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Interface formation during silica encapsulation of colloidal CdSe/CdS quantum dots observed by *in situ* Raman spectroscopy

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We investigate the encapsulation of CdSe/CdS quantum dots (QDs) in a silica shell by *in situ* Raman spectroscopy and find a distinct shift of the CdS Raman signal during the first hours of the synthesis. This shift does not depend on the final silica shell thickness but on the properties of the initial core-shell QD. We find a correlation between the Raman shift rate and the speed of the silica formation and attribute this to the changing configuration of the outermost layers of the QD shell, where an interface to the newly formed silica is created. This dependence of Raman shift rate on the speed of silica formation process will give rise to many possible studies concerning the growth mechanism in the water-in-oil microemulsion, rendering *in situ* Raman a valuable instrument in monitoring this type of reaction. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4979515>]

I. INTRODUCTION

During the last few years, colloidal quantum dots (QDs) have gained more and more interest for their potential application in bioimaging.^{1–3} Among other inorganic fluorophores,^{4–8} functionalized QDs used as probes in medical or biological applications instead of dye molecules could offer high brightness and finely tunable optical properties, which have been researched for many years with the focus on optoelectronic applications such as light emitting devices (LEDs), solar cells, and even lasers.^{9–13} Especially their high quantum yield and intense and broad absorption spectrum, together with their long-term stability, provide advantages compared to conventional organic fluorophores.^{1–3} For those applications, however, the QDs need to be stable in aqueous solution and require a barrier that prevents oxidation and diffusion of ions from their insides.

These limitations can be solved by coating QDs with a biocompatible material such as silica, as previously shown by several groups.^{14,15} Here, the microemulsion technique has become the method of choice for the silica encapsulation of such hydrophobic nanocrystals.¹⁶ It relies on aqueous nanodroplets, or reverse micelles, dispersed in an oil phase and stabilized by surfactant molecules. These micelles can be used as nanoreactors for the synthesis of a large variety of nanoparticles, including silica, via a classic sol-gel reaction based on the hydrolysis and condensation of an alkoxysilane precursor.^{17,18} The actual mechanism for the silica encapsulation of hydrophobic nanocrystals in the microemulsion is not fully elucidated; it is however assumed that before the hydrophobic nanocrystals, which are initially located in the oil phase, can migrate into the aqueous micelles, the organic ligands

which originally passivate the nanocrystal surface need to be substituted by hydrolyzed silica monomers and/or surfactant molecules.^{19,20}

How the growth of a silica shell influences the QDs is mostly studied by photoluminescence (PL) and absorption spectroscopy. In this way, one quantifies the quality of the encapsulation, while adjusting the synthesis for optimal quantum yield and stability. As the overall optical properties of the QD will however strongly depend on the properties of the interface between the QD surface and the silica shell, it is of utmost importance to gain a better understanding of the interaction. Acebrón *et al.*²¹ made use of ¹H NMR spectroscopy to follow the species that interacts with the organic ligands, but this technique does not provide direct microstructural information on the QDs. Ethiraj *et al.*²² used Raman spectroscopy mainly to show that QDs remain intact after silica encapsulation and to find similarities between the features that appear for the encapsulated sample compared to pure silica. Apart from their study, Raman spectroscopy is rarely applied to study this kind of heteronanostructures, despite it being widely used for the analysis of colloidal nanocrystals and nanocrystal-complexes in general.^{23,24} The information to be gained from this method is diverse and covers structural information on the lattice configuration, such as strain or temperature-dependent expansion, and more complex quantities like the electron-phonon coupling or the location of electronic states by resonance Raman spectroscopy.^{25–29}

Here, we study the formation of a silica shell around CdSe/CdS core/shell QDs by *in situ* Raman spectroscopy, where we monitor variations of the different Raman modes as a function of time. Most notably, we observe the shifting of the CdS longitudinal optical (LO)-like phonon mode towards the CdS bulk frequency. Increasing the rate of silica formation does not change the total shift of this phonon line, yet it shortens the time the shift takes to reach its final value. We thus

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conclude that this shift of the CdS LO phonon is a characteristic of the initial stage of the silica growth and we attribute it to the enhanced coordination of the CdS shell's surface atoms by silica, a finding which suggests the formation of a solid/solid interface between both. Additionally we show that the Raman intensities are sensitive to the local dielectric environment of the QD during synthesis and thus provide an additional signal to monitor silica shell growth. Overall, our results emphasize that *in situ* Raman spectroscopy is an extremely beneficial technique to monitor structural changes in nanocrystals and nanoparticles during synthesis, where especially in the case of heteronanostructures, it provides detailed information on the interaction between the different materials involved.

II. EXPERIMENTAL SECTION

CdSe/CdS quantum dots were synthesized according to the *flash* procedure described by Cirillo *et al.*³⁰ For the majority of this work, QDs consisting of a 4.0 nm CdSe core and a total diameter of 7.2 nm (QD A) are studied. These are later compared to QDs with a 3.6 nm core and a total diameter of 9.1 nm (QD B). The average size of the QDs was determined based on TEM observations. The concentration of the QDs' solutions was determined based on their absorbance in toluene at 300 nm and 350 nm, using the corresponding intrinsic absorption coefficients of the CdSe/CdS. These were calculated from the Maxwell-Garnett effective medium theory depending on the ratio between the CdSe core and CdS shell volumes.^{31,32} As synthesized flash CdSe/CdS QDs are passivated with a cadmium oleate ligand.³³ The silica encapsulation is performed via the microemulsion technique described by Aubert *et al.*,¹⁴ who have shown both a high photoluminescent quantum yield and a long term stability for "flash"-synthesized QDs even after silica encapsulation and dispersion in water. The synthesis was adjusted to operate in a cyclohexane solution, since the Raman signal of the solvent can be separated well from that of the QDs. In a typical microemulsion synthesis, 0.2 nmol of QDs in 1 mL of cyclohexane is mixed with 0.32 mL of surfactant (Brij30) and 55 μ L of a 3% ammonia solution in water. After 1 h of stirring, a varying amount of the silica precursor tetraethyl orthosilicate (TEOS) is added to the microemulsion in order to analyze different reaction speeds and final silica shell thicknesses. The mixture is left stirring for the whole duration of the reaction, to keep the synthesis stable.

Raman measurements were performed using the 487 nm line of an Ar⁺-ion laser (Spectra Physics Stabilit, Coherent Fred), with a macro-Raman setup and a Dilor XY triple monochromator. The solution of QDs was contained in a macro-cuvette (Thorlabs, for wavelengths between 200 nm to 3 μ m) and was constantly stirred during the whole experiment with a magnetic stirrer. To prevent laser induced heating, the incident power was kept below 10 mW and a cooling fan was directed onto the cuvette. To assess the evolution of the Raman signal over time, measurements with 180 s integration time were taken in 10 min intervals.

III. RESULTS AND DISCUSSION

A typical Raman spectrum of the wurtzite CdSe/