated state of the particles or the large diameter.
Moreover, as mentioned before, there is often the need for a second calcination step to crystallize the particles which aggravates agglomeration.\textsuperscript{43,49,51} Some synthesis methods\textsuperscript{23,42} yield unagglomerated and crystalline (sub 10 nm) particles but have the drawback that they use large quantities of surfactants and expensive precursors.

The most interesting method was the solvothermal synthesis presented by Buha et al. They were able to form HfO\textsubscript{2} particles at a low temperature (220 °C) starting from the relatively economical material HfCl\textsubscript{4}.\textsuperscript{50} The synthesis uses benzyl alcohol as a solvent, which is an environmentally friendly chemical that is used in the food industry. However the synthesis of Buha et al. features the typical drawbacks of solvothermal syntheses:

- a long reaction time
- a broad size distribution
- the agglomerated state of the particles

In this chapter\textsuperscript{53} we describe how to overcome these limitations. To speed up the reaction and to obtain smaller size dispersions, we use a microwave assisted solvothermal synthesis. Microwaves couple directly to the molecules in the reaction mixture, resulting in a more efficient energy transfer and an often significant enhancement of the reaction rate.\textsuperscript{54–56} Metal oxide nanoparticle synthesis in a microwave is already reported\textsuperscript{21,57,58} but to the best of our knowledge no literature is available for HfO\textsubscript{2} nanocrystals. We also investigated the reaction mechanism in both the autoclave and the microwave reaction. In contrast to the suggestion of Buha et al. we found proof of an ether elimination reaction in the autoclave synthesis. In the microwave synthesis, several side products were identified but the principal reaction mechanism remains the ether elimination. To tackle agglomeration, the post–synthetic surface modification of nanoparticles, synthesized in benzyl alcohol, was already reported for iron oxide, zirconia and indium tin oxide.\textsuperscript{59,60} Related approaches are briefly introduced here and elaborated upon in Chapter 3 for hafnium oxide nanocrystals.

2.2 Experimental

2.2.1 Synthesis procedures

Anhydrous benzyl alcohol and dibenzyl ether were purchased from Sigma Aldrich and hafnium/zirconium chloride was purchased from Alfa Easar.
To synthesize HfO$_2$ NCs in an autoclave, 0.2 g (0.625 mmol) of HfCl$_4$ was added to 45 mL of benzyl alcohol (0.014 M Hf) under ambient conditions in a stainless steel autoclave with Teflon liner and a total reactor volume of 100 mL. The autoclave was sealed with screws and heated in an oven to 220 °C for 3 days (no stirring). The resulting precipitate was washed with ethanol and diethyl ether.

HfO$_2$ NCs were also synthesized via a microwave-assisted solvothermal process. Under vigorous stirring, 4.5 mL of benzyl alcohol was added to 0.135 mmol of hafnium chloride in a 10 mL microwave vial under ambient conditions. The hafnium concentration is thus 0.3 M. The solution was subjected to microwave heating with the following temperature settings: 5 minutes at 60°C and 3 hours at 220°C (medium stirring is applied). The microwave device was of the type CEM discover equipped with an auto sampler and IR temperature detection. A typical temperature/power/pressure profile is shown in Figure 2.1.

After synthesis, the resulting suspension was centrifuged and the precipitate was washed with diethyl ether and finally dispersed in ethanol for TEM measurements or dried at 60 °C for XRD measurements.

### 2.2.2 Analysis Techniques

For Dynamic Light Scattering (DLS) and zeta potential measurements a Malvern Nano ZS was used in backscattering mode (173°). Quantitative analysis of metals was obtained by calibration of a Rigaku CG EDXRF analyzer working with the fundamental parameters based quantitative analysis (RPF–SQX). TEM measurements were performed on a JEOL JEM–2200FS TEM with Cs corrector. NMR spectra were recorded with a Bruker 500 MHz AVANCE III spectrometer equipped with a BBI–probe. Qualitative GC–MS experiments were performed on a Hewlett Packard G1800B GCD and quantitative measurements for organic compounds were obtained from a Hewlett Packard 5890 CD2 GC with FID detection. Statistical analysis was performed with SPSS Statistics 19. For XRD characterization a Thermo Scientific ARL X’tra X–ray diffractometer was used with the CuKα line as the primary source. To estimate the crystallite diameter from the XRD diffractogram, the Scherrer equation was applied

$$d = \frac{0.95 \lambda}{B \cos \theta}$$

where $\lambda$ is the wavelength of the X–rays, $\theta$ is the diffraction angle and $B$ is related to the width $\Delta$ of the Gaussian fit by
2.3 Results

2.3.1 Autoclave synthesis

To properly compare the microwave synthesis developed here with a conventional heating approach, first the solvothermal synthesis of Buha et al. was executed and fully characterized. After three days at 220 °C, a precipitate was retrieved from the autoclave, washed and suspended in ethanol. From the TEM image in Figure 2.2A it can be noted that the suspension consists of ellipsoidal nanoparticles with a varying aspect ratio between 0.5 and 0.9. Since the particles have no uniform shape, we use the effective di-

\[ B = \frac{4\pi}{360} \Delta \sqrt{m^2} \]  

(2.2)
ameter to analyze sizes and assess size distributions. This effective diameter is determined as the diameter of a 2D circle with the same surface area as the projection of the particle obtained in the TEM image. A statistical representation of the size distribution was made based on a significantly large population of particles (Figure 2.2B). This distribution matched well with the applied Gaussian fit. The average effective diameter is 5.2 nm with a standard deviation of 1.5 nm, giving a size dispersion of \( \approx 30\% \). However, it is already indicated by the TEM images that the particles form large aggregates.

![Figure 2.2](image)

**Figure 2.2:** Characterization of the HfO\(_2\) particles, solvothermally prepared in the autoclave. A. TEM image B. size distribution obtained from TEM C. powder XRD diffractogram.

The crystallinity of the nanoparticles is confirmed by the XRD diffraction pattern, in which the monoclinic phase is recognized and the different planes were indexed, see Figure 2.2C. Due to the small size of the nanocrystals (NCs), the reflections in the XRD pattern are broadened and often overlap. Nevertheless, the (-111) and the (111) reflections remain fairly isolated and their width can be associated with the diameter \( d_{\text{XRD}} \) of the crystallites by the Scherrer equation. For the (-111) reflection we find \( d_{\text{XRD}} = 6.3 \) nm and for the (111) reflection \( d_{\text{XRD}} = 8 \) nm. Although the method clearly overestimates the absolute size in this case (vide supra), it again points out the anisotropy of the NCs. The observed differences of \( d_{\text{XRD}} \) for the (-111) and (111) planes indicate that there is a larger periodicity of the (111) planes, compared to the (-111) planes. Indeed, this is confirmed by HRTEM measurements (Figure 2.3). From the Fourier transform of the image and measurements in real space, the interplanar distance was determined and related to the appropriate XRD reflection. One can now clearly see that the (-111) planes are directed parallel to the long axis of the ellipsoid and the
(111) planes parallel to the short axis. Hence, the periodicity of the (111) planes is more extensive, resulting in a more narrow XRD reflection.

![Figure 2.3: HRTEM images of the HfO$_2$ particles, solvothermally prepared in an autoclave. The inset shows the Fourier Transform (FFT) of the image.](image)

After synthesis, stability measurements on the suspensions in ethanol were performed and a positive zetapotential (+47 mV) was observed. Notwithstanding this very high value, a considerable fraction of the nanocrystals precipitates and it was only possible to stabilize the particles in extremely diluted conditions. Even then, the NCs themselves are not stabilized but rather form large agglomerates.

### 2.3.2 Microwave Synthesis

Comparable conditions as in the autoclave synthesis (temperature and filling ratio) were applied in the microwave assisted synthesis. The reaction time was systematically varied from 1 to 3 hours and of each sample the reaction yield and the effective diameter were estimated via XRF (X-ray Fluorescence) and TEM, respectively. The results are displayed in Figure 2.4 and it is clear that almost full yield is obtained after three hours. This is a significant reduction in reaction time compared to the autoclave synthesis (3 days). After two hours the average effective diameter changes only slightly but the yield inflates from about 75 % to about 100 %.

The microwave prepared particles have an ellipsoidal shape, as is confirmed by TEM images (Figure 2.5A). So at this point, there is no difference with the autoclave synthesized particles. However, the average effective diameter of the microwave prepared particles (Figure 2.5B) is smaller and the size distribution is much more narrow. The average diameter of the microwave particles is 4 nm compared to 5.2 nm for the autoclave particles. The standard deviation of the Gaussian fit is also reduced from 1.5 to 0.86 nm, giving a size dispersion of ±20 %. So we can conclude that the microwave synthesis
Figure 2.4: Yield and size evolution in function of the reaction time in a microwave assisted set up.

yields smaller and more monodisperse hafnium oxide nanoparticles than the autoclave synthesis. In addition, the reaction time is considerably shorter. Prolonged reaction times (up to 12 hours) in the microwave do not yield significant changes in shape or size distribution of the particles, which indicates that the observed differences with the autoclave synthesis are not caused by different reaction times.

In Figure 2.5C, XRD diffractograms of the particles at different stages of the reaction are displayed. Although the particles show already some crystallinity after two hours, the quality of the XRD diffractogram improves considerably during the last hour of reaction. Again, the peaks are broadened extensively and show often overlap, even more than in Figure 2.2C. This can be explained by the smaller average size and the smaller size distribution. The latter is important since larger particles contribute more to a sharp and clear peak (higher repetition of the unit cell). In an autoclave synthesis, the maximum effective diameter is about 8 nm while for the microwave synthesis this is 5 nm. The high crystallinity of the particles is confirmed by the high resolution TEM images where well developed lattice fringes are visible (Figure 2.6). Again, it was found that the (111) planes are parallel to the short axis of the ellipsoidal particle, so the growth direction was not changed by applying microwave heating.

Regarding the stability of the suspension of microwave prepared NCs in ethanol, an average zeta potential of +25 mV was measured. This is lower
Figure 2.5: Characterization of the HfO$_2$ NCs, obtained after 3 hours of microwave assisted solvothermal synthesis. A. TEM image B. size distribution C. powder XRD pattern of particles obtained after 1, 2 and 3 hours of reaction.

Figure 2.6: HRTEM images of the HfO$_2$ particles, solvothermally prepared in the microwave. The inset shows the FFT of the image.

compared to the zeta potential of the autoclave synthesized NCs (+47 mV). Hence, the microwave prepared NCs form less stable suspensions. Additional zeta potential measurements in water were performed to estimate the iso–electric point of hafnium oxide, which to our knowledge has never been determined. To keep the ionic strength constant for all measurements, all samples contain 0.01 M NaCl and the pH was adjusted via 0.01 M HCl and 0.01 M NaOH solutions. The average zeta potential and the standard deviation at different pH values are depicted in Figure 2.7. The data are closely described by a sigmoidal function, which goes through zero at pH = 8.3, thereby identifying the iso–electric point. To ensure good colloidal stability, the absolute value of the zeta–potential needs to be higher than 25 mV. Therefore, we conclude from the graph that stable suspensions of
hafnium oxide NCs are feasible at pH values lower than 6 or higher than 10.

![Image](image-url)  
**Figure 2.7:** The zeta potential of the HfO$_2$ NCs is positive below pH 8 and negative above pH 8. Hence the determination of the iso-electric point at pH = 8.

### 2.3.3 Colloidal stability improvement

Although all samples which have a zeta potential of more than 25 mV should in principle be colloidally stable, large agglomerates of particles are present in suspension as indicated by DLS (Chapter 3). To obtain a suspension of individual particles, several strategies were applied. The addition of triethanolamine before microwave treatment resulted in amorphous but well dispersed hafnia particles. Regarding their applications, crystallinity is however indispensable for the particles. They also need to be perfectly stable and inert in a YBa$_2$Cu$_3$O$_{7-\delta}$ precursor solution since the harsh growth conditions of the superconductor could otherwise lead to agglomeration or dissolution of the particles. Therefore, another procedure was selected. The synthesis itself was not altered but after synthesis the surface of the already crystalline particles was modified to break up the clusters in non-agglomerated particles. The advantage of post-synthetic modification over a direct surfactant assisted synthesis is that much less surfactant is needed. Dopamine has been shown to stabilize titania and iron oxide in situ and to provide solubility in polar solvents. Long chain carboxylic acids or alkylamines on the other hand were used by researchers to solubilize zirconia and indium–tin oxide nanoparticles respectively in apolar solvents (here defined as solvents with a dielectric constant, $\epsilon < 5$) after a benzyl alcohol
We tried to modify the surface of the synthesized particles with dodecanoic acid (DDAc). In contrast to the case of ZrO$_2$ described by Grote et al., the addition of dodecanoic acid did not bring the particles fully in suspension, unless oleylamine was also added to the dispersion. By following this procedure, the surface modification lasts only five minutes and yields a completely transparent solution in chloroform. The choice for chloroform instead of hexane or toluene lies in the high solubility of benzyl alcohol in chloroform. Hence, the desorption of benzyl alcohol during the post-synthetic modification is favored. Note that in order to obtain a completely transparent dispersion, the concentration of HfCl$_4$ in the initial reaction mixture is critical: 0.09 M versus 0.03 M corresponds to transparent versus turbid (the NC size remains the same). Unfortunately, increasing the concentration to 0.09 M also leads to a larger NC size (5 nm) and a broader size distributions. In Chapter 3 we characterize and discuss in detail the de-agglomeration and explain the differences with the observations of Grote et al.

### 2.3.4 Synthesis of ZrO$_2$ NCs

The synthesis strategy is not limited to HfO$_2$ NCs. Changing the precursor to ZrCl$_4$ yields monoclinic zirconia NCs, see Figure 2.8. The same rice like shape is observed as for HfO$_2$ NCs. Although the same surface modification scheme is used to deaggregate the NCs in chloroform, a different precursor concentration (0.13 M) is necessary to obtain a transparent suspension. Inexplicably, this optimized concentration corresponds to the same precursor mass as the optimized HfCl$_4$ concentration.

### 2.4 Discussion on the reaction mechanism

It is clear from the results that there are some profound differences between a solvothermal and a microwave assisted synthesis technique whereas other features are not altered by the change of heating system. In both cases, crystalline particles in the monoclinic phase were retrieved. From high resolution TEM measurements we derived that also the orientation of the crystallographic planes inside the ellipsoidal particles is identical in both synthesis methods. The (-111) planes are parallel to the long axis of the ellipsoid and the (111) planes parallel to the short axis. In contrast to these similarities, the reaction time in the microwave setup is much shorter (3 hours versus 3 days). The microwave synthesized particles are also smaller
Figure 2.8: A. TEM image of ZrO$_2$ NCs, synthesized at 220 °C for 4 hours in the microwave and dispersed in ethanol. B. XRD diffractogram.

and have a smaller size dispersion.

To investigate whether these differences reflect a change in reaction mechanism, we analyzed the reaction mixture of both the autoclave and the microwave assisted synthesis. Concerning the HfO$_2$ synthesis in an autoclave, Buha et al. suggested a reaction mechanism based on a benzyl chloride elimination.$^{50}$ However, the only species that we could identify in the autoclave reaction mixture, both by GC–MS and NMR analysis, were benzyl alcohol and dibenzyl ether ($^{13}$C NMR spectrum in Figure 2.9). Especially the presence of dibenzyl ether suggests a different two–step process. We propose that in the first step, a ligand exchange takes place according to Equation 2.3, where the chloride is partly replaced by benzyl alcoholate. In the second step, the oxygen is provided to the metal via an ether elimination reaction (Equation 2.4).

\[
\begin{align*}
\text{HfCl}_4 + \text{BnOH} & \rightarrow \text{HfCl}_4 - x \text{(OBn)}_x + x \text{HCl} \quad (2.3) \\
2\text{HfX}_3(\text{OBn}) & \rightarrow \text{HfX}_3 - \text{O} - \text{HfX}_3 + \text{BnOBn} \quad (2.4)
\end{align*}
\]

In this equation, the ligands not participating in the reaction are denoted by ‘X’. This mechanism is very similar to what was proposed for the synthesis of oxide nanoparticles with alkoxides as a reagent.$^{47,63}$ The observed quantity of ether (80 % of the reaction mixture) is however much larger than expected if only the oxide formation reaction would have proceeded. This has also been observed for a comparable SnO$_2$ synthesis and it was assumed that the
syntetized metal oxide could catalyze the etherification. However, a more straightforward explanation for the extensive ether formation is the acid catalyzed condensation of alcohols (Equation 2.5). This reaction typically requires a strong acid and elevated temperatures. In our case, the acid (HCl) is provided by the ligand exchange reaction (Equation 2.3).

\[ 2 \text{BnOH} \xrightarrow{\text{HCl}} \text{BnOBn} + \text{H}_2\text{O} \] (2.5)

**Figure 2.9:** $^{13}$C APT NMR spectrum of the reaction mixture (HfCl$_4$ and benzyl alcohol) in acetone-$d_6$ after three days in the autoclave at 220 °C.

GC and NMR measurements were also conducted on the microwave reaction mixture. In $^{13}$C NMR, only benzyl alcohol and dibenzyl ether were detected. In $^1$H NMR some additional low intensity resonances were observed but their interpretation was not straightforward. Some authors lower the concentration of BnOH to get a better NMR signal of the other compounds. We however refrain from doing so since it might alter the reaction mechanism. GC–MS has a lower detection limit and could identify various new compounds that were not detected in the autoclave reaction mixture. In Table 2.1 the different reaction products and their molar percentage (as determined from GC–FID) are displayed. We also performed and analyzed a reaction of 0.12 M HCl in BnOH at 220 °C in the microwave. The amount of HCl is equivalent to a full ligand exchange of 0.03 M HfCl$_4$ to Hf(OBn)$_4$.

From Table 2.1, it is clear that the main reaction product is dibenzyl ether, next to unreacted benzyl alcohol. As commented earlier, this is mostly likely due to the reaction in Equation 2.5. Dibenzyl ether could also be the result of Equation 2.4. It is noted that much less dibenzyl ether is present in
Table 2.1: The molar percentages of different products identified in the microwave reaction mixture by gas chromatography. Two types of experiments were studied. Sample 1 with 0.03 M HfCl\textsubscript{4} in 4.5 mL BnOH and sample 2 with an equivalent amount of HCl (0.12 M).

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>BnCl</td>
<td>0.19</td>
<td>0.17</td>
</tr>
<tr>
<td>BnOH</td>
<td>69.2</td>
<td>63.4</td>
</tr>
<tr>
<td>BnOBn</td>
<td>29.2</td>
<td>34.9</td>
</tr>
<tr>
<td>(\phi - CH = CH - \phi)</td>
<td>0.42</td>
<td>0.37</td>
</tr>
<tr>
<td>(\phi - CH_2 - C_6H_4 - CH_2 - OH) (o)</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>(\phi - CH_2 - C_6H_4 - CH_2 - OH) (m)</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>(\phi - CH_2 - C_6H_4 - CH_2 - OH) (p)</td>
<td>0.51</td>
<td>0.60</td>
</tr>
<tr>
<td>(\phi - CH_2 - CH_2 - \phi)</td>
<td>0.16</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Apart from the compounds already found in the autoclave, in the microwave HfO\textsubscript{2} reaction mixture (sample 1) other molecules such as benzyl chloride are present that could be elimination products of an oxide formation (Equation 2.6). However, benzyl chloride is also observed in the sample with pure HCl (sample 2), see Table 2.1. BnCl can be formed via Equation 2.7, an SN\textsubscript{1} reaction of BnOH with HCl.

\[
\text{HfX}_3\text{Cl} + \text{BnO} - \text{HfX}_3\text{H} \rightarrow \text{HfX}_3 - \text{O} - \text{HfX}_3 + \text{BnCl} \quad (2.6)
\]
\[
\text{HCl} + \text{BnOH} \rightarrow \text{BnCl} + \text{H}_2\text{O} \quad (2.7)
\]

Indeed, the 'OH' leaving group is activated by a proton and subsequently detached from the molecule. The intermediate benzylic cation is sufficiently stabilized by delocalization over the aromatic ring. Attack of the nucleophilic chloride on the cation results then in the formation of BnCl. So BnCl could be formed during oxide formation but it could also be formed by HCl which is released in the ligand exchange. This complicates the analysis. In addition, the same reasoning can be applied for all the other compounds listed in Table 2.1. All are present in the sample 2.

In literature, the formation of 1-ethoxy-1,2-diphenylethane (\(\phi - CH_2 -\))
$CH(OH) - \phi$ was observed in the synthesis of $\text{Nb}_2\text{O}_5$ and explained by the transition state (TTS) in Figure 2.10. We could assume that the TTS applies also in our case but in contrast to the synthesis of $\text{Nb}_2\text{O}_5$, we work in acidic medium. Therefore, the formed 1-ethoxy-1,2-diphenylethane undergoes a subsequent elimination reaction to cis-stilbene ($\phi - CH = CH - \phi$), see Equation 2.8. However, again, cis-stilbene is also present in sample 2.

$$\phi - CH_2 - CH(OH) - \phi \rightarrow \phi - CH = CH - \phi + H_2O \quad (2.8)$$

![Figure 2.10: The transition state to explain the formation of $\phi - CH_2 - CH(OH) - \phi$.](image)

Although the absolute amount of stilbene is too low to ascribe the oxide formation fully to that mechanism, it will probably play a role. However, the most important reason for the observed differences between autoclave and microwave synthesis will most likely be purely kinetic. In a microwave reaction, the final reaction temperature of $220^\circ C$ is reached at a heating rate of $40^\circ C/min$. The furnace in which the autoclave is placed has a slow heating rate of $4.5^\circ C/min$. Even when the furnace reaches the final temperature, the reaction mixture itself is not yet equilibrated. In contrast, microwaves are much more efficient since they couple directly to the molecules of the reaction mixture. This considerable difference in heating rate could have an influence on the nucleation and growth process, thereby leading to smaller and monodisperse particles in the microwave. In addition, we believe that the presence of the new compounds in the microwave reaction mixture (compared to the autoclave) could be caused by local superheating effects. This enables reactions to overcome activation energies which are too high in situations of thermal equilibrium.
2.5 Conclusion

We compared a microwave assisted solvothermal synthesis of HfO$_2$ nanocrystals with a conventional heating system (autoclave). The results of the solvothermal synthesis of Buha et al. proved to be reproducible but we found evidence for another reaction mechanism, involving an ether elimination. Compared to an autoclave synthesis, the microwave synthesis is considerably faster and yields more monodisperse and smaller particles. The reaction mechanism was again investigated but the use of chlorides as reagents makes the analysis very difficult. By ligand exchange with benzyl alcohol, HCl is formed and can catalyze reactions that yield the same compounds as the oxide formation reaction. In order to obtain non-agglomerated particles, post-synthetic modification was successfully performed with dodecanoic acid and oleylamine.
References


Understanding the surface modification mechanism with $^1$H solution NMR$^1$

*Succes is how high you bounce when you hit the bottom*  
– General George S. Patton

### 3.1 Introduction

As mentioned in Chapter 2, surfactant–assisted syntheses excel in synthesis control, delivering monodisperse and colloidal stable dispersions, albeit at the expense of robustness and atom economy. Nonaqueous surfactant–free syntheses on the other hand are robust but provide less control and suffer from agglomeration, the latter being their main drawback, especially in the light of superconducting nanocomposites.

A possibly generic solution to form stable, aggregate–free dispersions of

\footnote{adapted from: De Roo, J.; Van den Broeck, F.; De Keukeleere, K.; Martins, J. C.; Van Driessche, I.; Hens, Z. Unravelling the Surface Chemistry of Metal Oxide Nanocrystals, the Role of Acids and Bases. Journal of the American Chemical Society \textbf{2014}, \textit{136}, 9650–9657}
metal oxide nanocrystals (MONCs) generated by an economic, surfactant–free synthesis could be a post–synthetic surface modification in nonpolar solvents (here defined as solvents with a dielectric constant, $\epsilon < 5$) where a small amount of pristine ligands is introduced, providing stabilization by steric hindrance. In addition, traces of unwanted side products can be removed concomitantly. In some respects, this concept is the reverse of transferring colloidal nanocrystals (NCs) — synthesized using hot injection — to polar solvents via ligand exchange\textsuperscript{1,2} and a few examples can already be found in the literature. Aggregate–free suspensions of ZrO$_2$\textsuperscript{3,4} and Fe$_3$O$_4$\textsuperscript{5} NCs — synthesized via surfactant–free methods — were obtained with fatty acids, which was ascribed to their strong and selective interaction with the MONC surface. On the other hand, the surface modification of ITO\textsuperscript{3} (indium tin oxide) proved successful with long–chain primary amines, albeit due to a weak interaction and in the case of HfO$_2$ NCs, only a combination of fatty acid and alkylamine led to a stable dispersion of individual NCs (see Chapter 2). Although all examples illustrate the benefit of the approach by the minimal amount of surfactant required to obtain a stable, aggregate–free dispersion of MONCs, the diversity and apparent randomness of the recipes indicate that a rational basis for the surface functionalization of MONCs is lacking. In this respect, an in–depth understanding of the surface chemistry during all stages of synthesis and functionalization would allow for more judicious surface modification schemes.

In this chapter,\textsuperscript{6} we take the observation that two types of surfactants are needed to obtain stable, aggregate–free dispersions of HfO$_2$ or ZrO$_2$ NCs — synthesized using the respective metal chloride and benzylalcohol — as a starting point to study the surface chemistry of these MONCs. As–synthesized HfO$_2$ or ZrO$_2$ NCs are charge stabilized in polar media by an acid/base equilibrium and as we show here, have hydrogen chloride adsorbed at their surface in nonpolar media. Focusing on HfO$_2$ NCs, we demonstrate with solution $^1$H NMR (Nuclear Magnetic Resonance) and infrared spectroscopy that exposure of the NCs to a mixture of carboxylic acids and alkylamines results in HfO$_2$ NCs capped by carboxylate ligands whereas alkylamines are lost during successive purification steps. The bound ligands exhibit a self–exchange upon addition of excess carboxylic acid similar to CdSe NCs synthesized in the presence of carboxylic acids using hot injection.\textsuperscript{7} However, unlike CdSe or PbS NCs,\textsuperscript{7,8} we find that HfO$_2$ NCs also accommodate protons on their surface, in an amount that matches that of the carboxylate moieties. The fact that the MONCs are stabilized by dissociated Brønsted acids, i.e., a proton and the conjugated base, and not by the conjugated base only is most likely linked to the higher Brønsted basicity of oxygen as compared to the heavier chalcogens. During the polar–apolar
phase transfer, the long-chain amine is also found to act as a Brønsted base, enabling the replacement of the initially present strong acid (hydrogen chloride) by the weaker carboxylic acids. We thus conclude that MONCs can exhibit a surprisingly rich surface chemistry, where the presence of acid/base equilibria extends the prevailing picture of metal sulfide, selenide or phosphide NCs synthesized by hot injection.\textsuperscript{9,10}

### 3.2 The NMR toolbox

The following chapters will rely heavily on \textsuperscript{1}H NMR (Nuclear Magnetic Resonance) spectroscopy, as very useful NMR techniques have been developed to probe the interaction of organic ligands with the inorganic nanocrystal.\textsuperscript{11} Here we review the resulting toolbox and introduce the necessary concepts for understanding this chapter. NMR is a non-destructive technique, identifying ligands and their dynamic behaviour \textit{in situ} in the colloidal dispersion.

#### 3.2.1 1D proton NMR

A normal \textsuperscript{1}H NMR spectrum of a regular-sized molecule such as oleic acid features resonances with narrow line widths and fine structure, resulting from homonuclear scalar couplings, as featured in Figure 3.1. In contrast, a molecule tightly bound to a NC, suffers from extensive line broadening (Figure 3.1) and its resonances will appear at a slightly different chemical shift, the positive or negative variation of which is solvent dependent (to the right in chloroform and to the left in toluene). The difference in line width originates from the different relaxation behaviour of a free/bound molecule.

In short, there are two types of relaxation, $T_1$ and $T_2$ relaxation. $T_1$ relaxation is the recovery of the original $Z$-axis oriented magnetization, after the perturbation (= the measurement). $T_2$ relaxation determines how fast the NMR signal decays. The exponential decay is characterized by a time constant: the $T_2$ relaxation time constant, i.e. the time it takes for the NMR signal to decline until 37% of its original intensity (Equation 3.1).

$$S = S_0 e^{-t/T_2} \quad (3.1)$$

Consequently, the smaller $T_2$, the faster the decay. Importantly, the $T_2$ is related to the resonance line width by $\nu_{1/2} = \frac{1}{\pi T_2}$. Fast relaxation (small $T_2$) leads thus to broad lines. The efficiency (= rate) of relaxation depends on the rotational freedom of the nuclei. Small or medium-sized molecules tumble fast and their resonances relax slowly while large molecules — like polymers or big proteins — tumble slowly and relax faster. Hence restricted
rotational freedom can be intuitively associated with enhanced $T_2$ relaxation. Imagine now a small molecule that is bound to a big entity (e.g., a nanocrystal). It moves (in rotation and translation mode) together with the big NC and will thus tumble slower, resulting in severe line broadening of its resonances. Differences between resonances of the same ligand may, however, be noticed because of a different internal mobility. Note that the resonances 1 and 2 in Figure 3.1 are broadenend beyond recognition while the other resonances — located further away from the surface — show only moderate broadening.

Importantly, we will use throughout this dissertation the ERETIC quantification method as provided by the Bruker software. This method requires the acquisition of a $^1$H NMR spectrum of a reference sample — with known concentration — under quantitative condition: a tuned, matched and shimmed probe, a calibrated 90 degree pulse and a sufficient recovery delay (> $5T_1$). The concentration of other samples, acquired under the same conditions, can then easily be determined. From the concentration of bound ligands and the concentration, size and shape of the NCs, we will calculate the ligand density, i.e., the number of ligands per nm$^2$ of nanocrystal surface.

3.2.2 2D DOSY (Diffusion Ordered Spectroscopy)

As already hinted upon in the previous section, a bound molecule diffuses together with the larger NC and the solvodynamic radius ($r_s$) will consist
of two contributions: the NC core radius and the thickness of the ligand shell \( r_s = r_{\text{core}} + r_{\text{ligand}} \). The solvodynamic radius is related to the diffusion coefficient \( D \) by the Stokes–Einstein equation and for spherical particles this condenses to Equation 3.2 with \( k_B \) the Bolzmann constant, \( T \) the absolute temperature and \( \eta(T) \) the temperature dependent viscosity. Hence temperature stability is of the utmost importance during diffusion measurement.

\[
D = \frac{k_B T}{6\pi \eta(T) r_s}
\]  

(3.2)

Simply put, the DOSY measurement comprises the application of a \( z \)-dependent magnetic field gradient, \( G(z) \), applied for a time \( \delta \), which causes the spins to precess at a different frequency depending on their position along the \( z \)-axis.\(^{12} \) After this gradient, a certain period — called the diffusion delay \( \Delta \) — allows time for the spins to diffuse and thus change position in the sample. When the same but opposite gradient, \( -G(z) \), is applied, the \( z \)-dependent frequency evolution may be refocussed depending on the rate of diffusion. In the absence of any motion, the resulting intensity after refocussing would be the same (neglecting relaxation). However, the spins have a translational moment and are found, after the diffusion delay, at a slightly different position along the \( z \)-axis and will therefore experience a slightly different amplitude for the opposite magnetic field gradient and refocussing will not be complete, resulting in signal attenuation. This signal attenuation is described by the Stejskal–Tanner Equation (Equation 3.3) with \( D \) the diffusion coefficient, \( \gamma \) the gyromagnetic ratio, \( \delta \) the gradient pulse duration, \( \Delta \) the diffusion delay and \( g \) the gradient strength.\(^{13;14} \)

\[
I = I_0 e^{-D\gamma^2\delta^2 g^2(\Delta-\delta/3)}
\]  

(3.3)

To avoid problems with relaxation, the DOSY measurement is acquired by varying the gradient strength \( (g) \) rather than the diffusion delay \( (\Delta) \). Fitting the intensity decay to Equation 3.3 delivers the diffusion coefficient. In the case of overlapping signals, e.g., of slow and fast diffusing species, biexponential fitting manages to separate the resonances along the diffusion axis (see further in this chapter).

### 3.2.3 2D NOESY (nuclear Overhauser effect)

One could be tempted to assume \(^1\)H and 2D DOSY NMR is all one needs for the characterization of the nanocrystal ligand shell. Although the above methods are indeed perfectly suited for tightly bound ligands, they fail to
identify ligands that exchange fast (on the NMR time scale) between a predominant free state and a minor bound state. In that case, NOESY provides the necessary information. The nOe is an effect of spin polarization transfer arising from cross–relaxation between dipolarly coupled spins after perturbation. The sign of the nOe depends on the interplay between zero quantum and double quantum cross–relaxation, two processes counteracting each other. Which cross–relaxation process will dominate the nOe, depends on the size and tumbling behaviour of the molecule. Avoiding theory and focussing on the result, Figure 3.2 shows that small molecules have a moderately positive nOe and large molecules have a pronounced negative nOe, which also builds up faster than the positive nOe. Note that the x–axis represents the rotational correlation time, the average time required for a molecule to rotate through an angle of 1 radian about any axis. Small molecules tumble fast and big molecules tumble slowly.

![Figure 3.2: The sign and magnitude of the nOe depends on the size (tumbling) of the molecule.](image)

The nOe is apparent as a cross peak in the 2D NOESY spectrum (Figure 3.3). The spectrum is processed so that the diagonal peaks have a negative sign and the cross peaks can either have the same or opposite sign. For the remainder of this dissertation, the diagonal will be colored black and positive cross peaks will be colored red. Positive cross peaks are typical for small molecules such as oleylamine, see Figure 3.3A. Negative cross peaks have the same sign as the diagonal and will also be black. When oleylamine is bound to the larger nanocrystal the cross peaks are negative (Figure 3.3B), since oleylamine has acquired large molecule behaviour and tumbles more slowly. Interestingly, oleylamine is not tightly bound to the nanocrystal and exchange fast between a free and a bound state. However, the rapid negative
nOe build-up in the bound state outweighs the slow positive nOe buildup in the free state and this allows us to identify a ligand in fast exchange, even if the bound fraction is low.

![Figure 3.3](image.png)

**Figure 3.3:** A. Oleylamine as a free molecule features only positive (red) cross peaks in the NOESY spectrum. The inset shows a ZQ artefact. B. Bound oleylamine features intense, negative cross peaks. CDCl₃ was used as solvent.

It is worth mentioning that the weak positive nOe cross peaks are often overshadowed by zero quantum (ZQ) coherence artefacts in the case of strongly, scalarly coupled protons. They are easily recognized because they have both positive and negative components (see inset in Figure 3.3A). Such artefacts can, in principle, be removed but involve a more elaborate experimental setup and we choose here to employ a standard NOESY pulse program as the ZQ artefacts only arise when the molecule has extensive rotational mobility, thus being a free ligand.

### 3.2.4 2D ROESY (Rotating frame nuclear Overhauser effect)

In the NOESY experiment, cross peaks can arise not only from the nuclear Overhauser effect but also due to chemical exchange. Consider the case of two chemical species which are in slow exchange on the frequency time scale. Two separate resonances will be detected in the corresponding 1D ¹H NMR spectrum. However, if the exchange is fast enough to happen during
the mixing time of the NOESY experiment (typically, 100–300 ms) then a negative cross peak is detected in the 2D NOESY spectrum. To distinguish exchange peaks from negative nOe peaks, a ROESY experiment is advised where nOe peaks are positive for all sizes and the chemical exchange peaks are negative.

3.3 Experimental

3.3.1 Synthesis

Colloidally stable HfO$_2$ NCs were synthesized via a microwave–assisted solvothermal process. The precursor preparation was executed in a nitrogen filled glovebox. Under vigorous stirring, 0.5 mL of dibenzyl ether was added to 0.4 mmol (0.13 g) hafnium chloride in a 10 mL microwave vial. Then quickly 4 mL of benzyl alcohol is added, yielding a clear and colorless solution after 5 minutes of stirring. The solution was subjected to microwave heating with the following temperature settings: 5 minutes at 60°C and 3 hours at 220°C. The microwave device was of the type CEM discover equipped with an auto sampler and IR temperature detection.

After synthesis the phase separated mixture is transferred to a plastic centrifugation tube and 3 mL of diethyl ether is added. After mild centrifugation (2000 rpm, 2 min) two clear and transparent phases are observed. The organic (top) phase is removed and ethanol is added to the aqueous (bottom) phase yielding 2 mL of a clear suspension. The particles are precipitated and washed once with diethyl ether.

Finally the particles are redispersed in chloroform and typically 0.2 mmol of fatty acid is added to the milky suspension and the suspension is subjected to ultrasound treatment to disperse the particles. Under stirring, oleylamine (OAm) was added until a colorless and transparent suspension is obtained. As a standard protocol, 0.15 mmol (i.e., 50 µL) is used since this already results in optically clear dispersions. The particles can be purified by adding a non–solvent (acetone), followed by centrifugation and resuspension in chloroform. ZrO$_2$ NCs were synthesized via the same protocol but with a different precursor quantity (0.56 mmol zirconium chloride) and reaction time (4 hours at 220°C).

3.3.2 Comments on synthesis

During the workup, two phases are retrieved. The organic phase is the top phase (diethyl ether, benzyl ether and benzyl alcohol) and the bottom phase
comprises colloidally stable HfO$_2$ (or ZrO$_2$) nanoparticles in only 400 µL of water. The concentration of particles in the water phase is considerably high (0.9 M of hafnium). Without the water phase at this point, no colloidal stabilization nor subsequent surface functionalization is possible. This demonstrates the influence of the precursor (HfCl$_4$) concentration. When the concentration of HfCl$_4$ is low, the amount of released etherification catalyst (HCl) is minute (see chapter 2). The amount of water thus produced is too low and a precipitate is the final result.

The amount of fatty acid (0.2 mmol) is an excess, as is the amount of amine (0.15 mmol). As suggested by the chloride density (see further), only 0.05 mmol of both would actually be needed. 0.15 mmol oleylamine corresponds to 50 µL and this works very well in all cases. It allows a standard procedure irrespective of slight variations in yield or the higher metal concentration in case of zirconia. We don’t intend to impose strict amounts of surfactants but only offer guidelines. If higher concentrations of one or both surfactants are used, the outcome remains successful but this is a waste of reagent.

### 3.3.3 General Characterization

For Dynamic Light Scattering (DLS) and zeta potential measurements a Malvern Nano ZS was used in backscattering mode (173°). Semi–quantitative analysis was obtained by calibration of a Rigaku CG Energy Dispersive X–ray Fluorescence (EDXRF) analyzer working with the fundamental parameters based quantitative analysis (RPF–SQX). Photometric determination of chloride was performed with the VWR chloride test nr. 1.14897.0001. Transmission electron microscopy (TEM) images were taken on a JEOL JEM–2200FS TEM with Cs corrector. For X–ray diffraction (XRD) characterization a Thermo Scientific ARL X'tra X–ray diffractometer was used with the CuKα line as the primary source. For infrared measurements a Perkin Elmer FT–IR spectrometer spectrum 1000, equipped with a HATR module was used.

### 3.3.4 Solution $^1$H NMR Characterization

Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance III Spectrometer operating at a $^1$H frequency of 500.13 MHz and equipped with a BBI–Z probe. For each NMR measurement a 750 µL ampule of dry deuterated solvent was used. The sample temperature was set to 298.2 K. One dimensional (1D) $^1$H and 2D NOESY (Nuclear Overhauser Effect Spectroscopy) spectra were acquired using standard pulse sequences from the Bruker library. For the quantitative 1D $^1$H measurements, 64k data
points were sampled with the spectral width set to 16 ppm and a relaxation delay of 30 sec. NOESY mixing time was set to 300 ms and 2048 data points in the direct dimension for 512 data points in the indirect dimension were typically sampled, with the spectral width set to 11.5 ppm. Off–resonance ROESY (Rotating–frame Nuclear Overhauser effect Spectroscopy) was implemented as described by Desvaux and Goldman.\textsuperscript{17} ROESY mixing time was set to 150 ms and 4 k data points in the direct dimension for 512 data points in the indirect dimension were typically sampled, with the spectral width set to 13 ppm. Diffusion measurements (2D DOSY) were performed using a double stimulated echo sequence for convection compensation and with monopolar gradient pulses.\textsuperscript{12} Smoothed rectangle gradient pulse shapes were used throughout. The gradient strength was varied quadratically from 2–95 % of the probe’s maximum value (calibrated at 50.2 G/cm) in 32 or 64 steps, with the gradient pulse duration and diffusion delay optimized to ensure a final attenuation of the signal in the final increment of less than 10 % relative to the first increment. For 2D processing, the spectra were zero filled until a 2048 – 2048 real data matrix. Before Fourier transformation, the 2D spectra were multiplied with a squared cosine bell function in both dimensions, the 1D spectra were multiplied with an exponential window function. Concentrations were obtained using the ERETric method. The diffusion coefficients were obtained by fitting the appropriate Stejskal–Tanner equation to the signal intensity decay.\textsuperscript{14}

3.4 Results

3.4.1 From aggregates to stable dispersions

HfO\textsubscript{2} NCs were synthesized using HfCl\textsubscript{4} and benzyl alcohol in a microwave–assisted solvothermal synthesis. Immediately after synthesis, the NCs could be dispersed in water, ethanol or methanol. Figure 3.4 depicts DLS measurements and TEM images of HfO\textsubscript{2} NC suspensions in ethanol. The DLS size distribution is centered at 37 nm and comparison with TEM images ascertains that individual NCs (d = 5.0 nm) are aggregated in the polar solution.

It was possible to precipitate and wash the hafnia NCs with diethyl ether and subsequently redisperse them in chloroform by the addition of two surfactants: oleylamine (OAm) and dodecanoic acid (DDAc). The combination of the two was essential to obtain a transparent colloidal suspension. The addition of only OAm or only DDAc resulted in dispersions turbid upon visual inspection. Moreover, in chloroform the average solvodynamic diam-
The solvodynamic diameter (nanocrystal and ligand shell) is 9 nm according to DLS (Figure 3.4). The TEM pictures in the inset also confirm the absence of large aggregates in chloroform. In conclusion, the combination of OAm and DDAc allowed the phase transfer from polar to nonpolar media and the concomitant de-aggregation of the hafnia NCs.

By optimizing the precursor concentration and the reaction time, we were also able to obtain colloidal stable zirconium oxide NCs via the same synthesis protocol. In contrast to ZrO\textsubscript{2} NCs synthesized from zirconium isopropoxide and benzylalcohol, these particles showed no affinity towards carboxylic acids only and again the addition of OAm was indispensable. In addition, TEM and DLS analyses showed very similar results to those of hafnia oxide (Figure 3.5). We infer that the surfactant requirements are not dominated by the nature of the metal, but also determined by the nature of the metal precursor.

3.4.2 Characterization of the as-synthesized nanocrystals

The HfO\textsubscript{2} and ZrO\textsubscript{2} nanocrystal aggregates in ethanol feature a positive zeta potential (+31 mV) and are therefore charge stabilized by a positive charge. In addition, XRF measurements evidenced the presence of chlorine in the suspension. From Chapter 2 we know that the metal chloride precursor undergoes partial exchange with benzyl alcohol, resulting in the release of...
HCl and the formation of hafnium oxide via a subsequent ether elimination step. In addition, HCl catalyzes the direct conversion of benzyl alcohol to dibenzyl ether and water. In line with zeta potential measurements in aqueous solutions from Chapter 2, we conclude that released protons can adsorb on the surface of the formed NCs, ensuring charging of the surface and thus colloidal stability of the NC clusters.

When the suspension is precipitated and washed once with diethyl ether prior to functionalization, charge neutrality must be preserved and an equal amount of chloride will co–precipitate to compensate for the adsorbed protons. To measure photometrically the chloride quantity, the NCs were re-suspended in ethanol and diluted with water after the last washing step. The measurement was repeated three times to estimate the error. Finally, the amount of adsorbed chloride was determined to be $50 \pm 2 \mu\text{mol}$ for one batch of HfO$_2$ NCs which is equivalent to a chloride density on the nanocrystal surface of $3.7 \pm 0.2\text{ nm}^{-2}$ (procedure and calculations in Appendix A). This value remained the same when the NCs were washed multiple times with diethyl ether. Similarly, a chloride density of $3.4 \pm 0.4\text{ nm}^{-2}$ was determined for ZrO$_2$ NCs. The chloride densities are almost identical for hafnia and zirconia which amounts in both cases to about 50 % of the metal (Hf or Zr) surface density. Indeed, both ZrO$_2$ and HfO$_2$ NCs have the monoclinic crystal structure and have only slightly different lattice parameters (data in Appendix A).
3.4.3 Characterization of the Nanocrystal Surface after Functionalization

After surface modification, the NCs are sterically stabilized, providing stable dispersions in nonpolar solvents. In order to elucidate the role of the two surfactants, we examined the functionalized NCs with solution $^1$H NMR techniques. Figure 3.6 depicts representative $^1$H spectra of HfO$_2$ NCs stabilized with DDAc and OAm. Sample a was purified only once with a mixture of acetone and acetonitrile, sample b was purified 5 times. For purifications purposes, we used aprotic non-solvents to avoid possible exchange reactions with the ligands.\textsuperscript{18}

![Figure 3.6: $^1$H NMR spectra of HfO$_2$ NCs in CDCl$_3$ stabilized with DDAc and OAm after 1 (spectrum a) and 5 (spectrum b) purification steps, concentration: 40 mg HfO$_2$/mL. Greek letters refer to resonances from the solvent and the nonsolvents used during purification. Roman numerals are used to assign the protons of DDAc and OAm. The broad resonance (clover symbol) is attributed to an ammonium moiety (\textit{vide infra}).](image)

The resonances below 2 ppm are signals of aliphatic moieties that are present in both OAm and DDAc (see assignments in Figure 3.6). Hence the difficulty to distinguish between both molecules in this chemical shift region. However, OAm has a characteristic resonance due to the alkene group at 5.35 ppm so by observing that signal, information specific to OAm can be obtained. Since the alkene signal has decreased to only 1% of the CH$_3$ signal in spectrum b, we conclude that OAm was largely removed by the purification, yielding a clean spectrum with only resonances belonging to DDAc. The resonances 1 and 2 of DDAc however, are not observed since...
they are severely broadened due to their impaired mobility so close to the surface.

It is typical for bound ligands to display excessive $T_2$ relaxation and consequently feature broadened resonances.\textsuperscript{11} Spectrum $b$ clearly displays this behavior — indicating bound DDAc — but the spectrum of sample $a$ is more difficult to interpret. However, in order to assess ligand binding 2D NOESY NMR is more conclusive. As indicated in Figure 3.7A, very clear negative nOe cross peaks are visible for the distinct alkene resonance belonging to OAm, clearly indicating its proximity to the NC surface in sample $a$. The nOe cross peaks between the aliphatic moieties in Figure 3.7B also confirm that dodecanoic acid interacts with the NCs in sample $b$. Furthermore, from a DOSY experiment on sample $b$, a diffusion coefficient for dodecanoic acid of $77.1 \pm 0.4 \mu m^2/s$ could be extracted. This corresponds to a solvodynamic diameter of 10.5 nm, which is comparable to the DLS analysis in chloroform shown before (Figure 3.4), hereby confirming that DDAc is tightly bound to the HfO$_2$ NCs. Finally, a concentration of 22.5 mM bound DDAc (spectrum $b$) was determined, corresponding to a ligand density of 2.8 ligands/nm$^2$. This value matches reasonably well the earlier determined chloride density, a result that already hints at the interplay between both. In addition, very similar results were observed in case of ZrO$_2$ NCs.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/3.7}
\caption{A. 2D NOESY spectrum of the HfO$_2$ NC dispersion in CDCl$_3$ after 1 purification step. The negative nOe cross peaks of oleylamine are highlighted. A zoom of the spectrum is provided in Appendix A. B. 2D NOESY spectrum after 5 purification steps.}
\end{figure}
3.4.4 Binding mode of the carboxylic acid

Given the similarity between HfO$_2$ and ZrO$_2$, we concentrate on the former for a detailed study of the ligand–surface interaction. Since OAm can be completely removed from the surface by repetitive purification, this concerns the binding of the carboxylic acids. For the next experiment we preferred oleic acid (HOAc, note that the acidic hydrogen is explicitly written) instead of DDAc because the alkene resonance strongly facilitates the interpretation of NMR spectra. Since both HOAc and DDAc will bind to the NC via the carboxylic acid functionality, this change of ligand will not affect possible conclusions on ligand binding.

Spectrum a in Figure 3.8A represents a thoroughly purified sample of HfO$_2$ NCs stabilized with HOAc. The sole occurrence of broadened resonances confirms that only bound HOAc is retained. Spectrum b was recorded after addition of excess HOAc — one equivalent with respect to the bound OAc — to the sample. Superimposed upon the broad alkene resonance of bound HOAc, a second, sharper resonance appears. Although the width of the peak suggests that this feature corresponds to free HOAc, negative nOe cross peaks are observed for both the broadened and the sharp resonance (Figure 3.8B).

This peculiar behavior was already observed for CdSe NCs stabilized with oleic acid and was explained by equilibria between three states of acid: free, entangled in the ligand shell (physisorbed) and chemically bound. Fast exchange between the free and the entangled state results in one single resonance with properties of both states. The bound state emerges as a separate resonance due to slow exchange with the entangled state. In this case it is difficult to show this exchange unambiguously in the NOESY spectrum as the broad and sharp resonances overlap (Figure 3.8B inset). However, experimentally, we observed that the addition of dodecanoic acid to oleic acid capped NCs, results in NCs capped with dodecanoic acid, confirming the chemical exchange.

The surface composition of PbS and CdSe NCs is already well understood and it was reported that a cation–rich core is charge balanced by negatively charged carboxylates. The question arises whether this is also the case for post–synthetically modified MONCs. A straightforward distinction between adsorbed oleic acid (HOAc) or oleate (OAc$^-$) is however not possible with NMR since the acidic protons, close to the surface, are indiscernible due to T$_2$ relaxation. The only way to detect these protons is to exchange them for deuterium ions.

For the exchange experiment, deuterated oleic acid ($d_1$-OAc) was prepared,
Figure 3.8: A. $^{1}H$ NMR spectra of HfO$_2$ NCs in CDCl$_3$, stabilized with OAc and OAm (spectrum a) after 5 purification steps and (spectrum b) after subsequent addition of 1 equivalent of HOAc with respect to bound oleic acid. Greek letters refer to resonances from the solvent and the nonsolvents used during purification. The protons of OAc are denoted by roman numerals. B. 2D NOESY spectrum of the HfO$_2$ NCs stabilized with OAc after addition of 1 equivalent of excess HOAc. The dotted lines are drawn to discern cross peaks of the broad and the sharp alkene resonances.

see Appendix A. The notation $d_1$-OAc signifies that only the acidic proton was replaced with deuterium. We added $d_1$-OAc (5 equivalents with respect to bound HOAc) to a thoroughly purified, water–free suspension of oleic acid capped HfO$_2$ NCs in CDCl$_3$. The detailed procedure can be found in Appendix A. The above mentioned exchange processes between bound HOAc and excess $d_1$-OAc occur and the alleged surface protons — if any — can be exchanged for deuterium, see Equations 3.4–3.5 in case of carboxylate or carboxylic acid ligands respectively.

\[
\text{HfO}_2 \cdot \text{R}_1 \text{COO} + \text{R}_2 \text{COOD} \rightleftharpoons \text{HfO}_2 \cdot \text{R}_2 \text{COO} + \text{R}_1 \text{COOD} \quad (3.4) \\
\text{HfO}_2 \cdot \text{R}_1 \text{COOH} + \text{R}_2 \text{COOD} \rightleftharpoons \text{HfO}_2 \cdot \text{R}_2 \text{COOD} + \text{R}_1 \text{COOH} \quad (3.5)
\]

Note that this exchange is a purely stochastic event and merely causes a redistribution of proton and deuterium nuclei. The observed proton concentration (derived from the carboxylic acid signal at 12 ppm) relative to the total concentration of oleic acid molecules (from the alkene resonance)
was plotted in Figure 3.9, together with the theoretical predictions according to Equations 3.4–3.5. Even in the case of carboxylates on the surface (Equation 3.4) the [H]/[OAc] ratio is larger than naught because of the incomplete deuteration of $d_1$-OAc (92.34 % deuterated). The calculations are available in Appendix A. The experimental [H]/[OAc] ratio matches the prediction based on equation 3.5, which indicates that there are exactly as many protons near the surface as there is bound oleate.

![Figure 3.9](image)

**Figure 3.9**: The ratio of the proton concentration and the total oleic acid concentration for the addition of 5 equivalents of $d_1$-OAc. The experimental and theoretical values — dependent of the assumption of carboxylate or carboxylic acid on the surface — are given.

Having the quantitative information of NMR, it would seem legitimate to regard these MONCs as stabilized by neutral carboxylic acids molecules. However, the complete absence of a carboxylic acid absorption — expected at 1710 cm$^{-1}$ — in the infrared spectrum of DDAc capped HfO$_2$ NCs (Figure 3.10) conflicts with this hypothesis. In contrast, a carboxylate peak is detected at 1548 cm$^{-1}$. In addition, around 3388 cm$^{-1}$, a broad band is observed which is typical for hydrogen bonded O–H. The small peak at 3670 cm$^{-1}$ is attributed to single hafnol moieties, Hf–O–H, similar to freestanding titanol. This again confirms (qualitatively) the presence of hydrogen atoms on the surface, however not bound to the carboxylate but directly to the nanocrystal. We conclude that the carboxylic acid is able to dissociate on the stoichiometric HfO$_2$ NC surface.

### 3.4.5 Is OAm Imperative for Stabilization?

The surface chemistry before and after modification utterly clarified, the question remains why OAm is indispensable. The experiment in section 3.4.3 points out that OAm is not strongly bound to the surface of the
Understanding the surface modification

Figure 3.10: ATR-FTIR spectrum of dried HfO$_2$ NCs capped with dodecanoic acid.

NCs. Even more, OAm seems not even relevant to the stabilization process as the NCs are perfectly stable after OAm being removed. To determine unambiguously the influence of the amine, a combination of 10-undecenoic acid and OAm was used since both have different characteristic resonances outside the aliphatic region. Figure 3.11 displays the $^1$H NMR spectra of HfO$_2$ NCs with 10-undecenoic acid in CDCl$_3$, before and after addition of OAm. Note the presence of diethyl ether ($\beta$) which was used to wash the NCs prior to suspension in chloroform. Before any OAm was added, only sharp resonances of 10-undecenoic acid were observed. This suggests that the acid does not interact with the NC surface, a conclusion confirmed by the 2D NOESY spectrum (Figure 3.12A) which only features small, positive nOe crosspeaks and zero quantum coherences typical of free ligands. The particles precipitate quickly, as could be expected for an unstabilized system.

Upon addition of only 13 mM of OAm (i.e., 10 mol % with respect to hafnium) — an amount insufficient to fully de-aggregate and stabilize the turbid suspension yet enough to avoid precipitation — the resonances of OAm appear in the $^1$H NMR spectrum and a slight broadening of all signals (except the solvent) is observed (see Figure 3.11, spectrum b). Moreover, both 10-undecenoic acid and OAm now feature negative nOe’s, indicating interaction with the NC surface (see Figure 3.12B). In line with this conclusion, DOSY yields two diffusion coefficients for the terminal olefinic resonances of 10-undecenoic acid, corresponding to free (842 ± 2 $\mu$m$^2$/s) and
Figure 3.11: Proton spectra of HfO\textsubscript{2} NCs in CDCl\textsubscript{3} with a. 10–undecenoic acid and b. with 10–undecenoic acid and OAm. Concentration: 28 mg HfO\textsubscript{2}/mL. $\beta$ refers to the resonance from the nonsolvent used during purification. The broad resonance (clover symbol) is attributed to an ammonium compound (\textit{vide supra}).

bound (96 ± 6 $\mu$m\textsuperscript{2}/s) moieties, respectively. The alkene signals of OAm on the other hand exhibit a mono exponential decay in DOSY, with a diffusion coefficient of 307 ± 5 $\mu$m\textsuperscript{2}/s in between that of free OAm (864 ± 1 $\mu$m\textsuperscript{2}/s) and bound OAm. As observed previously with CdSe, CdTe, PbS and ZnO NCs, this indicates that OAm is in fast exchange between a bound and a free state,\textsuperscript{15} a conclusion in line with the observation that OAm is readily removed by successive purification. However, the most far–reaching result is that the carboxylic acid will only bind to the NC surface if OAm is present, i.e., although absent in the eventual ligand shell, the amine is essential to the ligand exchange.

Returning to section 3.4.3, XRF measurements indicate that traces of chlorine are still present in sample a (purified only once) but not in sample b (purified 5 times). Together with the removal of chlorine the broad resonance — indicated by the clover symbol in Figure 3.6 — disappears upon successive purification. The clover resonance might be assigned to an ammonium moiety and this suggests that the purification removes oleylammnonium chloride together with the excess of OAm. Further indication that the clover resonance is OAm related is given by Figure 3.11 where again the broad feature is observed upon addition of OAm, although with a somewhat different chemical shift. This is not uncommon since the ammonium proton is easily exchanged, which makes its position dependent on the amount of
Figure 3.12: A. 2D NOESY of HfO$_2$ NCs in CDCl$_3$ with 10-undecenoic acid B. 2D NOESY of HfO$_2$ NCs in CDCl$_3$ with 10-undecenoic acid and OAm.

amine present in the sample and its chemical environment.

Provided that OAm merely serves as a base, the use of other bases — together with carboxylic acids — should equally lead to the successful surface modification of HfO$_2$ or ZrO$_2$ NCs. In Figure 3.13, DLS measurements are shown of three samples modified with three different bases. In case of OAm and triethylamine, only a stoichiometric amount was needed to ensure immediate stabilization, confirming that only a base is required. The small difference between triethylamine and OAm despite the similar pKa (in water) is attributed to steric hindrance of the tertiary amine. However, in case of pyridine, significant aggregation persists, even when used in large excess. As discussed below, this is attributed to insufficient basicity.

<table>
<thead>
<tr>
<th>Amines</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAm</td>
<td>10.6</td>
</tr>
<tr>
<td>Et$_3$N</td>
<td>10.8</td>
</tr>
<tr>
<td>pyridine</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Chapter 3

Figure 3.13: DLS measurements of HfO$_2$ NCs in CHCl$_3$ (15 mg HfO$_2$/mL) prepared by post modification with DDAc (50 mol% with respect to Hf) and either oleylamine (50 mol% with respect to Hf), triethylamine (50 mol% with respect to Hf) or pyridine (270 mol% with respect to Hf).

3.5 Discussion

In line with previous studies on CdSe,$^7$ PbS$^{22,23}$ and InP$^{24}$ NCs, we have demonstrated that carboxylic acids bind as carboxylates to HfO$_2$ and ZrO$_2$ NCs. Using IR spectroscopy, similar conclusions were arrived at for Fe$_2$O$_3$, MFe$_2$O$_4$ (M = Fe, Mn, and Co),$^{26}$ ZnO$^{27}$ and ZrO$_2$,$^{28}$ NCs, yet the combination with NMR spectroscopy enables us to complement this finding with the observation that in the case of HfO$_2$ and ZrO$_2$, the negative charge on the carboxylate moieties is balanced by surface adsorption of protons rather than by excess metal cations. Moreover, carboxylic acids will only bind as carboxylates on the as–synthesized NCs provided that a sufficient amount of oleylamine is supplied, which removes hydrogen chloride, initially present at the surface. This provides us with the possibility to use cheap chloride precursors without excluding applications where chloride is detrimental.

This set of results can be rationalized by considering the occurrence of acid–base reactions at the MONC surface. Before surface modification, in aqueous (or other polar) media, protons adsorb on the surface of the MONCs, thereby charging the surface (Equation 3.6). Since the system in chloroform has to be charge neutral, the MO$_2$ NC precipitates are more likely described as MO$_2\{\text{H}^+\text{Cl}^-\}_a$, i.e., as NCs having Brønsted acid adsorbed at their surface. Importantly, this notation does not imply that the
proton and the chloride ion are bound to one another. They may well occupy different adsorption sites on the NC. During the surface modification the chloride anions are replaced by carboxylates resulting in a stabilized colloidal suspension of aggregate-free MONCs (Equation 3.7).

\[
\text{MO}_2(s) + \text{HCl}_{(aq)} \rightarrow \text{MO}_2(\text{H}^+)_{(aq)} + \text{Cl}^-_{(aq)} \quad (3.6)
\]
\[
\text{MO}_2(\text{H}^+\text{Cl}^-) + \text{RCOOOH} \rightarrow \text{MO}_2(\text{H}^+\text{RCOO}^-) + \text{HCl} \quad (3.7)
\]
\[
\text{MO}_2(\text{H}^+\text{Cl}^-) + \text{OAm} \rightarrow \text{MO}_2 + \text{OAmH}^+\text{Cl}^- \quad (3.8)
\]
\[
\text{RCOOOH} + \text{OAm} \rightarrow \text{RCOO}^- + \text{OAmH}^+ \quad (3.9)
\]
\[
\text{MO}_2 + \text{RCOOH} \rightarrow \text{MO}_2(\text{H}^+\text{RCOO}^-) \quad (3.10)
\]
\[
\text{MO}_2(\text{H}^+\text{Cl}^-) + \text{RCOO}^- \rightarrow \text{MO}_2(\text{H}^+\text{RCOO}^-) + \text{Cl}^- \quad (3.11)
\]

This reaction is however unfavorable in chloroform because of the high solubility of the carboxylic acid, the low solubility of HCl and the difference in pKa. The role of OAm is to lower the activity of either the adsorbed protons (Equation 3.8) or the proton of the carboxylic acid (Equation 3.9). In the first case the acid can subsequently dissociate on the bare NC surface (Equation 3.10) and in the latter case the carboxylate can exchange for the chloride (Equation 3.11) but the net effect remains the same, i.e., the equilibrium of Equation 3.7 is displaced to the right by the formation of an ammonium chloride salt. In apolar solutions, the salt remains in the ligand shell, until it leaches out during the purification with polar solvents. A model for the overall reaction during the surface modification is presented in Figure 3.14, which indicates the changes in surface chemistry and stresses the role of the amine as a base. In general any base would comply but in practice the options are limited due to solubility and basicity, e.g., pyridine is too weak a base (pKa = 5.2), which means that it cannot fully deprotonate the carboxylic acid.

Figure 3.14 shows that MONCs charge stabilized in polar media by the (dissociative) adsorption of a Brønsted acid can be transferred to apolar media by acid exchange. It indicates that the factors governing this exchange reactions are the pKa of the two acids, the binding affinity of the conjugate bases to the MONC surface and the solubility of the reagents and products involved. Working on similar functionalization experiments in the case of indium tin oxide NCs, Grote et al. deducted from TGA experiments that benzyl alcohol (BnOH) is present on the surface of as-synthesized ITO NCs and the authors concluded that amines do not bind sufficiently strong to replace the BnO\(^-\) groups. In regard of the above surface chemistry model,
Figure 3.14: In the first step the surface modification mechanism is displayed. The amine captures a proton of the carboxylic acid. Subsequently the carboxylate exchanges for the chloride. The chloride is paired with the ammonium compound as a salt and remains in the ligand shell. In the second step the NC are purified (precipitated and redispersed) with polar solvents and the salt leaches out of the ligand shell. The final result is a dissociated carboxylic acid on the HfO$_2$ or ZrO$_2$ NC surface.

we can conclude that an important parameter preventing this exchange will be acidity. To remove the BnO$^-$ moiety, it would need to be protonated (pKa of BnOH $\approx$ 15) but the amines are too weak an acid (pKa $\approx$ 35) to render this exchange possible. Hence the use of our model to understand the surface chemistry of MONCs and judiciously modify their surface.

The observation that dissociated carboxylic acids are present on the MONC surface in nonpolar media — see the end result of Figure 3.14 for visual representation — is unprecedented. Metal sulfide, selenide and telluride nanocrystals for example were always found to be stabilized by carboxylate or phosphonate moieties that are charge balanced by a metal cation excess, a combination that can be described as the salt of the metal and the conjugated base of a carboxylic or phosphonic acid. Although Figure 3.14 specifically represents the surface modification of HfO$_2$ and ZrO$_2$ synthesized via benzyl alcohol and metal chlorides, the underlying surface chemistry model of stabilization by a dissociated Brønsted acid may apply to MONCs in general. Indeed, since the ability of a NC surface to adsorb protons will depend on the Brønsted basicity of the chalcogen, dissociative adsorption of acids is unlikely for metal chalcogenide NCs of the heavier chalcogens (S, Se, Te) yet it can be a common characteristic of MONCs. The observation that at least for HfO$_2$ and ZrO$_2$, the NC surface provides a medium where acid base reactions can proceed in nonpolar solvents extends considerably the possibility for ligand exchange reactions with these MONCs. Instead of only exchanging the anionic species — as
is common practice with metal sulfide, selenide or telluride NCs — the MONC surface can be modified by exchanging the proton for other cations. Moreover, Brønsted acids should now be seen as an overall neutral, yet dissociating ligand rather than a single anionic ligand, which implies that the need for proton transfer will no longer restrict ligand exchange processes. As a result, adsorption/desorption equilibria can exist between a dissolved Brønsted acid and the adsorbed conjugate base/proton pair and the direct exchange of this conjugate base/proton pair for non-dissociating neutral ligands (e.g., amines, phosphines) may be possible. This will be further explored in the next chapter.

3.6 Conclusion

We have elucidated the surface modification mechanism of HfO$_2$ and ZrO$_2$ NCs, synthesized via surfactant-free nonaqueous methods from the respective metal chlorides and benzyl alcohol. We showed that the carboxylic acid is unable to replace the initially present hydrogen chloride without the presence of a suitable base such as oleylamine. Furthermore, oleylamine is only weakly entangled in the ligand shell and can be removed by simple purification together with undesired traces of chloride, leaving a clean surface suitable for various applications. After surface functionalization of the metal oxide NCs, the carboxylic acids feature the same dynamical behavior in solution as metal chalcogenide NCs stabilized with carboxylates. However, we established the crucial difference that in case of metal oxides the negative charge of the carboxylate is not balanced by excess of cations but by protons which are adsorbed on different adsorption sites on the surface than the carboxylates. We conclude that carboxylic acids can dissociate on the surface of the metal oxide NCs which is an unprecedented and fascinating result that opens new possibilities for the manipulation of metal oxide NCs in general.
References


Understanding the surface modification and Binding. *Journal of the American Chemical Society* 2013, 135, 18536–18548.


The NC(X)$_2$ binding motif, extending the covalent bond classification\textsuperscript{1}

\textit{The essence of science is that it is always willing to abandon a given idea for a better one}  
- H.L. Mencken

4.1 Introduction

Colloidal nanocrystals (NCs) are hybrid objects where the properties of the core and surface both determine the characteristics of the entire NC. The surface is often capped by a shell of (in)organic ligands which determine the stability of NC dispersions and the physical and chemical properties of NCs and NC assemblies.\textsuperscript{1-4} As a result, NC surface chemistry, i.e., the understanding of and control over the ligand shell, has become one of the central themes in NC research.

In contrast to CdSe NCs, the surface of ZnO, TiO$_2$, ZrO$_2$ and HfO$_2$ NCs can adsorb protons. In case of fatty acid capped ZrO$_2$ and HfO$_2$ NCs, we showed in chapter 3 that both carboxylate and proton bind separately to the metal oxide NC surface. Although we suggested that this internal proton source could result in new exchange reactions, no evidence for this was given yet. In this chapter, we investigate exchange and self-adsorption of oleic acid on HfO$_2$ and ZrO$_2$ NCs, benchmarked against oleate stabilized CdSe NCs. We observe clear differences when both NC dispersions are titrated with octylamine, an L-type ligand. This results in a gradual displacement of oleic acid from the oxide NCs, opposite from CdSe NCs where the immediate release of cadmium oleate is observed. Moreover, oleic acid added to a purified HfO$_2$ dispersion binds to the NCs, a behavior that is not observed in case of CdSe. These findings indicate that the dissociated carboxylic acid bound to HfO$_2$ NCs can be described by an NC(X)$_2$ binding motif, i.e., a combination of a cationic X-type ligand (H$^+$) and an anionic X-type ligand (RCOO$^-$). This new binding motif results in exchange characteristics comparable to that of simple L-type ligands.

### 4.2 The Covalent Bond Classification

The Covalent Bond Classification (CBC) provides an apt framework to describe NC–ligand binding motifs. Ligands are defined as L-, X- or Z-type depending on the number of electrons that the neutral ligand contributes to a NC–ligand bond (2, 1 or 0 respectively). This classification is unambiguous and convenient to conceptualize and understand covalent interactions. It allows to label distinct NC–ligand model systems (Figure 4.1) and to rationalize ligand exchange reactions. L-type ligands such as amines and phosphines are neutral donors of a free electron pair. In apolar solvents, they coordinate to the surface metal ions of stoichiometric NCs to yield overall charge-neutral objects. Z-type ligands are neutral electron-pair acceptors (e.g., metal carboxylates) that bind to the surface anions of stoichiometric NCs. In NC surface chemistry, X-type ligands are often presented as negatively charged ligands (RCOO$^-$, Cl$^-$) that bind to excess surface cations of non-stoichiometric NCs. Although this concept is certainly correct, it is a too restrictive description as we argue in this chapter. According to the original CBC, ligands must be classified in their neutral form. X-type ligands are thus formally regarded as radicals (Figure 4.1).

Obviously, desorption or adsorption of L- and Z-type ligands involves the separation or combination of two neutral, closed shell moieties. In contrast,
Chapter 4

Figure 4.1: The Covalent Bond Classification (CBC) considers L–type ligands as Lewis bases and Z–type ligands as Lewis acids. X–type ligands are radicals.

self–desorption of X–type ligands implies the formation of either radicals or charged species. The former process is generally unfeasible and the latter is thermodynamically unfavorable in apolar media due to the low dielectric screening. For the same reason, it would be impossible to exchange X–type ligands for L–type ligands. Anionic X–type ligands can only be traded for other anionic X–type ligands by the transfer of a proton or trimethylsilyl group.\cite{5,12,16–19}

4.3 Experimental

HfO$_2$ and ZrO$_2$ NCs were synthesized according to the methods described in the previous chapters.

4.4 nm CdSe QDs were synthesized using the method developed by Jaseniak et al.\cite{20} A homogeneous ODE–Se precursor was prepared by heating up 3.5 mmol of Se powder in 35 mL of ODE under nitrogen atmosphere for 2 h and 30 min. The cadmium oleate precursor was prepared by dissolving 1.55 mmol of CdO in 12.4 mmol of oleic acid and 11.6 mL of ODE and heating up to 250 °C until complete dissolution.

The synthesis was performed by adding 3 mL of the Cd precursor solution to 7.75 mL of ODE in a three neck flask and flushing the mixture at 100 °C for 30 min. Subsequently the temperature was raised to 260 °C and 3 mL of the ODE–Se precursor were injected into the reaction mixture. After injection, the reaction was carried out at 235 °C for 50 min. The obtained solution was purified 3 times by precipitating the particles with methanol and redissolving them in toluene. The final product was dissolved in 3 ml of toluene.
4.4 Results and discussion

4.4.1 Establishing ligand exchange

HfO$_2$, ZrO$_2$ and CdSe NCs were synthesized according to established procedures and oleic acid (HOAc) was each time employed as ligand. Note that HOAc can populate 3 different states; chemisorbed to the NC, physisorbed in the ligand shell and free in solution (see also Chapter 3). However, the $^1$H NMR spectrum of a purified HfO$_2$ NC dispersion features only broadened signals of chemically bound HOAc (Figure 4.2), i.e., no free or physisorbed acid is present in the sample. Upon addition of octylamine (Am), the alkene resonance changes and a new signal appears at a slightly lower chemical shift (Figure 4.3A). This is a mixed state resonance, the result of fast exchange between physisorbed and free HOAc, featuring a population averaged chemical shift and line width. Indeed, this signal becomes more intense and sharpens with increasing Am concentration, indicating the increasing contribution of the free state to the average. However, the physisorbed contribution is still apparent from the negative nOe cross peaks which are characteristic for bound states (Figure 4.3B).

Regarding the resonances of the amine, we focus on the $\alpha$–CH$_2$ of Am (2.5 ppm) since it is well–separated from the aliphatic resonances of HOAc. Only a single resonance without fine structure is observed and this resonance clearly leads to negative nOe cross peaks (Figure 4.3B). From these two features we infer that Am is in fast exchange between a bound and a free state. The above results thus suggest that HOAc is displaced by Am.

As reported by Owen et al. the addition of amines to oleate capped CdSe
NCs results in a release of coordinated cadmium oleate. Although no subtle changes in the alkene resonance were analyzed — probably because of the considerably higher amine concentration — this raises the question as to whether our results with HfO$_2$ could be explained by a release of hafnium oleate instead of oleic acid. We therefore repeated the Am titration with a CdSe NC dispersion, adding similar amounts of amine as with the HfO$_2$ NCs.

Again, a sharper alkene resonance appears at a lower chemical shift (see Figure 4.4A). Since this signal features negative nOe cross peaks (Figure 4.4B), we again attribute it to a mixed state resonance with, however, slightly different characteristics. Firstly, the fraction of mixed state — the released species — is much larger for CdSe than for HfO$_2$ NCs, as determined by deconvolution of the alkene resonance (Figure 4.5). Secondly, a comparison of the blue spectra in Figure 4.3A and 4.4A, both having a more or less equal amount of released alkene (Figure 4.5), shows that the mixed resonance of CdSe NCs appears at lower chemical shifts and is more narrow. We thus conclude that the free state is more predominant in case of cadmium oleate release. Indeed, even a first hint of scalar coupling fine structure is observed for the mixed resonances in Figure 4.4A, typically a characteristic of free molecules. Since cadmium oleate can be further coordinated in solution by excess Am, it will populate less the physisorbed state due to steric hindrance. This sort of behavior is not observed in the titration of HfO$_2$ NCs, giving a first indication that the released species is not hafnium oleate.
**Figure 4.4:** A. A new alkene resonance appears upon addition of Am to a CdSe NC dispersion in toluene-$d_8$. B. 2D NOESY spectrum of the sample with 7.2 equivalents of octylamine. Although there is an impurity, the resonance shows only positive, red nOe cross peaks (see dashed oval) and thus the impurity doesn’t interact with the surface.

**Figure 4.5:** Am releases a higher fraction of original ligand at CdSe NCs than at HfO$_2$ NCs. The deconvolution spectra are provided in Appendix A

### 4.4.2 The nature of the released species

To further confirm the nature of the released species we combined IR, NMR and XRF analysis. Upon addition of Am to HfO$_2$ NCs, the expected carboxylic acid band at 1720 cm$^{-1}$ is absent in the IR spectrum (Figure 4.6). However, if HOAc were released during ligand exchange, it could be deprotonated by the excess of Am and form an ion pair. Indeed, the shape and
position of the carboxylate peak (1570 cm\(^{-1}\)) of Am treated NCs is essentially the same as for a mixture of HOAc and Am. However, IR does not allow to differentiate between the ion pair and hafnium oleate. Therefore, we precipitated the Am treated NCs with methanol. After centrifugation, the supernatant was dried under vacuum and the resulting oil was dissolved in deuterated methanol and measured in NMR and XRF. An alkene resonance with fine structure was observed in the \(^1\)H NMR spectrum (see Figure A.6 in Appendix A) indicating the presence of a free species. The intensity of the resonance was comparable to the mixed state resonance in the titration experiment, confirming that we were able to quantitatively separate the NCs from the released species. In addition, no hafnium was detected by XRF analysis (see Figure A.7 in Appendix A) so we finally conclude that the displaced species is oleic acid and not hafnium oleate.

\[ \text{NC(HOAc)} + 2 \text{Am} \rightleftharpoons \text{NC(Am)} + [\text{OAc}^-\text{HAm}] \quad (4.1) \]

The reaction comprises three equilibria; the desorption of oleic acid (Equa-
tion 4.2), the adsorption of octylamine (Equation 4.3) and the formation of an ion pair (Equation 4.4).

\[
\text{NC(HOAc)} \rightleftharpoons \text{NC}^* + \text{HOAc} \quad (4.2)
\]

\[
\text{NC}^* + \text{Am} \rightleftharpoons \text{NC(Am)} \quad (4.3)
\]

\[
\text{HOAc} + \text{Am} \rightleftharpoons [\text{OAc}^-\text{HAm}] \quad (4.4)
\]

We calculated a reaction quotient of \(2.0\pm0.6 \times 10^{-5}\) for the overall exchange reaction (Equation 4.1), confirming that carboxylic acids bind stronger to the NC surface than amines (calculation in Appendix A). Importantly, the reaction quotient remains only constant for different amine concentrations if equilibrium 4.4 is included (Figure 4.7).

![Figure 4.7: The exchange reaction quotient in function of amine concentration, with and without the inclusion of Equation 4.4.](image)

This highlights the central role of the ion–pair formation in the exchange reaction, which becomes even more clear from the exchange reaction’s temperature dependence. Indeed, somewhat surprisingly, we find that with increasing temperature the exchange equilibrium is displaced to the left, i.e., less HOAc is removed from the surface by Am (Figure 4.8). The exchange is therefore reversible and exothermic. This would have been difficult to understand if the exchange was regarded as a combination of Equation 4.2 and
4.3. Such a reaction would be endothermic since amines bind weaker than carboxylic acids. However, reaction 4.4 is apparently sufficiently exothermic to render the whole exchange exothermic. Hence the identification of reaction 4.4 as the main driving force of the exchange.

The same temperature dependence is observed for the CdSe system (Figure 4.8). In that case, the driving force for exchange is most likely the exothermic coordination of octylamine to the cadmium oleate complex, again rendering the overall reaction exothermic. In practice, this means that at high temperatures — typical for NC syntheses — the adsorption of amines is negligible compared to the binding of metal carboxylates or carboxylic acids.

4.4.3 Auto–desorption and auto–adsorption of carboxylic acids

Auto–desorption of HOAc (Equation 4.2) does not take place without external driving force. Even when the temperature was raised to 130 °C, no indication of free HOAc was observed in the ¹H NMR spectrum (Figure 4.9). Although heating induces the appearance of a small alkene signal at 5.33 ppm, we refrained from attributing it to released oleic acid because the latter would have been involved in fast exchange between a bound and a free state, resulting in a broadened resonance. However the new resonance is sharp and even features fine structure. In addition we observe in the
spectrum at 60 °C a broadened resonance at 3.6 ppm which we ascribe to ethanol. Indeed this molecule is also bound to the surface as evidenced by negative nOe cross peaks (Figure 4.10A).

Figure 4.9: The purified dispersion of HfO$_2$ NCs features only broadened resonances of bound oleic acid at 60 °C in dichlorobenzene-$d_4$, $[\text{HOAc}] = 19$ mM. New resonances appear in the spectrum upon heating to 130 °C.

Together with the sharp alkene resonance, also a quadruplet at 4 ppm increases in intensity and both resonances are clearly correlated (see Figure 4.10B). Therefore we assume that the ethyl ester of oleic acid is formed but we will elaborate further on this result in Chapter 5. In conclusion, no auto–desorption of oleic acid — as such — is observed.

However, we were able to demonstrate the reverse reaction, auto–adsorption, by gradually adding excess HOAc to a HfO$_2$ NC suspension which was purified 5 times with acetone (Figure 4.11A). The absolute concentration of bound ligand increased with 17 % (at 0.4 eq excess HOAc), as determined by deconvolution. HOAc is thus capable of spontaneous dissociation on the oxide surface at room temperature. The free adsorption sites probably emerged from the extensive purification. Indeed, DLS measurements (Figure 4.11B) confirm that aggregates are formed during the purification, an indication of ligand stripping. In contrast, HOAc does not display such unforced binding behavior towards CdSe NCs.$^5$
Figure 4.10: A. Cross peaks for bound oleic acid and ethanol appear in the NOESY spectrum. B. The concentration (relative to the total alkene resonance) of the quadruplet at 4 ppm and the free alkene resonance coincides very well over time.

Figure 4.11: A. Change of the alkene resonance upon progressive addition of excess oleic acid, $[\text{HOAc}]$. B. DLS measurements of HfO$_2$ NCs directly after surface modification in CHCl$_3$ and after 5 subsequent purification steps with acetone.
4.4.4 Implications and generalization

Figure 4.12 summarizes the ligand exchange processes we observed at HfO$_2$ NCs. First, there is the exchange of carboxylic acids for amines, typical L–type ligands. Note that the actual driving force is the acid–base ion pair formation. Second, self–adsorption of carboxylic acids on the HfO$_2$ surface was recognized.

These reactions can be rationalized within the concepts offered by the CBC. An X–type ligand is a radical, which can either take an electron from the NC (RCOO$^-$) or donate its own electron (H$^+$) upon formation of an ionic NC–ligand bond, turning the X–type ligand in either an anion or a cation. Hence, dissociative adsorption of carboxylic acids brings two X–type moieties on the NC surface, proton and carboxylate, in a binding motif we classify as NC(X)$_2$. Opposite from a single X–type ligand, this overall charge neutral pair of X–type ligands can be exchanged for L–type ligands, either by direct release of the (X)$^+$(X)$^-$ combination or by the formation of complexes such as the ion pair observed here, see Equations 4.5 and 4.6.

$$NC(X)_2 + L \rightarrow NC(L) + (X)^+(X)^- \quad (4.5)$$

$$NC(X)_2 + 2L \rightarrow NC(L) + [(LX)^+(X)^-] \quad (4.6)$$
To explore the general implications of these findings, we repeated the Am titration using ZrO$_2$ NCs capped with HOAc. Importantly, the ZrO$_2$ NCs were synthesized with a different precursor, leading to a crystallographic phase and initial surface chemistry different from that of the HfO$_2$ NCs used before. Nevertheless, also in this case we observe the release of HOAc acid upon titration with Am (Figure 4.13), a result indicating that our model may apply to metal oxide NCs in general. Indeed, the ability to accommodate protons on the surface depends on the basicity of the anion rather than on the nature of the metal although the latter’s influence cannot be fully excluded.

![Figure 4.13](image)

**Figure 4.13:** A. $^1$H NMR spectrum of ZrO$_2$ NCs capped with oleic acid in toluene-$d_8$, [HOAc] = 21.3 M. B. Change of the alkene resonance upon progressive addition of octylamine (Am).

### 4.5 Conclusion

In conclusion, we have shown that octylamine releases oleic acid from HfO$_2$ and ZrO$_2$ NCs while cadmium oleate is released from CdSe NCs. The ligand exchange reaction is rendered exothermic and thus impeded at high temperatures — relevant for NC syntheses — by the formation of an acid/base pair in case of oxide NCs or a metal complex in case of CdSe NCs. Finally, oleic acid features self-adsorption at the oxide but not at the CdSe NC surface.

We argue that the exchange characteristics of carboxylic acids bound to metal oxide NCs result from their dissociative adsorption. The NC surface thus contains equal amounts of anionic and cationic X–type ligands, a binding motif we label as NC(X)$_2$. Importantly, acknowledging the occurrence of the NC(X)$_2$ binding motif brings about a new class of NC–ligand systems
— stoichiometric NCs with overall neutral pair of X–type ligands — in addition to cation rich NCs with anionic X–type ligands and stoichiometric NCs with neutral Z–or L–type ligands. Our work indicates that this new NC–ligand class will be most relevant to understand the surface chemistry of metal oxide NCs in general.
References


Oxide Nanocrystals, the Role of Acids and Bases. *Journal of the American Chemical Society* 2014, 136, 9650–9657.


Ligand displacement and catalysis

The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time.
– Rudolf Diesel

5.1 Introduction

Over the last 20 years, colloidal nanocrystals (NCs) have emerged as a new and extremely versatile state of matter. The physical and chemical properties of these hybrid objects depend both on the inorganic core and the ligand–capped surface with the latter also determining the colloidal stability. Controlling the surface has proven indispensable for all NC applications, ranging from thermoelectrics and thin film electronics to electrochromic applications. In this respect, metal oxide nanocrystals stand out from other nanocrystals as carboxylic acids adsorb on their surface by dissociation in carboxylates and protons (see Chapter 3 and 4), the latter already proving

1 adapted from: De Roo, J.; Van Driessche, I.; Martins, J. C.; Hens, Z. Colloidal metal oxide nanocrystal catalysis by sustained chemically driven ligand displacement Nature materials 2016 doi:10.1038/nmat4554
Chemical exchange and catalysis is essential in electron transfer reactions.⁶

### 5.1.1 The Covalent Bond Classification 2.0

The first step in surface manipulation is understanding the NC–ligand bond and the Covalent Bond Classification (CBC) provides an apt theoretical framework for this purpose.⁷ Although the CBC was already explained in Chapter 4, we will quickly revisit it here since we modified the implementation of the CBC to nanocrystals in that same chapter. Ligands are defined as L−, X− or Z− type depending on the number of electrons that the neutral ligand contributes to the NC–ligand bond (2, 1 or 0 respectively, see Figure 5.1). L− type ligands are Lewis bases,⁸,⁹ Z− type ligands are Lewis acids,¹⁰ both coordinating to stoichiometric NCs and the respective binding motifs are NC(L) and NC(Z). X− type ligands are radicals in their neutral form, that can turn into ionic species when forming an ionic bond with the NCs. X− type ligands such as hydroxide,¹¹ halides¹² and carboxylates¹³ bind to surface cations in a NC(MXₙ) binding motif. Only in the special case of metal oxide NCs, it was shown that carboxylic acids provide two X− type moieties, retrieved as surface adsorbed protons and carboxylates and denoted as NC(X)₂.¹⁴,¹⁵

![The covalent bond classification](image)

**Figure 5.1:** L− type ligands are Lewis bases, donating 2 electrons to the NC–Ligand bond. Z− type ligands are Lewis acids, offering an empty orbital. X− type ligands offer 1 electron to the NC–ligand bond and are thus formally regarded as radicals.

### 5.1.2 Ligand exchange or displacement in apolar solvents

Charge balancing requirements restrict ligand exchange reactions in apolar solvents, in first instance, to L− for L and X− for X exchange processes (see Figure 5.2).⁸ These processes are governed by adsorption enthalpy (L−
and X–type) and acidity (X–type), hampering exchange for weaker binding and/or less acidic ligands. More elaborate reactions involve L–type ligands that promote the desorption of Z–type cadmium carboxylates\textsuperscript{10} from CdSe NCs (note that NC(MX\textsubscript{2}) = NC(Z)) or the displacement of carboxylic acids\textsuperscript{15} (NC(X)\textsubscript{2}) from HfO\textsubscript{2} NCs, see Figure 5.2. These reactions are facilitated by an enthalpy gain since the leaving ligand forms a complex or ion pair with the L–type ligands. Nevertheless, these reactions still rely on a huge excess of new ligand and work best for strong Lewis bases such as amines whereas obtaining nanocrystals stabilized by, for example, alcohols proved nearly impossible.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_2.png}
\caption{L–for–L exchanges, X–for–X exchanges and Z–type displacements are illustrated with the model system of CdSe but could be extended to other NCs such as PbS, PbSe, CdS, ZnS, etc. NC(X)\textsubscript{2} type displacements are only known for oxides, e.g., HfO\textsubscript{2}.}
\end{figure}

In this chapter,\textsuperscript{16} we show that in the case of HfO\textsubscript{2} NCs, weakly binding ligands such as amines and alcohols chemically convert tightly bound carboxylic acids in non-coordinating amides or esters and thus promote acid/amine and acid/alcohol ligand displacement. Furthermore, the ester formation is sustained when the ligand shell is continuously replenished with carboxylic acids, a reaction not occurring in the absence of the NCs. We relate this un-
expected colloidal nanocatalysis to the dissociative NC(X)$_2$ binding of carboxylic acids to oxide NCs and further underscore its potential by showing that colloidal HfO$_2$ NCs also catalyze transesterifications. While promising, as it may combine the benefits of heterogeneous and homogeneous catalysis,$^{17}$ colloidal nanocatalysis is often problematic since surface-adsorbed ligands, needed for colloidal stability, prevent reagents from reaching catalytically active surface sites.$^{18}$ Hence the description of thiol ligands as a double-edge sword for catalytic CO oxidation by Au nanoclusters$^{19}$ and a general preference for heterogeneous approaches using supported, ligand-stripped nanocrystals over colloidal nanocatalysis.$^{18,20,21}$ By using reagents as ligands however, chemically driven ligand displacement bypasses this colloidal stability / catalytic activity conundrum, thus turning colloidal nanocrystals into effective nanocatalysts.

5.2 Experimental

5.2.1 Esterification catalysis

HfO$_2$ NCs were synthesized via an established microwave-assisted solvothermal process, see Chapter 3. CdSe NCs were synthesized using the method developed by Jaseniak et al.$^{22}$ The HfO$_2$ NC dispersion in chloroform is evaporated and deuterated o-dichlorobenzene (DCB) is added. The total content of NCs is 21.8 mg (0.104 mmol) in 500 µL DCB. Although at room temperature, the oleic acid capped NCs are not colloidal stable in DCB, heating to 60 °C or more yields a colorless and transparent suspension. The warm suspension is transferred to a screw capped NMR tube and the concentration of bound oleic acid is determined to be 21.4 mmol/L (yielding a ligand density of 2.4 nm$^{-2}$ for the NCs with a diameter of 5 nm and an acid loading of 0.5 mmol/g). Ethanol (4 µL) and oleic acid (8 µL) are added and the final concentration, measured at 60 °C, was 115 mmol/L ethanol and 70 mmol/L HOAc (bound + excess). The temperature is subsequently raised in a stepwise manner to 130 °C and kept there for 3 hours while 1D spectra are continuously recorded.

5.2.2 Characterization

Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance II Spectrometer operating at a $^1$H and $^{13}$C frequency of 500.13 MHz and 125.77 MHz respectively and featuring a $^1$H, $^{13}$C, $^{31}$P TXI-Z probe. The sample temperature was set to 298.15 K unless otherwise stated. One-dimensional (1D) $^1$H and 2D $^1$H-{$^{13}$C} HSQC, 2D $^1$H-{$^{13}$C}
Chapter 5

HMBC, TOCSY and NOESY (Nuclear Overhauser Effect Spectroscopy) spectra were acquired using standard pulse sequences from the Bruker library. For the quantitative 1D $^1$H measurements, 64k data points were sampled with the spectral width set to 16 ppm and a relaxation delay of 30 sec. NOESY mixing time was set to 300 ms and 4096 data points in the direct dimension for 512 data points in the indirect dimension were typically sampled, with the spectral width set to 11.5 ppm. For 2D processing, the spectra were zero filled to a 4096 - 2048 real data matrix. Before Fourier transformation, the 2D spectra were multiplied with a squared cosine bell function in both dimensions, the 1D spectra were multiplied with an exponential window function. Concentrations were obtained using the Digital ERETIC method as provided in the Bruker Software package. Diffusion measurements (2D DOSY) were performed using a double stimulated echo sequence for convection compensation and with monopolar gradient pulses. Smoothed rectangle gradient pulse shapes were used throughout. The gradient strength was varied linearly from 2-95 % of the probe’s maximum value (calibrated at 50.2 G/cm) in 64 steps, with the gradient pulse duration and diffusion delay optimized to ensure a final attenuation of the signal in the final increment of less than 10 % relative to the first increment.

5.3 Results

5.3.1 Ligand displacement

HfO$_2$ NCs were synthesized by a solvothermal process and subsequently capped with oleic acid to ensure colloidal stability, a process resulting in a ligand shell of oleates and protons. The NC-oleate binding was apparent from the broadened oleyl resonances in the $^1$H NMR spectrum of the dispersion in o-dichlorobenzene-$d_4$, see Figure 5.3. Note that the spectrum was acquired at 60 °C since the NCs are not dispersible in o-dichlorobenzene-$d_4$ at room temperature.

Our general strategy to have carboxylic acids replaced by amines on HfO$_2$ NCs is illustrated in Figure 5.4A. Rather than a direct amine-for-acid exchange, which proved an unfavorable process, see Chapter 4 we envisaged here a process where one amine equivalent converts one acid equivalent in an amide, which is released from the surface, allowing a second amine equivalent to bind to the uncovered surface site. A first indication of this process occurring is the appearance of (green) resonances pertaining to the octyl amide of oleic acid in the $^1$H NMR spectrum of a mixture of oleic acid capped HfO$_2$ NCs and octylamine, kept at 130 °C (Figure 5.4B, detailed
Chemical exchange and catalysis

Figure 5.3: Purified dispersion of HfO$_2$ NCs in o-dichlorobenzene-$d_4$ (DCB) features only broadened resonances of bound oleic acid, [HOAc] = 19 mM, measured at 60 °C since the NCs were not dispersible in DCB at room temperature. A spectrum of HOAc in DCB without particles was measured as a reference.

resonance assignment can be found in Appendix A). The alkene resonance (5.5 ppm) comprises both a broad resonance of remaining bound oleic acid and a sharp resonance of the formed amide. The width and fine structure of the latter suggest that the amide does not coordinate to the NCs, a conclusion confirmed by positive (red) cross peaks in the NOESY spectrum (Figure 5.4C). In contrast, the resonances of octylamine and the remaining oleic acid feature negative (dark-blue) nOe cross peaks, indicative of bound ligands. Hence, amide formation coincides with the development of a mixed ligand shell, comprising both oleic acid and octylamine.

The same strategy applied to the replacement of carboxylic acids by alcohols via ester formation, Figure 5.5A. Again, its success follows from the sharp (blue) ester resonances showing up in the $^1$H NMR spectrum (Figure 5.5B, detailed resonance assignment in Appendix A) and the ethanol resonances featuring clear negative cross peaks in the NOESY spectrum (Figure 5.5C).

The DOSY spectrum (Figure 5.6) sheds more light on the dynamic nature of the NC-ligand bond. The diffusion coefficient of the remaining oleic acid is small (36 µm$^2$/s), corresponding to a solvodynamic diameter of 9 nm (inorganic core + organic ligand shell). Oleic acid is thus tightly bound to the NCs as opposed to ethanol (or octylamine), which exchanges rapidly between a free and a bound state as evidenced by the combination of its large diffusion coefficient (1524 µm$^2$/s) and its negative nOe cross peak. 24
Figure 5.4: A. Carboxylic acid ligands are converted to amides, leading to amine binding. B. $^1$H NMR spectra of a HfO$_2$ NC suspension, stabilized by oleic acid, before and after addition of 10 equivalents of octylamine and reaction at 130 °C for three hours. Spectra acquired at 60 and 130 °C respectively. C. Room temperature NOESY spectrum of the resulting suspension. Note how the N-H resonance moved downfield due to the temperature change.
Figure 5.5: A. Carboxylic acid ligands are converted to esters, leading to alcohol binding. B. $^1H$ NMR spectra of a HfO$_2$ NC suspension, stabilized by oleic acid in o-dichlorobenzene-$d_4$, before and after addition of 7 equivalents of ethanol and reaction at 130 °C. Spectra acquired at 60 and 130 °C respectively. C. Room temperature NOESY spectrum of the resulting suspension. The alkene resonance of bound oleic acid is not observed due to the combination of its short T$_2$ relaxation time, the length of the convection compensating pulse program and the large NC size.
Figure 5.6: Room temperature DOSY spectrum after heating a HfO$_2$ NC suspension, stabilized by oleic acid and with excess of ethanol at 130 °C for 3 hours.

5.3.2 Tuning the ligand shell composition

In contrast to aggressive stripping reagents, ligand displacement by amide or ester formation is a rather gentle reaction. Since it was performed in-situ in the NMR spectrometer, the gradual change in ligand shell composition could be monitored (Figure 5.7A). A conversion plateau is observed, indicating that this reaction is fully equilibrium controlled and thus reversible. However, the reaction proved kinetically impeded below 100 °C, which makes for a ready tailoring of the ligand shell composition by adjusting the reaction time at 130 °C and subsequently locking that configuration at lower temperature, see Figure 5.7B. Furthermore, the equilibrium could be manipulated to almost full displacement by, e.g., the addition of a larger excess alcohol or amine (however still far below the quantities used in reference 10, Figure 5.8). Interestingly, we found that opposite from the original oleic-acid-only ligand shell, a mixed oleic acid / octylamine (or ethanol) capping, renders HfO$_2$ NCs dispersible in o-dichlorobenzene also at room temperature, a result emphasizing the practical importance of ligand shells with a finely tuned composition.
Figure 5.7: A. The fraction of bound oleic acid decreases gradually with time until equilibrium when the HfO$_2$ NC suspension in $o$-dichlorobenzene-$d_4$ is heated with either 7 equivalents of ethanol or 10 equivalents of octylamine. B. The fraction of bound oleic acid is decreasing at 130 °C due to amide formation with 8 equivalents of octylamine. However at 60 °C, even before equilibrium is reached, that fraction remains constant, i.e. kinetic trapping of the ligand shell composition.
Figure 5.8: When 30 equivalents of amine are used and the reaction mixture is heated for 12 hours, most of the bound oleic acid is transformed in amide, effectively stripping the surface.

5.3.3 Esterification catalysis

Since esters are industrially important chemicals, the outcome of the chemically driven ligand displacement - esters and HfO$_2$ NCs with loosely bound alcohol ligands - inspired us to use this ligand displacement reaction for catalysis, Figure 5.9A. After esterification, an adsorption site is left for the excess alcohol to bind. However, if both alcohol and carboxylic acid are present in excess, alcohol binding will be suppressed by carboxylic acid adsorption. This may lead to a sustained ester formation while the HfO$_2$ NCs maintain their carboxylic acid capping, i.e., a catalytic process.

We thus added oleic acid and ethanol to oleic acid capped HfO$_2$ NCs and monitored the development of the ester resonances at 130 °C, Figure 5.9B. Initially, the ester resonances linearly increase with time (Figure 5.9C), the ethanol resonances decrease and the bound oleic acid resonances keep a steady intensity during the whole experiment (Figure A.10 and 5.10, respectively).
Figure 5.9: A. Starting from pristine hafnium oxide NCs, the alcohol penetrates the ligand shell and reacts with the bound acid to form an ester. This leaves a free adsorption site which is subsequently occupied by a new carboxylic acid molecule and the catalytic cycle continues. B. NMR spectra in o-dichlorobenzene-d₄ acquired at different reaction times at 130 °C for the esterification of oleic acid and ethanol with HfO₂ NCs as catalyst. Ratio of HOAc and EtOH = 1:1.6. C. The esterification rate at different temperatures.
Since no ester was formed in a control experiment without HfO$_2$ NCs (Figure A.11), this indicates that all free adsorption sites — created by ester formation — are immediately replenished by fresh oleic acid, restoring the surface composition of the catalyst.

The overall activation energy of the reaction was estimated at approximately 88 kJ/mol in the temperature interval 110–130 °C (see Figure 5.11). In addition, the esterification reaction was monitored using methanol and after three hours, equilibrium was reached with a catalytic turnover number, TON = 3.4, further underpinning the catalytic nature of the process (Figure 5.12).

In a control experiment, in the absence of nanocrystals, no ester was detected (Figure A.11 in Appendix A) and similarly CdSe NCs - featuring a binding motif where X–type carboxylates bind to excess surface Cd$^{2+}$ (without co-adsorption of protons) - did not catalyze ester formation (Figure A.12 in Appendix A). This emphasizes the importance of the NC(X)$_2$ type binding motif and the underlying chemistry of the metal oxide surface - providing both acidic and basic adsorption sites - for catalysis. A tentative reaction pathway is represented in Figure 5.9A, where the carbonyl carbon is rendered electrophilic by coordination of the carboxylate to hafnium and back-bonding of the surface proton. In addition, attraction of the alcohol proton by an oxygen anion may increase the alcohol’s nucleophilicity. The scheme highlights the role of the metal oxide surface where the Lewis acid and base properties of the metal cations and the oxygen anions can both

![Figure 5.10: Upon heating a HfO$_2$ NC dispersion at 130 °C with excess oleic acid and ethanol, the broadened resonance (bound oleic acid) increases ever so slightly, the mixed state resonance (free + physisorbed acid) decreases and the resonance with fine structure (ester) increases.](image-url)
facilitate ester formation, whereas the presence of surface-adsorbed protons at the HfO$_2$ surface makes for reaction conditions where, unlike oleate stabilized CdSe NCs, ester formation can proceed through water elimination.

To our knowledge, there is no previous account of HfO$_2$ as an esterification catalyst and in comparison with earlier reports on porous, single metal oxide catalysts, the operating temperature of colloidal HfO$_2$ NCs is much lower (130 °C vs. 300–450 °C). Other common (solid state) esterification catalysts, e.g., (doped) zeolites, ion exchange resins, sulfated zirconia, or sulfated tin oxide, are more complex in architecture, demand higher synthesis temperatures or activation treatments. In addition, the surface areas are rather small while the surface area of colloidal nanocrystals can easily be increased by decreasing the NC diameter. Single metal (hafnium) oxide NCs may thus open a new class of esterification catalysts.

5.3.4 Transesterification catalysis

Further exploring HfO$_2$ NC catalysis, we found that heating oleic acid capped HfO$_2$ NCs to 130 °C in the presence of ethyl acetate leads to the formation of ethanol and acetic acid, i.e., ester hydrolysis (Figure 5.13), which did not occur in the absence of the NCs (Figure A.13 in Appendix A). This effect is probably caused by the dissociative adsorption of small amounts of residual water as H$^+$ and OH$^-$ (NC(X)$_2$) on the metal oxide surface (see Figure A.14). More importantly, nothing prevents the thus formed acetic acid or alcohol in getting involved in ester formation with a second alcohol or acid respectively, i.e., transesterification, see Figure 5.14A.
Figure 5.12: The development of the ester resonances in a sample with 21.8 mg HfO₂ nanocrystals in 500 µL dichlorobenzene-d₄, to which excess oleic acid and methanol was added so that the concentrations were 95 mM HOAc (10 µL) and 600 mM methanol (15 µL) at 25 °C. The TON was calculated as the ratio of the ester resonance and the original ligand concentration because the latter represents the number of catalytically active surface sites. The initial rate is quasi-linear, as in the case with ethanol, but in the end, equilibrium is reached. At that point the number of catalytic turnovers is more than 3, thereby further underpinning the catalytic activity of the HfO₂ NCs.

This is exactly what is observed when heating a mixture of oleic acid capped HfO₂ NCs, ethyl acetate and methanol, where NMR analysis confirms the primary formation of methyl oleate and methyl acetate, as indicated in green and blue in the ¹H NMR spectrum (Figure 5.14B). In addition, residual resonances of ethyl acetate and methanol, as well as of the byproduct of reaction, ethanol, are observed. Such assignments are corroborated by the ¹H–¹³C HMBC spectrum (Figure 5.14C).

In addition, 22% of the oleic acid is converted in ethyl oleate, quite consistent with the original 1:3 ratio of ethyl acetate and methanol, indicating about equal rate of esterification and transesterification. Since solid-state acid catalyzed transesterification usually demands higher temperatures, the observed simultaneous catalysis of esterification and transesterification reactions by HfO₂ NCs is an interesting feat for, e.g., biodiesel applications where cheap feed stocks contain both triglycerides and free fatty acids. Note that in this experiment the original ligand is consumed in the reaction, without being replenished from the reaction mixture. Eventually, oleic acid is almost completely converted to ester (see the alkene resonance at 5.4 ppm).
Chemical exchange and catalysis

Figure 5.13: To a HfO$_2$ NC dispersion, ethylacetate was added (bottom spectrum) and the resulting mixture was heated to 130 °C, causing the appearance of ethanol in the spectrum (middle spectrum). The intensity is however rather low and the resonance has no fine structure, indicating interaction with the surface. Therefore, methanol was added as a competing ligand to drive ethanol from the ligand shell and present its appearance more clearly (top spectrum).

in Figure 5.14B) and the NC are stabilized by only a very small amount of residual oleic acid as recognized by weak negative nOe cross peaks in the NOESY spectrum, Figure 5.14D. In addition, ethanol and methanol are dynamically interacting with the surface as evidenced by their negative nOe cross peaks.

5.4 Discussion

Colloidal metal nanocrystals have attracted wide attention as nanocatalysts since they can show enhanced catalytic activity as compared to bulk materials,\textsuperscript{31} combine the advantages of homogeneous and heterogeneous catalysts\textsuperscript{17} and constitute model systems to obtain molecular insight in catalytic processes.\textsuperscript{21} For practical purposes however, the enhanced catalytic activity often conflicts with the need to ensure colloidal stability as capping ligands tend to block catalytically active surface sites.\textsuperscript{32} From this point of view, chemically driven ligand displacement not only unexpectedly turns metal oxide NCs like HfO$_2$ into a useful colloidal nanocatalyst, it also shows how the colloidal stability / catalytic activity tradeoff can be overcome. By turn-
Figure 5.14: **A.** Esters are converted in new esters by adding new alcohol and simultaneous with transesterification, esterification takes place. **B.** $^1$H NMR spectrum acquired after 2 hours at 130 °C of a HfO$_2$ NC suspension in o-dichlorobenzene-d$_4$ with 5 equivalents of ethyl acetate and 15 equivalents of methanol (with respect to bound oleic acid). **C.** The HMBC spectrum, correlating the carbonyl carbons to neighbouring protons, confirmed the existence of 4 ester species in the synthesis mixture. **D.** NOESY spectrum. Negative cross peak are observed for ethanol, methanol and oleic acid proving a bound state. The ester resonance only features zero quantum coherences.

Incorporating steric stabilizers into reagents and supplying them in excess, full access to the catalytic sites is warranted without compromising colloidal stability. Importantly, the example of transesterification catalysis already shows that this approach extends beyond reactions where the originally present ligand is the only reacting/stabilizing species and similar processes are conceivable that involve small molecules, stabilizing NC dispersion in polar media. Moreover, as the catalytic activity is linked to intrinsic properties
of the HfO$_2$ NC surface — preserved during the catalytic reaction — this approach makes for a far more robust nanocatalyst than nanocrystals functionalized by catalytically active ligands,\textsuperscript{32,33} where the catalytic properties are lost upon ligand desorption.

5.5 Conclusion

Given the extensive range of metal oxides that can be synthesized as nanocrystals and the almost unlimited possibilities to tune their composition and the variety of ligands they support, chemically driven ligand displacement on metal oxide nanocrystals may offer a new route towards low-cost, durable and versatile catalytic processes. We thus conclude that the joint catalysis of esterification and transesterification by HfO$_2$ nanocrystals merely constitutes a first unique example of a much wider range of catalytic processes and metal oxide nanocatalysts to be explored in the near future.
References


Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *Journal of the American Chemical Society* 2013, 135, 18536–18548.


6

Nanocomposites of YBa$_2$Cu$_3$O$_{7-\delta}$ coated conductors; the need for ligand exchange$^{1}$

Limited in his nature, infinite in his desire, man is a fallen god who remembers heaven. (translated from French)
– Alphonse de Lamartine

6.1 Superconductivity and nanocrystals

In the previous chapters, we have established the synthesis and surface chemistry of HfO$_2$ and ZrO$_2$ NCs and we found unexpected catalytic properties of HfO$_2$ NCs. However, in this chapter we focus on the primarily envisaged applications of these NCs; artificial pinning centers in YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors.

$^{1}$adapted from: De Roo, J.; Coucke, S.; Rijckaert, H; De Keukeleere, K; Sinnaeve, D.; Hens, Z; Martins, J. C.; Van Driessche, I. Amino acid based stabilization of oxide nanocrystals in polar media; limits and opportunities of solution $^1$H NMR characterization. *Langmuir* **2016** doi:10.1021/acs.langmuir.5b04611
6.1.1 Superconductivity, basic principles

Superconductivity is the phenomenon of zero resistivity at temperatures above 0 K and was first discovered in mercury, see Figure 6.1. The temperature at which a given material changes to the superconducting state, is called the critical temperature ($T_c$).

Superconductors behave as perfect diamagnets, expelling magnetic fields but there is a limit to that behaviour. Subjected to a magnetic field higher than the critical magnetic field ($H_c$), the superconducting state breaks down. The critical magnetic field is temperature dependent, according to Equation 6.1 with $H_0$ the critical magnetic field at 0 K.

$$H_c = H_0 \left(1 - \left(\frac{T}{T_c}\right)^2\right)$$

(6.1)

Since a current represents moving charges, it creates a magnetic field and therefore, there exists a critical current ($I_c$). However, it is more convenient to use $J_c$, the critical current density since this quantity is independent of the dimensions of the material ($J_c = I_c/A$ with $A$ the cross section area of the conductor). If the current exceeds $J_c$, or the temperature exceeds $T_c$ or the magnetic field exceeds $H_c$, the material returns to the normal state and superconductivity is lost.

Superconductors can be classified in type I and type II superconductors, depending on the phase transformation behaviour. A type I superconductor changes abruptly from the superconducting to the non-superconducting
state, see Figure 6.2. Metals and alloys typically show this behaviour. Note that the superconducting state is a different thermodynamic phase but the crystal structure remains unchanged.

![Figure 6.2: Phase diagram of a type I and a type II superconductor.](image)

Type II superconductors show a more gradual collapse of the superconducting state. From $H_{c1}$ on, the magnetic flux starts penetrating the superconductor but only at $H_{c2}$ the last trace of superconductivity has disappeared (see Figure 6.2). In between $H_{c1}$ and $H_{c2}$, the material persists in a mixed state, characterized by small, cylindrical, non–superconducting areas, surrounded by paramagnetic supercurrents, called vortices (see Figure 6.3). The magnetic flux lines can penetrate the non–superconducting channels.

![Figure 6.3: Illustration of the mixed state in type II superconductors with characteristic vortices.](image)

A second, more arbitrary classification is the division in High Temperature and Low Temperature Superconductors (HTS vs. LTS). LTS typically show the transition to the superconducting state below 30 K and require liquid helium cooling. HTS are materials with a higher superconducting $T_c$, often above the boiling point of $N_2$ (77 K), and are thus commercially quite in-
Interesting since liquid nitrogen is a significantly cheaper coolant than liquid helium.

6.1.2 Superconducting materials

The ceramic oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) is a type II High Temperature Superconductor and is widely studied as the second generation of superconductors. The optimal value for $\delta$ is 0.07 and in that case YBCO has a $T_c$ of 92 K. This is not a record $T_c$ but oxides with a higher $T_c$ feature important disadvantages such as toxicity, expensive synthesis techniques and higher anisotropy.

The unit cell of YBCO (see Figure 6.4) comprises three pseudo–perovskites, resulting in an orthorombic crystal structure with $a = 0.382$ nm, $b = 0.389$ nm and $c = 1.168$ nm. YBCO has CuO chains along the $b$–axis and CuO$_2$ planes parallel with the $a$–$b$ plane. The planes are responsible for the charge transport and almost no current is flowing along the $c$–axis, hence YBCO’s anisotropy.

![Figure 6.4: Unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$](image)

There are several difficulties in the applications of YBCO as a superconducting wire. First, due to the anisotropy of conduction, the orientation of the different crystal grains is of utmost importance. Second, YBCO is a ceramic material and thus brittle, which make it impossible to pull wires from the material. The solution for both problems is the coated conductor architecture. In this approach, the excellent mechanical properties of a biaxially textured, metallic substrate are transferred to an epitaxially grown YBCO thin film. As a result, the $a$–$b$ planes of all the crystal domains are parallel with the substrate’s surface and critical current densities of 3.5 MA/cm$^2$ and
higher, are achieved. To achieve epitaxial growth, both physical vapour deposition and wet chemical techniques are used. In this dissertation we focus on chemical solution deposition as this method proves promising for industrial application due to scalability and cost-effectiveness. The precursor solution contains yttrium, barium and copper ions, stabilized by trifluoroacetate, in methanol.

6.1.3 Nanocrystals as artificial pinning centers

YBCO is a type II superconductor and therefore enters the mixed state when the critical magnetic field exceeds \( H_{c1} \) (see Figure 6.2). In this mixed state, vortices of 2–3 nm are present with an average distance of 10–30 nm in between. When a current \( I \) is introduced in the superconductor, these vortices start to move due to the Lorentz force \( F_L = I \times B \). This process causes energy dissipation, equivalent to resistance and hence loss of superconductivity. However, if the vortices are pinned at a fixed position, the material remains superconducting. The condition for pinning is thus a higher pinning force \( F_p \) than the Lorentz force. The critical current can now be defined as the current which yields a Lorentz force equal to the pinning force (Equation 6.2). Again, we normalize the critical current over the cross section area of the superconductors to the critical current density \( J_c \).

\[
F_p = F_L = I_c \times B \quad (6.2)
\]

Pinning actually originates from non–superconducting defects in the crystal structure. Therefore a perfect YBCO crystal would have a negligible \( J_c \). In principle, the formation of a vortex involves sacrificing part of the superconducting phase for a volume of non–superconducting material through which the magnetic flux lines can penetrate the material. This is associated with an energy penalty, the superconducting condensation energy. However, when a magnetic flux line passes through a defect there is no sacrifice of superconducting material since the defect was never superconducting in the first place. Therefore the magnetic flux line prefers to remain where it is, being effectively pinned.

Rather than relying on the intrinsic defects of the superconducting material, researchers seek to enhance \( J_c \) through the introduction of artificial pinning centers. Pinning centers have been created by introducing nanoscale, non–superconducting phases, e.g., BaSnO\(_3\) nanocolumns and BaZrO\(_3\) nanocrystals. The precursors of the nanoscale inclusions were added to the superconducting precursor and nucleation and growth occurs during the
growth of the superconductor itself (called, the in–situ approach). However, recently, research efforts were directed to the separate synthesis of nanocrystals and the stabilization of these preformed nanocrystals in the superconducting precursor solution. We believe that this approach provides more control over the final nanocrystal properties (e.g., size and shape) and is industrially more feasible since the in–situ approach requires a precisely controlled heat treatment, an impossible feat for meters–long furnaces.

In this chapter, we will first review the existing ligand exchange methodologies and argue them inadequate for application in the superconducting precursor solution. We then introduce a new approach to transfer oxide NCs to methanol, the main solvent of the superconducting precursor solution. Finally, we present the deposition of the YBCO precursor solution with oxide NCs on an appropriate substrate and the obtained superconducting nanocomposite after heat treatment.

6.2 Ligand exchange and phase transfer to polar solvents

The emergence of nanocrystals (NCs) has provided material science with extremely versatile building blocks with regard to size, shape, chemical composition and crystal structure. Here, the NC surface is an indispensable part of these building blocks since its composition determines colloidal stability in various solvents and influences the nanocrystal’s physical and chemical properties. With its typical capping of hydrophobic ligands, the surface composition of as–synthesized nanocrystals however, is ill suited for application that require solubility in polar solvents, complete ligand removal, or subtle doping of the surface. This applies in particular to the formation of all–inorganic nanocomposites, comprising a matrix and nanoscale inclusions, for which NCs, soluble in polar solvents, are typically needed. Examples include (i) capacitor or superconducting nanocomposite thin films formed using a methanol–based precursor solution containing both molecular precursors for the matrix and dispersed metal oxide NCs (ii) Nanocrystal–in–glass composites, fabricated from aqueous dispersions of indium tin oxide or (iii) mesoporous materials, constructed from NC building blocks by electrostatic interaction with a structure directing block–copolymer.

In order to achieve stability in polar solvents, the original hydrophobic ligands need to be exchanged for organic or inorganic polar ligands. Several strategies have already been developed to transfer metal, metal selenide
and metal sulfide NCs to polar solvents, yet these exchange schemes cannot be simply transferred to metal oxide NCs. Sulfide or selenide based ligands for example, proved excellent for ligand exchange on metals and metal sulfides, selenides, phosphides or arsenides but show little affinity towards oxide NCs. In addition, ligand exchange schemes tend to use solvents with high dielectric constants (e.g., formamide, $\varepsilon = 111$ or N-methylformamide, $\varepsilon = 180$) that favor electrostatic stabilization. However, the application of those high boiling, unstable and toxic solvents is limited. Furthermore, most accounts in literature describe procedures providing electrostatic stabilization in basic conditions, and with negatively charged surfaces. The formation of nanocomposites however, may involve acidic matrix precursor solutions whereas the uptake of nanoparticles by immune cells was found to be enhanced by positive surface charges. Potentially useful procedures in this respect involve the use of stripping agents such as NOBF$_4$, RO$_3$BF$_4$ (R = alkyl), and BF$_3$ which operate in acidic conditions, or dopamine, which stabilized titania NCs by a positive surface charge. The former approach however, does not lead to long term stable dispersions whereas dopamine is an important neurotransmitter, involved in addictive behaviour, and therefore a restricted chemical.

Here, we present a new ligand exchange strategy to transfer metal oxide nanocrystals capped with apolar ligands to a variety of common polar solvents. The method is based upon exposure of metal oxide NCs to short-chain amino acids under acidic conditions, implying that it does not introduce additional metal ions to the dispersion and uses reagents that are all perfectly stable in air and moisture. Using mostly hafnium oxide as a metal oxide NC model system with a well understood surface chemistry — and potentially useful as luminescence host, as dielectric for electronics and for therapeutic applications in medicine — we can elucidate the ligand exchange mechanism through a combination of FTIR, zeta potential measurements and advanced solution $^1$H NMR techniques. The latter is especially popular to probe the dynamic behavior of ligands in situ, in solution and is mostly used to characterize NCs in apolar media, stabilized by long, steric ligands. Having amino acid stabilized metal oxide NCs available however, enables us to explore the possibilities of the technique for the detection of short-chain adsorbates that only have protons close to the nanocrystal surface. While these prove in general broadened beyond detection, we show that in situ titration experiments with competing ligands makes released ligands observable. Most interesting however, is the finding that the resonance of a methyl moiety, present in certain bound amino acids, can be discerned in the $^1$H NMR spectrum due to its high internal
mobility. As they are inherent to the size of the ligand and not the nature of the nanocrystal, these results set the scene for the characterization of small ligand binding to a variety of NC surfaces.

6.3 Experimental

6.3.1 Nanocrystal stabilization

Anhydrous benzyl alcohol and dibenzyl ether were purchased from Sigma Aldrich and hafnium/zirconium chloride was purchased from Alfa Easar. HfO$_2$ and ZrO$_2$ NCs were synthesized according to a microwave-assisted benzyl alcohol synthesis. Briefly, 0.13 g of the metal chloride was dissolved in 0.5 mL dibenzylether and 4 mL benzyl alcohol, and heated at 220 °C in the microwave. After synthesis, the NCs were stabilized in 4 mL chloroform by a post synthetic surface functionalization with dodecanoic acid (DDAc). The concentration of the HfO$_2$ NC solution was 0.06 M in metal. The particles were washed three times with acetone. In a typical ligand exchange, 1 mL of the HfO$_2$ dispersion was precipitated with acetone and centrifuged. Then 0.4 mmol trifluoroacetic acid (TFA) in 1 mL of methanol was added (together with 0.05 mmol of amino acid, typically glutamine). After 30 min sonication, a clear suspension was obtained. The NCs were precipitated with toluene, to remove excess of ligands, and redispersed in methanol, acetone, butanol, ethanol, DMSO, isopropanol or acetonitrile. In some cases it was necessary to add again 0.1 mmol TFA to obtain a stable dispersion.

6.3.2 Superconducting nanocomposite formation

The preparation of the TFA–YBCO precursor solution is described elsewhere. NCs were introduced in a TFA–YBCO precursor solution at different mol%. The resulting suspension was deposited on 5 mm x 5 mm LaAlO$_3$ (LAO) single crystal substrates via spin coating, at 6000 rpm for 2 min. The layers are thermally treated for pyrolysis and subsequent crystallized into the final YBCO nanocomposite thin films. Generally, the pyrolysis treatment was performed in a tubular furnace under a humid oxygen gas flow (0.07 L min$^{-1}$) at 310 °C for 30 min. The crystallization treatment was performed at 810 °C for 180 min in a wet N$_2$ atmosphere with an O$_2$ partial pressure of 200 ppm. Finally, the superconducting YBCO phase was obtained by oxygen annealing at 450 °C for 210 min. To start from an LAO substrate with an interfacial YBCO seed layer, first a 0.375 M total metal concentration of TFA–YBCO precursor is deposited on the LAO substrate.
and spin–coated. This layer is pyrolyzed, without the dwell of 30 min, before the NCs–YBCO suspension is deposited.

6.4 Results and discussion

6.4.1 Phase transfer with and without amino acids

Dodecanoic acid capped HfO$_2$ NCs, dispersed in chloroform, were synthesized using established procedures.$^{39,49}$ Dodecanoic acid is dissociatively adsorbed on the HfO$_2$ NC surface (Figure 6.5A), a binding motif classified as NC(X)$_2$.$^{38}$ Since it was already previously shown that ligand exchange processes with such X–type ligands are governed by acidity$^{14,39,52,53}$ and that it proved possible to transfer NaYF$_4$ NCs to water by simple protonation of the original oleate ligand,$^{53}$ we sought to transfer the HfO$_2$ NCs to methanol with the same principle. The HfO$_2$ NCs were precipitated with acetone and a methanol solution of trifluorosulphonic acid (TFSA) was added. However, even after prolonged ultrasound treatment the dispersion remains turbid and unstable. Curiously, a similar treatment with trifluoroacetic acid (TFA), another strong organic acid, did result in a transparent dispersion. Dynamic Light Scattering (DLS) measurements confirm that the solvodynamic radius in chloroform and methanol are about the same (Figure 6.5B). Such TFA stabilized HfO$_2$ NCs have a zeta potential of $-22$ mV and the methanolic dispersion has a pH of $-0.04$ (measured with a standard pH meter). Admittedly, pH is only perfectly defined in aqueous solutions yet the deviation in value is rather small in methanol. Since a negative zeta potential was measured, there must be more negatively charged species adsorbed on the surface than positively charged species. Although the solution is very acidic, the adsorption of trifluoroacetate anions (TFA$^-$) is thus apparently preferred over the adsorption of protons, see Figure 6.5A, route A. A negative zeta potential at such low pH values is remarkable and has — to our knowledge — never been reported. Furthermore, we rationalize the differences between TFSA and TFA by their differences in acidity and nucleophilicity. TFA has a pKa in water of -0.03 while TFSA has a pKa of -12. TFSA is therefore classified as a superacid and has thus negligible nucleophilic properties and does not bind to the NC surface.

Unfortunately, the TFA stabilized HfO$_2$ NCs are neither colloidally stable upon dilution nor over a longer period of time (a few days). In addition, the NCs cannot be precipitated by the addition of apolar solvents such as toluene — the dispersion remains stable — and thus purification of the NCs is problematic. However, these issues are readily solved by the addition of
glutamine (Gln) to the NC dispersion. The HfO$_2$ NCs are subsequently precipitated with toluene and redispersed in methanol. As attested by DLS, the solvodynamic diameter remains the same, see Figure 6.5B. The dispersion in methanol is colorless, optically fully transparent (inset in Figure 6.5B) and displays an excellent colloidal stability (for months).

**Figure 6.5:** A Surface chemistry models representing the various ligand exchange strategies, starting from dodecanoic acid capped metal oxide NCs. In route A, the NCs are treated with trifluoroacetic acid (TFA). In route B, the NCs are treated with TFA and glutamine (Gln). We do not mean to impose stoichiometry relationships during the exchange. Note that all charges are balanced. B DLS measurements of HfO$_2$ NCs in chloroform with dodecanoic acid or in methanol with TFA and/or glutamine Gln. The inset displays a dispersion of HfO$_2$ NCs with Gln and TFA.
The impact of Gln on the NC surface chemistry, is also clearly reflected in the changes in zeta potential to +26 mV. A pH of 1.92 was measured and as the pKa values of Gln in water are 2.17 and 9.31 — and very likely, slightly higher in methanol — most of the Gln is present as positively charged, fully protonated species. The positive zeta potential of the NCs is thus rationalized as cationic Gln\(^+\) adsorbed on the surface, see Figure 6.5A, Route B.

To further compare the HfO\(_2\) dispersions, either with or without Gln, both suspensions were dried during 24 hours in an oven at 60 °C. The subsequently measured IR spectra both clearly feature the characteristic absorption bands of C–F stretches (Figure 6.6), confirming the presence of TFA. The first spectrum certifies that, in the absence of Gln, TFA is bound to the HfO\(_2\) NC surface, because TFA is a volatile compound and all free molecules should have evaporated after the drying step. The second sample also still contains TFA and we infer trifluoroacetate is the counterion for protonated Gln, adsorbed on the HfO\(_2\) NC surface, see Figure 6.5A, Route B. Further support for this surface chemistry picture is found experimentally since the phase transfer to methanol proceeds with the combination of Gln and TFSA but not with Gln alone. We infer respectively that Gln may be protonated by any strong organic acid and that the zwitterionic form of Gln is unable to provide electrostatic stabilization.

![Figure 6.6: The IR spectra after evaporation of a purified HfO\(_2\) suspension, either stabilized with TFA alone or with TFA and Gln.](image_url)

The above results have led us to a general scheme to transfer carboxylic acid...
capped metal oxide NCs from apolar to polar solvents, see Figure 6.7A. After precipitation of the NCs with acetone, centrifugation and decantation, we added a methanolic solution of a strong organic acid and an amino acid. For purification purposes, the NCs are precipitated with toluene and could be redispersed in either methanol or various other polar solvents, showing the versatility of the approach, see 6.7B.

**Figure 6.7:** A Schematic overview of the NC phase transfer from apolar solvents to various polar solvents with amino acids. The colors are to guide the eye and are no reference to the real color of the suspension. B DLS measurements of HfO$_2$ NCs stabilized with TFA and Gln in various polar solvents.

We have verified the ligand exchange and phase transfer of HfO$_2$ and ZrO$_2$.
NCs, dispersed in chloroform or toluene, with most amino acids: lysine, glutamine, glycine, serine, arginine, aspartic acid, histidine, leucine, methionine, threonine, asparagine and glutamic acid. The choice of a specific amino acid has an influence on the surface charge which is reflected in a varying zeta potential, e.g., glutamine (+26 mV), lysine with an extra amine group in the side chain (+ 40 mV) or leucine, a nonpolar amino acid (+ 15 mV). Such differences might play a role in the interaction with structure directing agents in the synthesis of mesoporous materials. In addition, most amino acids contain only C, H, O and N, which burn off easily, and do not introduce new elements in, e.g., a nanocomposite.

6.4.2 $^1$H NMR characterization of the surface after phase transfer

Focussing on Gln/TFA stabilized HfO$_2$ NCs in methanol, the positive zeta potential of the HfO$_2$ NCs already suggested that Gln is bound to the NC surface. This is however an indirect deduction and does not give any information about the fate of the original ligand, dodecanoic acid. Therefore, we used the $^1$H solution NMR toolbox that was specifically developed to study the organic–inorganic interface of NC ligand shells, albeit mostly applied to bulky ligands in apolar solvents. In the $^1$H NMR spectrum of glutamine stabilized HfO$_2$ NCs, obtained after phase transfer to methanol (Figure 6.8A), resonances of both DDAc (dodecanoic acid, the original ligand) and Gln (glutamine, the new ligand) are recognized. The DDAc resonances (except a and b) comprise two components, characterized by sharp and broad resonances respectively, superimposed on each other (Figure 6.8A). Sharp resonances with fine structure are a typical feature of free molecules. In contrast, bound ligands lead to broad $^1$H signals due to their decreased rotational mobility and thus increased $T_2$ relaxation rate. This also explains the lack of bound a and b resonances, as the broadening becomes extreme as one approaches the NC surface since the local rotational freedom becomes more impaired. As a result, bound a and b resonances are broadened beyond detection. We conclude that the broad DDAc contributions belong to bound DDAc molecules. As the broad and sharp signals of resonances c and d overlap, the bound fraction was determined by deconvolution. Finally, a ligand density of 0.3 DDAc nm$^{-2}$ was determined. As the ligand density was 3.6 nm$^{-2}$ before ligand exchange, 92 % of the original ligand was thus removed from the surface. We infer that the remaining 8 % of DDAc ligands provide a steric contribution to the colloidal stabilization of the NCs, in addition to the electrostatic contribution, as provided by glutamine.
The bound state of DDAc was confirmed by DOSY and NOESY NMR techniques. The DOSY spectra were bi-exponentially fitted and a diffusion coefficient of $64 \pm 3 \, \mu m^2/s$ and $986 \pm 20 \, \mu m^2/s$ was obtained for the bound and free DDAc respectively. The diffusion coefficient of the bound DDAc was converted via the Stokes–Einstein Equation to a solvodynamic diameter ($d_s$) of $12.5 \, nm$. Since this is the same diameter as in the DLS analysis, these broad DDAc signals can be attributed to tightly bound ligands. Additional support is provided by the broad, negative nOe cross peaks in the NOESY
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spectrum (Figure 6.8B), a typical feature of bound ligands. Curiously, negative nOe cross peaks are also present between the sharp resonances (a–b and a–c) of ‘free’ DDAc, pointing towards a bound character. Although sharp resonances are usually associated with free ligands, this apparent contradiction can be explained by a fast exchange (on the NMR time scale) between a small pool of weakly bound ligands and a large pool of free ligands. The line width is a weight average and thus dominated by the free fraction while the efficient nOe effect of the bound state prevails in the NOESY spectrum. These so-called, transfer nOe cross peaks, were observed before in toluene for oleic acid and it was concluded that there are three possible ligand states: free, bound or weakly entangled in the ligand shell. We infer that the same scheme applies here for DDAc, binding to HfO$_2$ NCs in methanol.

The resonances of Gln however, are sharp (Figure 6.8A) and no slowly diffusing species (related to glutamine) is detected in DOSY. In addition, negative (transfer) nOe cross peaks are absent in the NOESY spectrum, and only zero quantum coherence (ZQ) artefacts are visible (Figure 6.8B). This suggests that the observed Gln is only present in a free state, and is therefore not interacting with the surface. In this respect, it is worth mentioning that the Gln concentration is rather low: 3 mM or 3 % of the original amount of Gln, indicating that most of the glutamine is removed during the purification step (precipitation of the NCs with toluene and re-suspension in methanol). Indeed, the supernatant contains a high concentration of glutamine, next to dodecanoic acid (Figure A.15). Other amino acids, e.g., lysine, asparagine, etc. show the same behaviour, i.e., their resonances feature no line broadening, no negative (transfer) nOe cross peaks and correspond to fast diffusing species.

6.4.3 Competitive titration as a work-around for line broadening

According to the above measurements, the observed Gln is not interacting with the surface of the HfO$_2$ NCs. However, based on the positive zeta potential, we inferred that Gln should be bound to the NC surface. A possible explanation could be that the bound Gln fraction features resonances that are broadened beyond detection due to impaired mobility and concomitant efficient T$_2$ relaxation, as proposed for the a and b resonances of DDAc. We tried to tackle the line broadening issue with typical techniques like HRMAS (to eliminate magnetic susceptibility line broadening) or measurements at elevated temperatures in DMSO (90 °C, to increase internal, rotational mobility) but to no avail. Finally, we gradually added another amino acid
(glycine, Gly), to a HfO₂ NC suspension, stabilized in MeOH–d₄ with TFA and Gln and purified with toluene. We expected Gly to compete with the — invisible — Gln on the surface, thus liberating Gln from the surface, see Figure 6.9A.

In the experiment, we monitored the DDAc, Gln and Gly resonances and in each titration step, 0.56 µmol glycine was added to the HfO₂ NC suspension, see Figure 6.9B. Throughout the titration, the amount of detected glutamine increases, confirming that Gln is detaching from the surface. In addition, in the first three titration steps, the differential increase in Gly (as observed in NMR) does not match the amount of Gly that was added in each titration step (Figure 6.9B). Therefore, there is a sink for Gly, which is the binding event to the NC surface. We conclude that Gly binds to the surface, releasing glutamine in the solution. In addition, the fraction of bound DDAc (against the total amount of DDA) decreases, from 77 % to 56 %, probably also due to the competitive ligand binding of Gly.

The same competitive titration could be performed on HfO₂ NCs, stabilized with only TFA in methanol, see Figure 6.10A. To this highly acidic solution (pH = - 0.04), 6.5 µmol Gln was added in each titration step and the fraction of bound DDAc increases (Figure 6.10B). Although this would seem rather odd because an additional, competing ligand is added, Gln also increases the pH of the solution, resulting in a shift of the equilibrium between free and bound DDAc. On the other hand, in the first titration step, the increase in Gln intensity was smaller than expected from the added Gln amount (Figure 6.10B), showing the binding event of glutamine. Therefore, the surface acts again as a sink for the amino acid. From this deficiency, the ligand density for Gln was quantified: 1 nm⁻². Together with the DDAc ligand density, as determined earlier, the total ligand density on the HfO₂ NCs surface amounts to 1.3 nm⁻².
Figure 6.9: A. General scheme of competitive titration. The addition of glycine ($R_2$) drives bound glutamine ($R_1$) from the surface into the solution as a free molecule. Note that the NC–ligand entity is positively charged. B. The fraction bound DDAc (with respect to the total amount of DDAc) decreases during the titration with Gly. The amount of Gln increases and the differential increase in Gly is lower in the first titration steps.
Figure 6.10: A. When Gln is added to HfO₂ NCs, stabilized with TFA, Gln will bind to the surface and become undetectable in NMR. Note that the NC–ligand entity is negatively charged before Gln addition and positively charged after Gln addition. B. The fraction of bound DDAc and the differential increase of glutamine upon gradual addition of Gln to TFA stabilized HfO₂ NCs in MeOH–d₄.
6.4.4 Methyl moieties in small, bound ligands are detectable.

The combination of the positive zeta potential and the competitive titration experiments, has proven qualitatively and quantitatively that Gln is bound to the HfO₂ NCs. However, we could not directly detect a resonance of strongly bound Gln ligands in the ¹H NMR spectrum. Since the lack of internal mobility, close to the surface, is the most important impediment, we proposed that methyl groups may afford to recover a signal for the bound species, as the rapid rotational motion of the methyl rotor may allow a decreased T₂ relaxation rate, see Figure 6.11A. Therefore, we used leucine (Leu), methionine (Met) and threonine (Thr) as amino acids in the ligand exchange and measured the resulting suspension in NMR. However, the methyl resonance of Thr and Leu overlaps with the alkyl resonances of DDAc (Figure A.16). Fortunately, the methyl (δ) resonance of Met appears in a different chemical shift range, together with its β resonance (Figure 6.11B). When closely examining the spectrum, it is clear that the signals around 2.1 ppm are a superposition of sharp β and δ signals, and a very broad contribution which we ascribe to the methyl (δ) resonance of bound methionine (Figure 6.11B, indicated in green). Unfortunately, this is the only visible resonance for the bound methionine ligand, thus no negative intramolecular nOe’s could be detected to support the bound nature of this species. However, it does feature a broad and negative nOe cross peak to the methylene resonances of the DDAc chain (δ to c, Figure 6.11C), albeit having an intermolecular nature, i.e., this peak arises from the dipolar interaction between the methyl group and protons from the DDAc ligand at the surface. DOSY measurements confirm this broad resonance to belong to tightly bound methionine as we obtain a small diffusion coefficient of 78 ± 10 μm²/s, corresponding to a solvodynamic radius of 10.3 nm and very close to the diffusion coefficient of bound DDAc: 63 ± 1 μm²/s. We conclude that methyl units of tightly bound, small ligands can be detected and thus provide a ‘probe’ to assess small ligand binding.
Figure 6.11: A. HfO$_2$ NCs stabilized with methionine (Met). The methyl group possesses complete rotational freedom. B. In the $^1$H NMR spectrum of HfO$_2$ NCs with Met in MeOH-$d_4$, the broad contribution under the $\delta$ resonance indicates bound Met. C. In the NOESY NMR spectrum of the same sample, a broad nOe peak is visible between DDAc and the Met.
Having addressed the broad resonance of bound Met, we turn to some additional interesting nOe cross peaks between the sharp Met resonances. As in the case of Gln, zero–quantum cross peak artefacts are apparent between the resonances $\gamma$ and $\beta$ or between $\alpha$ and $\beta$, see Figure 6.11C). Note that zero–quantum artefacts are particularly persistent between strongly scalarly coupled resonances, such as adjacent resonances. In contrast, between the resonances $\alpha$ and $\gamma$, we do observe a negative (transfer) nOe cross peak, indicating some contribution of an entangled state (*vide supra*). This entangled state is also apparent from the sharp intermolecular negative cross peak between $\delta$ and $c$, superimposed on the broad cross peak. Nevertheless, we infer that the entangled state will be poorly populated as the negative nOe’s are only small and not stronger than the eventual zero–quantum artefacts. The same picture is provided by the NOESY spectrum of Leu or Thr stabilized HfO$_2$ NCs (Figure 6.12 and A.17 respectively). Although mostly intramolecular negative nOe cross peaks are detected, there are still zero–quantum artefacts between some scalarly coupled resonances. Even Gln stabilized HfO$_2$ NCs feature weak negative nOe cross peaks if special precautions are taken to suppress the zero quantum coherences (Figure A.18). We thus conclude that all amino acids show more or less the same behaviour; the metal oxide NCs are primarily stabilized by a layer of strongly bound amino acids and residual DDAc molecules. Although the remaining, free amino acid fraction seems to interact very weakly with the NC surface or the ligand shell, this entangled state is far less populated than the entangled state of fatty acids$^{55}$ and seems hardly relevant for the stabilization.

![Figure 6.12](image)

*Figure 6.12:* In the NOESY spectrum of HfO$_2$ NCs with Leu in MeOH-$d_4$, sharp negative cross peaks are present.

We would like to emphasize that the correct assessment of ligand binding
can only happen through the combination of at least these three techniques: 1D, 2D NOESY and 2D DOSY \textsuperscript{1}H NMR. This allows to differentiate the dynamics of ligand binding. (i) Broadened resonances with negative nOe peaks and a slow diffusion coefficient are ascribed to tightly bound ligands. (ii) Sharp resonances with negative nOe peaks and intermediate or fast diffusion coefficients are originating from weakly bound ligand, exchanging fast between a free and a bound state. However, this is only useful when resonances are detectable and as we showed here, this is not the case for a tightly bound, small ligand, unless this small molecule contains a methyl moiety. Although some literature\textsuperscript{56,57} exists where resonances are ascribed to small, bound ligands, solely based on the 1D \textsuperscript{1}H NMR spectrum, such practices are risky. We emphasize that in all cases of ligand binding, and especially with small ligands, caution is needed and NOESY and DOSY experiments are an absolute necessity.

6.5 Superconducting nanocomposites

Finally, the NCs were added to the YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x} precursor solution (0.75 M total metal concentration). If stabilized with only TFA, the particles quickly precipitated. However, with TFA and Gln, the HfO\textsubscript{2} NCs possessed excellent colloidal stability, even at high loadings (see Figure 6.13). The solvodynamic radius is, \( d_H = 12 \text{ nm} \), and remains as such for at least three months, demonstrating the excellent stability of the NCs in the YBCO precursor solution. The same holds for ZrO\textsubscript{2} NCs, stabilized with glutamine and TFA. Note that water in the YBCO precursor is detrimental for the growth process and therefore, we employed trifluoroacetic anhydride instead of trifluoroacetic acid. The anhydride scavenges water molecules in the solution, forming trifluoroacetic acid.

The introduction of various NCs in the superconducting matrix has been the focus of other PhD theses\textsuperscript{58,59} and is here briefly mentioned for sake of completion. YBCO precursor solutions with various concentrations of ZrO\textsubscript{2} NCs were spin coated on LaAlO\textsubscript{3}(LAO) substrates and after heat treatment the superconducting layers were evaluated. High concentrations of zirconia led to poor YBCO growth and even low concentrations did not increase the physical properties of the layers, on the contrary. The disturbed YBCO growth is caused by the NCs, settling at the substrate before the YBCO growth. In order to promote epitaxial YBCO growth, first, a thin YBCO seed layer (without NCs) was deposited on the LAO substrate and pyrolyzed. On top of this seed layer, nanocomposite films with different
Figure 6.13: DLS measurements indicate that HfO$_2$ NCs remain colloidally stable in YBCO precursor solutions up to 50 mol % loading. The dispersion is optically transparent.

amounts of NCs were tested; 0, 3, 10 and 15 mol% ZrO$_2$ NCs. In all case, c–axis oriented YBCO was formed and the ZrO$_2$ NCs were transformed to BaZrO$_3$, as determined from XRD analysis (data not shown).

The size and distribution of the NCs in the YBCO layer were determined using HAADF–STEM and EDX. It is apparent from the TEM and EDX images displayed in Figure 6.14A and B, that the bottom 50–70 nm of the YBCO layer does not contain a Zr–rich phase, while the formed BaZrO$_3$ NCs are homogeneously distributed in the top YBCO layer. The individual NCs embedded in the layer coarsen from the initial 7 nm ZrO$_2$ NCs to 12–25 nm of BaZrO$_3$ NCs (see Figure 6.14C and D), similarly to the case of in situ nanocomposites, while some agglomeration is also clearly visible (Figure 6.14D). This agglomeration may already occur during the pyrolysis step, but it may also be induced during the growth process as a consequence of grain coalescence.

Finally, the layers were evaluated for their superconducting properties, see Figure 6.15. An overall increase in critical current density ($J_c$) is noted at high fields. The critical current density in self–field, $J_{c,sf}$, steadily increases for the layers with 0, 3 and 10 mol% zirconia, up to 4.6 MA/cm$^2$, compared to 3.35 MA/cm$^2$ for the YBCO film without NCs. At higher concentrations (e.g., 15 mol%) $J_c$ falls back. The addition of ZrO$_2$ NC did not decrease the critical temperature $T_c$. We thus succeeded for the first time in synthesizing
Ligand exchange and superconducting nanocomposites

Figure 6.14: A. HAADF STEM cross sectional image showing and B. EDX Zr map image of the YBCO nanocomposite with 10 mol% preformed NCs, indicating the presence of Zr in the layer. C-D. High-resolution HAADF STEM Z-contrast image of the same nanocomposite showing local microstructures of BaZrO$_3$ NCs randomly oriented and sometimes faceted by the YBCO (001) plane.

an improved YBCO film through an approach with preformed NCs, in which pinning at high magnetic fields is achieved.

6.6 Conclusion

We presented a versatile, amino acid based, ligand exchange method to stabilize metal oxide NCs in various polar media. We studied the mechanism of the ligand exchange and found that a strong acid is necessary to protonate the original carboxylic acid ligand, after which a positively charged amino acid adsorbs on the surface, electrostatically stabilizing the surface. In addition there is a small steric contribution to the colloidal stabilization due to some remaining carboxylic acid on the NC surface. The amino acids are tightly bound to the surface and their resonances are broadened beyond detection. However, we could prove the existence of this dark state by competitive titration experiments. In addition, a methyl moiety has a higher internal rotational mobility and its resonance is observed, even when it is located relatively close to the surface in a small, bound ligand.
Figure 6.15: The magnetic field dependence of the critical current density at 77 K and H // c of YBCO nanocomposites with 0, 3, 10, and 15 mol% of preformed ZrO$_2$ NCs.

DOSY measurements ascertained that the broad methyl resonance diffuses together with the nanocrystals and therefore, that the amino acid is really tightly bound to the NC surface. Note that it was only through the combination of 1D and 2D DOSY and NOESY techniques that the surface could be elucidated and we presented here a first exhaustive account on the NMR characterization of small, tightly bound ligands. Until now, small molecule binding was only proven via NOESY experiments in the case of fast exchange between free and bound molecules. These insights will facilitate further research, characterization and development of ligand exchange methods with small ligands. Regarding the application of metal oxide NCs as artificial pinning centers in YBa$_2$Cu$_3$O$_{7-δ}$ superconductors, we succeeded at forming a superconducting layer with NC inclusions and found 10 mol% addition of ZrO$_2$ NCs as an optimum for maximal $J_c$ enhancement.
References


BaMO$_3$-doped YBa$_2$Cu$_3$O$_{7-x}$ thin films (M = Zr, Sn). *Superconductor Science & Technology* 2008, 21, 032002.


[58] De Keukeleere, K. PhD, Ghent University, 2016.


Conclusion and future prospects

7.1 Conclusion

In our quest for superconducting nanocomposites, we started off with the synthesis of metal oxide nanocrystals. Subsequently, we studied the oxide formation mechanism and the surface modification. This led to interesting exchange and catalytic properties and finally we transferred the NCs from nonpolar to polar media and superior superconductors were synthesized.

First, we compared a microwave assisted solvothermal synthesis of HfO$_2$ nanocrystals (NCs), from hafnium chloride and benzyl alcohol, with a conventional heating system (autoclave). The results of the solvothermal (autoclave) synthesis of Buha et al. proved to be reproducible but we found evidence for another reaction mechanism, involving an ether elimination. By ligand exchange of HfCl$_4$ with benzyl alcohol, HCl is formed and this acid catalyzes more ether formation. Compared to an autoclave synthesis, the microwave synthesis is much faster and yields more monodisperse and smaller NCs. In addition, zirconia NCs were synthesized by the same synthesis strategy. In order to obtain non–agglomerated metal oxide NCs, a post–synthetic surface modification was successfully performed.
Second, we have elucidated the surface modification mechanism of HfO$_2$ and ZrO$_2$ NCs. We showed that the carboxylic acid is unable to replace the initially present hydrogen chloride without the presence of a suitable base such as oleylamine. Furthermore, oleylamine is only weakly entangled in the ligand shell and can be removed by simple purification, together with undesired traces of chloride, leaving a clean surface suitable for various applications. After surface functionalization of the metal oxide NCs, the carboxylic acids feature the same dynamical behavior in solution as metal chalcogenide NCs stabilized with carboxylates. However, we established the crucial difference that in case of metal oxides the negative charge of the carboxylate is not balanced by an excess of metal cations but by protons which are adsorbed on different adsorption sites on the surface than the carboxylates. We infer that carboxylic acids can dissociate on the surface of the metal oxide NCs (see Figure 7.1) which is an unprecedented and fascinating result that opens new possibilities for the manipulation of metal oxide NCs in general.

Third, we elaborated on the surface manipulation of metal oxides and showed that octylamine releases oleic acid from HfO$_2$ and ZrO$_2$ NCs while cadmium oleate is released from CdSe NCs. The ligand exchange reaction is rendered exothermic and thus impeded at high temperatures — relevant for NC syntheses — by the formation of an acid/base pair in case of oxide NCs or a metal complex in case of CdSe NCs. Finally, oleic acid features self-adsorption at the oxide but not at the CdSe NC surface. We argue that the exchange characteristics of carboxylic acids bound to metal oxide NCs result from their dissociative adsorption. The NC surface thus contains
equal amounts of anionic and cationic X type ligands, a binding motif we label as $X_2$. Importantly, acknowledging the occurrence of $X_2$ type binding brings about a new class of NC–ligand systems — stoichiometric NCs with overall neutral $X_2$ ligands — in addition to cation rich NCs with anionic $X$ type ligands and stoichiometric NCs with neutral $Z$ or $L$ type ligands. Our work indicates that this new NC–ligand class will be most relevant to understand to surface chemistry of metal oxide NCs in general.

Fourth, going one step further from ligand exchange to ligand displacement, we demonstrated that, on HfO$_2$ NCs, weakly binding ligands such as amines and alcohols chemically convert tightly bound carboxylic acids in non–coordinating amides or esters and thus promote acid/amine and acid/alcohol ligand exchange. Furthermore, sustained ester formation is observed when the ligand shell is continuously replenished with carboxylic acids. We relate this catalytic activity to the dissociative $X_2$ binding of carboxylic acids to oxide NCs and further underscore its potential by showing that HfO$_2$ NCs also catalyze transesterifications. These findings show that apart from a powerful yet subtle surface engineering tool, chemically driven ligand exchange bypasses the colloidal stability / catalytic activity conundrum in colloidal nanocatalysis — where ligands imparting colloidal stability block catalytically active surface sites — and thus provides a gateway to the application of colloidal nanocrystals in catalysis. Given the extensive range of metal oxides that can be synthesized as nanocrystals and the almost unlimited possibilities to tune their composition and surface termination, chemically driven ligand exchange on metal oxide nanocrystals may offer a new route towards low-cost, durable and versatile catalytic processes. We thus conclude that the joint catalysis of esterification and transesterification by HfO$_2$ nanocrystals merely constitutes a first unique example of a much wider range of catalytic processes and metal oxide nanocatalysts to be explored in the near future.

Finally, we returned to the aim of superconducting nanocomposites. We have presented a versatile, amino acid based, ligand exchange method to stabilize oxide NCs in various polar media. We studied the phase transfer mechanism from apolar to polar solvents, and found that TFA is necessary to protonate the original carboxylic acid ligand, after which a positively charged amino acid adsorbs on the surface, electrostatically stabilizing the surface. In addition there is a small steric contribution to the colloidal stabilization due to some remaining carboxylic acid on the NC surface. Although the bound state of most amino acids is undetectable by NMR, we could prove the existence of this dark state by competitive titration experiments. Furthermore, methyl moieties have a higher internal mobility
and their resonances are observed, even when located relatively close to the surface in a small, tightly bound ligand. In this respect, NOESY and DOSY NMR measurements have proven indispensable to correctly assess ligand binding. These insights will facilitate further research, characterization and development of ligand exchange methods with small ligands. The NCs stabilized with TFA and glutamine showed excellent stability in the TFA YBCO precursor solution, even at high loading and during an extensive period of time. We finally succeeded at forming superconducting layers with NC inclusions and found the 10 mol% addition of ZrO$_2$ NCs as an optimum for maximal $J_c$ enhancement, resulting in a $J_c$ of 4.6 MA/cm$^2$.

### 7.2 Perspectives

In this final section, I would like to state my personal opinion, concerning the future advancement of nanoscience. I started many conference presentations with: ‘Nanocrystals synthesis is useless, ..., unless you bridge the gap between synthesis and applications. This gap is surface chemistry.’ Too many researchers neglect the surface of NCs while virtually every NC property is influenced by it. In this respect, the covalent bond classification is an absolute necessity to understand and predict ligand exchange strategies. This is an incredibly powerful framework and its application to NC surfaces has finally provided the community with a rationale behind many unexplainable synthetic observations. Further advancement of NC science will thus surely be found, in part, in judicious studies of the surface.

In this thesis, we definitely altered the perspective of researchers towards oxide nanocrystals. We showed how their surface chemistry is different for classically studied NCs and we also introduced a new concept to the domain of catalysis. We showed here a catalytic process where the catalyst is not poisoned or hindered by the stabilizing ligands. The idea of using reagents as ligands is to be explored further, other metal oxides should be investigated as well and this could possibly lead to competitive (trans)esterification catalysts and finally even sustainable biodiesel production.

In the context of superconducting nanocomposites, this thesis proved the feasibility of using preformed nanocrystals as artificial pinning centers but there is still ample room for optimization. Future research should primarily concentrate on introducing smaller nanocrystals into the superconductor as now the final size of the pinning centers is an excessive 20 nm where we envisaged only 3 nm. The question, whether it is really possible to tune the final size by the initial NC size, is actually fundamental because this was one of the main arguments for our strategy.
During my research stays abroad, I have come to realize that certain nano-crystals synthesis and characterization methods, which I consider standard, are not generally applied in other labs around the globe. Therefore, by featuring these in this paragraph, I hope such techniques will find wider acclaim in nanoscience. Firstly, from my conclusions, one can appreciate that microwaves are the method of choice for solvothermal procedures, shortening the reaction significantly and thus tackling the main drawback of solvothermal syntheses. Therefore, every researcher is strongly encouraged to transfer their autoclave syntheses to the microwave. Note that this conviction has no relation with the so called, special non–thermal microwave effect, which has never been really proven, but the microwave is simply faster as the heat transfer proceeds more quickly. Secondly, as a material scientist, it was no walk in the park to shift my focus to learning NMR, but it is obvious that NMR was a major tool in my work and definitely worth the effort. NMR may seem a primarily organic chemistry tool but inorganic chemists should learn more about this highly relevant technique as it can give a wealth of information about reaction mechanisms, NC–ligands interactions and even structural information of solids.

Finally, there is a theory; there are two kinds of researchers. The first class of scientists is creative and seeks to synthesize new materials and push the boundaries of existing formulations. The second group has a desire to understand why the first group is succeeding, and develops a theoretical framework and structure. Subsequently, the first group wields the insights of the second group to accomplish the production of new concoctions. I think it is crucial to know which group you belong to, but I also think it equally important to sometimes attempt to be that other class, just to climb out of your scientific comfort zone.
A.1 Supporting info of Chapter 3

A.1.1 Photometric chloride determination and chloride density

One batch of hafnia NCs was suspended in 2 mL ethanol and the concentration was gravimetrically determined: 33 mg HfO$_2$/mL.

To 0.4 mL of that suspension diethyl ether was added to precipitate the NCs and after centrifugation, the NCs were washed once with diethyl ether and redispersed in 4 mL of ethanol with the aid of an ultrasonic bath (10x dilution). 1 mL of that resulting suspension was diluted with 10 mL deionized water. To measure the amount of chloride in the aqueous suspension the VWR chloride test 1.14887.0001 was used. 5 mL of sample was brought in a 20 mL vial. 2.5 mL of Cl-1 reagent was added and subsequently 0.5 mL of Cl-2 reagent was added. The samples were shaken and measured almost instantly with UV-VIS around 445 nm of wavelength. The absorbance at 445 nm (0.283 on average) was multiplied with the factor 28.2 to obtain the concentration of chloride in mg/L (8 mg/L on average). This number was then transformed to the amount of chloride in mmol in the one batch of
hafnia NCs.

\[
\frac{8 \text{ mg/L}}{35.45 \text{ g/mol}} \times 0.011 \times 4 \times \frac{2 \text{ mL}}{0.4 \text{ mL}} = 49.7 \mu\text{mol chloride} \quad (\text{A.1})
\]

Two measurements were executed with the 11 mL of sample. In addition, to check the reproducibility of the procedure, another 0.4 mL of original suspension was treated in the same fashion. The number was averaged and the error was calculated: 49.7 ± 2 µmol.

The same procedure was performed but the NCs were washed zero times or washed twice with diethyl ether and is graphically shown in Figure A.1. In conclusion, additional washing doesn’t change the chloride concentration.

![Figure A.1: The dependence of the amount of chloride in one batch of hafnia on the number of washing steps with diethyl ether.](image)

The chloride density was calculated: in one batch 66 mg of HfO₂ is present. This corresponds to 0.314 mmol of hafnium. With an average diameter from TEM of 5 nm, a volume of 65.45 nm³ per NC was calculated. The molar volume of hafnia is the molecular weight (210 g/mol) divided by the density (9.68 g/cm³): 21.7 cm³/mol. Consequently, the amount of HfO₂ per NC expressed as mol HfO₂ per NC is

\[
\frac{65.45 \text{ nm}^3/\text{NC}}{21.7 \text{ cm}^3/\text{mol}} 10^{-21} = 30.17 10^{-21} \text{ mol HfO}_2/\text{NC} \quad (\text{A.2})
\]

The number of particles in one batch will be:

\[
\frac{0.314 10^{-3} \text{ mol HfO}_2}{3.017 10^{-21} \text{ mol HfO}_2/\text{NC}} = 1.04 10^{17} \quad (\text{A.3})
\]
There is 49.7 \( \mu \text{mol} \) chloride in one batch so this corresponds to \( 2.99 \times 10^{19} \) chloride ions, so there are 287.3 chloride ions per NC. Also the surface area of one NC can be calculated as the surface of a sphere of 2.5 nm radius: 78.53 \( \text{nm}^2 \) and finally the chloride density is

\[
\frac{297.3 \text{Cl}^-/\text{NC}}{78.53 \text{nm}^2/\text{NC}} = 3.7 \text{Cl}^-/\text{nm}^2 \quad (A.4)
\]

In the case of zirconia nanocrystals, the same procedure and calculations apply and the result is 69.1 \( \pm \) 2 \( \mu \text{mol} \), in one synthesis batch of zirconia. This is higher than the case of hafnia but also the amount of zirconia is higher so everything taken into account, this corresponds to a ligand density of 3.35 \( \pm \) 0.2 Cl\(^-\)/nm\(^2\), which is comparable to the chloride density of hafnia NCs.

The similar chloride densities are no surprise since both hafnia and zirconia are monoclinic and have almost the same lattice parameters. (see Table A.1). The density of hafnium atoms on unreconstructed lattice planes, was calculated to be 3.75/\( \text{nm}^2 \) (010), 7.5/\( \text{nm}^2 \) (001) and 10/\( \text{nm}^2 \) (1-11). On average, the surface density of chloride is about 50 % of the surface density of hafnium. Our numbers are therefore realistic values.


<table>
<thead>
<tr>
<th></th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>( \beta ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfO(_2)</td>
<td>0.512</td>
<td>0.518</td>
<td>0.529</td>
<td>99</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>0.514</td>
<td>0.520</td>
<td>0.531</td>
<td>99</td>
</tr>
</tbody>
</table>
A.1.2 Zoom of 2D NOESY

Figure A.2: Zoom of Figure 3.7.

A.1.3 Titration with $d_1$-OAc

**Preparation of $d_1$-OAc.** Oleic acid with a deuterated carboxylic acid $d_1$-OAc was prepared by dissolving sodium oleate (100 mg, 99% pure) in a DCl/D$_2$O mixture (50 µL DCl (99 atom % D) in 2.0 mL D$_2$O (99.97 atom% D)), followed by a phase transfer of the formed $d_1$-OAc to cyclohexane-$d_{12}$ (500 µL - 99.6 atom% D). The organic phase was separated from the aqueous phase in an O$_2$ and H$_2$O free glove box. This was considered the $d_1$-OAc stock solution.

**NMR sample preparation.** Extreme care was taken to prevent contamination of NMR tubes and HfO$_2$ NCs samples by residual H$_2$O. This involved loading and drying of NMR tubes and a (5 times) purified oleic acid capped HfO$_2$ suspension in the glove box 48 hours prior to the NMR sample preparation. The required oleylamine for post-modification was removed during the purification. Finally, in the glovebox, CHCl$_3$ of the purified suspension was evaporated and dry CDCl$_3$ was added. This procedure was repeated and this was called the NC stock solution. No characteristic water resonance was observed in the spectra of the stock solution and after addition
of $d_1$-OAc to the nanocrystal suspension, the carboxylic acid resonance was observed at 12 ppm so that we can conclude that the samples are water-free.

**Experiments, observations and calculations.** 30 \( \mu L \) of $d_1$-OAc hexane solution was added to 490 \( \mu L \) CDCl$_3$. The concentration of OAc was determined via the ERETIC method to be 12.14 mM in the NMR sample which means the real concentration in the $d_1$-OAc stock solution was

\[
  c_{OAc} = \frac{12.14 \, mM \times 520 \, \mu L}{30 \, \mu L} = 210 \, mM
\]  

(A.5)

The degree of deuteration was determined from the residual carboxylic acid signal. When the integration of the alkene signal was set to 2, the integral of the carboxylic acid was 0.0766. So 7.66 \% of oleic acid molecules still have a proton. As a results 92.34 \% is deuterated. This gives an overall concentration of $d_1$-OAc in the $d_1$-OAc stock solution of $210 \times 0.9234 = 194 \, mM$.

600 \( \mu L \) of the NC stock solution was measured in NMR and the concentration of bound OAc was determined to be 12.87 mM. In the final experiment, 450 \( \mu L \) of NC stock solution was combined with 150 \( \mu L \) of the $d_1$-OAc stock solution. Useful numbers were calculated

\[
  450 \mu L \times 12.87 mM = 5.79 \, \mu mol \, \text{bound OAc} \quad \text{(A.6)}
\]
\[
  150 \mu L \times 210 mM = 31.5 \, \mu mol \, \text{excess OAc} \quad \text{(A.7)}
\]
\[
  5.79 + 31.5 = 37.29 \, \mu mol \, \text{total OAc} \quad \text{(A.8)}
\]
\[
  31.5 \mu mol \times 0.9234 = 29.09 \mu mol \, d_1\text{-OAc} \quad \text{(A.9)}
\]
\[
  31.5 \mu mol - 29.09 \mu mol = 2.41 \mu mol \, H_1\text{-OAc} \quad \text{(A.10)}
\]

The experimentally observed proton concentration (derived from the carboxylic acid signal at 12 ppm) relative to the total concentration of oleic acid molecules (from the alkene resonance) was $[H]/[OAc] = 18.6 \%$. We can also calculate the expected ratio for the situation when either there are or there aren’t protons on the surface.

\[
  \text{HfO}_2 \cdot R_1\text{COO} + R_2\text{COOD} \quad \implies \quad \text{HfO}_2 \cdot R_2\text{COO} + R_1\text{COOD} \quad \text{(A.11)}
\]
\[
  \text{HfO}_2 \cdot R_1\text{COOH} + R_2\text{COOD} \quad \implies \quad \text{HfO}_2 \cdot R_2\text{COOD} + R_1\text{COOH} \quad \text{(A.12)}
\]

If there are no protons on the surface, the only protons that will be visible are the ones from the incomplete deuteration: 2.41 \( \mu mol \). So the ratio would be
\[
\frac{[H]}{[OAc]} = \frac{2.41 \, \mu \text{mol} \, H}{37.29 \, \mu \text{mol} \, \text{total OAc}} = 6.5\% \quad (A.13)
\]

If there are as many protons on the surface as there are bound OAc then the total amount of protons would be: \(5.79 + 2.41 = 8.2 \, \mu \text{mol}\). However, not all these protons will be present in solution, they will be stochastically distributed among all the OAc molecules, bound (i.e. invisible proton) and unbound (i.e. visible protons). Thus the amount of visible protons will be \(8.2 \times 31.5/37.29 = 6.93\). This results in a ratio

\[
\frac{[H]}{[OAc]} = \frac{6.93 \, \mu \text{mol} \, H}{37.29 \, \mu \text{mol} \, \text{total OAc}} = 18.57\% \quad (A.14)
\]

Which is exactly the experimental number so there are as many protons near the surface as there are bound OAc.

A.2 Supporting info of Chapter 4

A.2.1 Titration of HfO$_2$ NCs with octylamine

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Figure A.3: Full spectrum of Figure 4.3.}
\end{figure}
A.2.2 Deconvolutions

Figure A.4: The deconvolutions of the alkene resonances in Figure 4.3, A. 4.9 and B. 8.4 equivalents
Figure A.5: The deconvolutions of the alkene resonances in Figure 4.4, A. 0.5, B. 3.6 and C. 7.2 equivalents
A.2.3 Separation of oleic acid and HfO₂ NCs

![Figure A.6](image)

**Figure A.6:** The black curve presents a zoom on the alkene region of the $^1$H NMR spectrum of a dispersion of HfO₂ NCs in toluene to which 30 equivalents of amine were added. Both a bound and a mixed state resonance are observed. The red curve is the $^1$H NMR spectrum of the supernatant after precipitation of the NCs with methanol. The supernatant was dried and the resulting oil was redissolved in methanol-$d_4$. The difference in solvents caused the difference in chemical shift of the alkene resonance.

A.2.4 Calculation of the equilibrium constant

Consider the exchange equilibrium (DDAc A.15). In table A.2, the specific nomenclature for this section are displayed.

\[
[\text{NC}^-\text{HOAc}] + 2\text{Am} \rightleftharpoons [\text{NC}^-\text{Am}]^+[\text{OAc}^-\text{HAm}] \quad (A.15)
\]

**Table A.2:** Overview of species notation, their meaning and their concentration notation.

<table>
<thead>
<tr>
<th>Species</th>
<th>Description</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{NC}^-\text{HOAc}]$</td>
<td>bound oleic acid</td>
<td>$[\text{HOAc}]_b$</td>
</tr>
<tr>
<td>Am</td>
<td>free octylamine</td>
<td>$[\text{Am}]_f$</td>
</tr>
<tr>
<td>$[\text{NC}^-\text{Am}]$</td>
<td>bound amine</td>
<td>$[\text{Am}]_b$</td>
</tr>
<tr>
<td>$[\text{OAc}^-\text{HAm}]$</td>
<td>ion pair of released acid and amine</td>
<td>$[\text{HOAc}]_{\text{mix}}$</td>
</tr>
</tbody>
</table>
For the calculation of the equilibrium constant, a fresh sample was prepared and treated with 5, 10, 15, 20 and 30 equivalents (with respect to bound acid) of octylamine. The total concentration of oleic acid was determined via integration of the whole alkene resonance; 11.3 mM. Deconvolution of the bound and the mixed (free + entangled) state was achieved by the multipeak fitting 2.0 package of IGOR pro. Two lorentzian functions were fitted to the alkene resonance region and the relative areas yielded the relative population and concentration; $[\text{HOAc}]_b$ and $[\text{HOAc}]_{\text{mix}}$. The latter we assume equal to the concentration of the ion pair.

The total concentration of octylamine, $[\text{Am}]_{\text{total}}$, was exactly determined via integration of the alpha CH$_2$ after substraction of the initial spectrum (of the particles with oleic acid, without addition of amine). No distinction could be made between resonances of bound or free/entangled octylamine in the spectrum. Therefore we assumed that one molecule octylamine replaces one molecule of oleic acid, i.e. the concentration of liberated acid is equal to the concentration of bound amine, $[\text{HOAc}]_{\text{mix}} = [\text{Am}]_b$. This allows to simplify the equilibrium constant to

$$Q_2 = \frac{[\text{HOAc}]_{\text{mix}} [\text{Am}]_b}{[\text{HOAc}]_b [\text{Am}]_b^2} = \frac{[\text{HOAc}]_{\text{mix}}^2}{[\text{HOAc}]_b ([\text{Am}]_{\text{total}} - 2[\text{HOAc}]_{\text{mix}})^2}$$ (A.16)

We call this $Q_2$ since the reaction quotient of the equilibrium without including the ion pair is denoted as $Q_1$

$$Q_1 = \frac{[\text{NC}^-\text{HOAc} + \text{Am} \rightleftharpoons [\text{NC}^+\text{Am}]^+\text{HOAc}}{[\text{HOAc}]_{\text{mix}} [\text{Am}]_b^2} = \frac{[\text{HOAc}]_{\text{mix}}^2}{[\text{HOAc}]_b ([\text{Am}]_{\text{total}} - [\text{HOAc}]_{\text{mix}})}$$ (A.18)

### A.2.5 XRF results

XRF measurements were performed on a blanc Teflon substrate and a Teflon substrate with 50 µL of supernatant (HfO$_2$ NCs + octylamine precipitated with methanol) after drying, see Figure A.7. The substrates feature a slight varying background of tantalum but clearly upon addition of the supernatant no signal of hafnium is detected.
Table A.3: Overview of the calculations of the reaction quotient for the exchange reaction with ion pair formation ($Q_2$) for different amine concentrations.

<table>
<thead>
<tr>
<th>$[Am]$ : $[HOAc]$</th>
<th>$[HOAc]_b$</th>
<th>$[HOAc]_{mix}$</th>
<th>$[Am]_{total}$</th>
<th>$Q_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.26</td>
<td>10.57</td>
<td>0.69</td>
<td>59.23</td>
<td>$1.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>9.41</td>
<td>9.79</td>
<td>1.47</td>
<td>106.00</td>
<td>$2.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>12.6</td>
<td>9.07</td>
<td>2.19</td>
<td>141.54</td>
<td>$2.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>17.2</td>
<td>8.78</td>
<td>2.48</td>
<td>193.60</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>24.6</td>
<td>8.10</td>
<td>3.16</td>
<td>277.00</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Mean: $2.0 \times 10^{-5}$

Standard deviation: $0.6 \times 10^{-5}$
**A.3 Supporting info of Chapter 5**

**A.3.1 Resonance assignment of the octylamide of oleic acid**

To allow for sufficient intensity of all the resonances in the 2D spectra, we added octylamine together with excess oleic acid to HfO$_2$ NCs, capped with oleic acid and heated the mixture for three hours. In Figure A.8, the different molecules (amine, acid and amide) and the assignment of their most important resonances are depicted.

We start with the resonances of oleic acid (a-d). The assignments follow from the reference spectrum in Figure 5.3. We will not discriminate between the alkene resonances of oleic acid and the amide of oleic acid since they overlap, both are referred to as (e). The same reasoning applies to the alkene neighbours (c), the aliphatic CH$_2$ units (1-1.5 ppm) and the methyl resonance (d). Hence the only characteristic signals of oleic acid are the alpha and beta CH$_2$ units, (a) and (b).
Figure A.8: Assignment of the different resonances to the various compounds in the mixture after heating a HfO$_2$ NC dispersion in dichlorobenzene with excess oleic acid and octylamine to 130 °C for 3 hours. Spectra acquired at 60 °C.

The characteristic resonances of octylamine are the alpha (1) and the beta CH$_2$ (2). The rest of the CH$_3$ units (1-1.5 ppm) overlap with similar resonances of oleic acid and the resulting amide. The same applies for the CH$_3$ resonance of octylamine as it is denoted as (d). For the amide of octylamine and oleic acid, the resonances (c-e) overlap with other resonances but the resonances (a'), (b') and (1') are observed separately in the 1D spectrum. Special attention goes to resonance (*) since this is the amide proton and
already proves the formation of an amide species.

Further confirmation for the previous assignments was sought in 2D NMR techniques. We measured $^1$H-$^{13}$C HMBC, $^1$H-$^{13}$C HSQC, and $^1$H-$^1$H TOCSY. In the HMBC, the carbonyl carbon of oleic acid (179.5 ppm) clearly correlates with the alpha (a) and beta (b) protons of oleic acid. The HMBC also proves that the carbonyl carbon of the amide (172 ppm) correlates with both resonances (1') and (a',b'). This underscores the fact that the amide is the product of octylamine and oleic acid since (1') pertains to the octylchain of the amide and (a') and (b') pertain to the oleylchain of the amide. The TOCSY provides us with the assurance that the amide resonance (*) correlates with (1'), confirming further the assignment of the amide molecule (see correlation [*-1']). TOCSY also confirms that (1) and (2) are connected, (a) and (b) are connected and (a') and (b') are connected. Finally, the HSQC confirms that (1', 1, 2, a, b, c, a' and b') are CH$_2$ units and (d) is a CH$_3$ unit. However more important, HSQC provides addition separation of resonances along the F1 ($^{13}$C) dimension and therefore, it allows us to clearly separate the somewhat overlapping resonances (a') and (c) or the resonances (2) and (b').

### A.3.2 Resonance assignment of ethylester of oleic acid

To allow for sufficient intensity of all the resonances in the 2D spectra, we added ethanol together with excess oleic acid to HfO$_2$ NCs, capped with oleic acid and heated the mixture for three hours. In Figure A.9, the different molecules (alcohol, acid and ester) and the assignment of their most important resonances are depicted.

Like in the assignment of the amide, we will not consider overlapping resonances. In this case this is the oleylchain (of oleic acid or the ester) except for the alpha protons (a and a'). The beta protons (b) already overlap both in the $^1$H NMR spectrum as in the HSQC. The resonances (1) and (2) pertain to ethanol. The resonances (1') and (2') belong to the ethylchain of the ester.

The HMBC shows a correlation of the ester carbonyl carbon (173 ppm) with both (1') and (a'), confirming the formation of the ester bond between ethanol and oleic acid. Also the correlation between the carbonyl carbon of oleic acid (178 ppm) and the alpha protons of oleic acid (a) is apparent. Furthermore, TOCSY show the correlation between (1) and (2) and between (1') and (2'), confirming the two ethyl chains in both ethanol and the ethyl ester. Finally HSQC confirm the CH$_2$ nature of (1, 1', a, a' and b) while (2) and (2') are recognized as CH$_3$ units.
Figure A.9: Assignment of the different resonances to the various compounds in the mixture after heating a HfO$_2$ NC dispersion in dichlorobenzene with excess oleic acid and octylamine to 130 °C for 3 hours. Spectra acquired at 60 °C.
A.3.3 Evolution of the ethanol concentration

Figure A.10: The ethanol concentration decreases quicker than the esterification reaction goes forward. Initially, there was a sufficient excess of ethanol with respect to oleic acid but this changes. This is because of evaporation and influences the esterification reaction’s equilibrium. Although in this paper we merely outline the concepts and possibilities, for practical use, the reaction vessel should be sealed tightly and pressurized so that volatile components cannot escape the reaction mixture.

A.3.4 Control experiment without nanocrystals

Figure A.11: Heating at 130 °C of a mixture of ethanol (5 µL) and oleic acid (15 µL) in dichlorobenzene does not result in ester formation.
A.3.5 Control experiment with CdSe NCs

Figure A.12: CdSe NCs with excess oleic acid and ethanol do not catalyze the esterification. The intensity of ethanol decreases over time, probably due to evaporation.

A.3.6 Control experiment; ethylacetate at 130 °C

Figure A.13: There is no sign of any hydrolysis (e.g., ethanol resonances) present in the sample when ethylacetate is heated in DCB to 130 °C for 1 hour.
A.3.7 Addition of water to enhance the hydrolysis rate

Figure A.14: To 500 µL of HfO$_2$ NC dispersion, ethylacetate was added and the resulting mixture was heated to 130°C with or without an additional 5 µL of water. The normalized concentration of ethylacetate, decreases faster with additional water, indicating faster hydrolysis.
A.4 Supporting info of Chapter 6

A.4.1 Purification

Figure A.15: The purification, using toluene, was monitored by NMR. The concentration of DDAc and Gln is lower in the $^1$H NMR spectrum of the purified NCs, with respect to the non-purified dispersion. In the spectrum of the supernatant, which is a 1:4 mixture of MeOH:tol-$d_8$, intense peaks of DDAc and Gln are present. Based on quantification, it was calculated that 88 % of DDAc and 97 % of Gln is washed away.
A.4.2 Ligand exchange with threonine, leucine and methionine

Figure A.16: In the $^1$H NMR spectra of HfO$_2$ NCs, stabilized with leucine, threonine and methionine MeOH-$d_4$, the peaks were assigned based on the reference spectra.

Figure A.17: In the NOESY NMR spectrum of HfO$_2$ NCs, stabilized with threonine, in MeOH-$d_4$, clear intramolecular negative nOe peaks are visible for Thr. However still, the zero–quantum coherence dominates the cross peak from $\beta$ to $\gamma$. 
Figure A.18: The NOESY spectrum recorded with a zero-quantum filter significantly reduced the zero-quantum artefacts. Weak negative nOe peaks appear between the $\beta$ and $\gamma$ signals of Gln.
B.1 Publications in international journals


17. De Keukeleere, K.; Cayado, P.; Meledin, A.; **De Roo, J.**; Rijckaert, H.; Pollefeyt, G.; Bruneel, E.; Van Tendeloo, G.; Puig, T.; Obradors, X.; Van Driessche, I. Vortex pinning by preformed metal oxide nanocrystals in YBa$_2$Cu$_3$O$_{7-δ}$ coated conductors enhances the critical current. *in preparation*


### B.2 Patents

- EP15157156.9 – Nanoparticles for the Use as Pinning Centers in Superconductors
- PF78142 – Crystalline nanoparticles of tantalum oxide and synthesis thereof via an in situ esterification method

### B.3 First author conference contributions

Jonathan De Roo, Freya Van den Broeck, Yolanda Justo, Katrien De Keukeleere, José Martins, Isabel Van Driessche and Zeger Hens. *The surface chemistry of metal oxide nanocrystals, how protons change the game*. (2015, april 6-10) MRS spring meeting, San Francisco (USA). Talk

Jonathan De Roo, Freya Van den Broeck, Katrien De Keukeleere, José Martins, Isabel Van Driessche and Zeger Hens. *The surface chemistry of*
metal oxide nanocrystals; a solution NMR study. (2014, November 24-25) YBMRS annual meeting, Spa (Belgium). Talk rewarded with presentation prize


Jonathan De Roo, Katrien De Keukeleere, Jonas Feys, Petra Lommens, Zeger Hens, Isabel Van Driessche. Synthesis of BaHfO3, Ta2O5 and HfO2 nanoparticles as artificial pinning centers in High Temperature Superconductors. (2013, March 6-9) JCF frühjahrssymposium, Berlin (Germany). Talk rewarded with presentation prize

B.4 Other conference contributions

Glenn Pollefeyt, Hannes Rijckaert, Max Sieger, Katrien De Keukeleere, Jonathan De Roo, Ron Feenstra, Jan Bennewitz, Jens Hänisch, Ruben Huehne, Michael Bäcker, Maximilian Hemgesberg and Isabel Van Driessche. Nanocomposite YBa2Cu3O7−δ thin films using low fluorine MOD and
preformed nanocrystals. Applied Superconductivity, 12th European conference (2015, September 6-10)

Hannes Rijckaert, Glenn Pollefeyt, Katrien De Keukeleere, Jonathan De Roo, Ron Feenstra, Jan Bennewitz, Michael Bäcker, Maximilian Hemgesberg and Isabel Van Driessche. Understanding growth and nucleation of nanocomposite YBa$_2$Cu$_3$O$_{7-\delta}$ thin films derived from low fluorine metal organic deposition. Applied Superconductivity, 12th European conference (2015, September 6-10)


Katrien De Keukeleere, Jonathan De Roo, Petra Lommens, Pascal Van Der Voort, José Martins and Isabel Van Driessche. Zirconia nanocrystals: effect of metal precursor on the crystalline phase and surface chemistry. European Ceramic Society, 14th International conference (2015, June 21-25)

Katrien De Keukeleere, Jonathan De Roo, Freya Van Den Broecke, Petra Lommens, José Martins and Isabel Van Driessche. Zirconia nanocrystals: effect of metal precursor on the crystalline phase and surface chemistry. MRS spring meeting (2015, april 6-10)

Katrien De Keukeleere, Jonathan De Roo, Pablo Llosa, Hannes Rijckaert, Glenn Pollefeyt, Petra Lommens, Susagna Ricart, Xavier Obradors and Isabel Van Driessche. Synthesis and incorporation of nanosized pinning centers for YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors. MRS spring meeting (2015, april 6-10)

Zeger Hens, Freya Van den Broeck, Jonathan De Roo, Ruben Dierick, Isabel Van Driessche, Jose C Martins. Surface chemistry of colloidal nanocrystals from semiconductors to metal oxides. Abstracts of papers of the american chemical society (2014, august 10)

Katrien De Keukeleere, Jonathan De Roo, Freya Van Den Broecke, Petra Lommens, José Martins, Isabel Van Driessche. *Zirconia nanocrystals: effect of metal precursor on the crystalline phase and surface chemistry.* Annual meeting of the Belgian Ceramic Society 2014 (2014, October 23)

Hannes Rijckaert, Katrien De Keukeleere, Jonathan De Roo, Jonas Feys, Isabel Van Driessche. *Synthesis and stabilization of ZrO$_2$ and HfO$_2$ as artificial pinning centers in YBCO superconductors.* 2th Chemistry conference for Young Scientists (ChemCYS 2014)

Katrien De Keukeleere, Jonas Feys, Jonathan De Roo, Glenn Pollefeyt, Petra Lommens, Isabel Van Driessche. *General approach for the development of YBa$_2$Cu$_3$O$_{7-\delta}$ high-temperature superconductors.* 17th International Sol-Gel Conference (Sol-Gel 2013)

Isabel Van Driessche, Petra Lommens, Pieter Vermeir, Jonas Feys, Melis Arin, Glenn Pollefeyt, Katrien De Keukeleere, Jonathan De Roo, Mieke Meire, Jonathan Watté, Klaartje De Buysser. *Complex oxide nanoparticles and thin films by chemical solution processing and deposition.* 2013 MRS Spring meeting and exhibition

Katrien De Keukeleere, Jonathan De Roo, Jonas Feys, Petra Lommens, Isabel Van Driessche. *Time-and energy efficient methods for the aqueous synthesis of ceramic BaZrO$_3$ nanocrystals.* 17th International Sol-Gel Conference (Sol-Gel 2013)

Katrien De Keukeleere, Jonathan De Roo, Petra Lommens, Isabel Van Driessche. *Innovative synthesis of metal oxide nanoparticles for use as artificial pinning centres in YBa$_2$Cu$_3$O$_{7-\delta}$ superconducting layers.* 2013 MRS Spring meeting and exhibition

Katrien De Keukeleere, Jonathan De Roo, Jonas Feys, Isabel Van Driessche. *Development of nanosized ZrO$_2$ and BaZrO$_3$ pinning centers for YBCO (YBa$_2$Cu$_3$O$_{7-\delta}$) superconductors.* Applied Superconductivity, 11th European conference, 2013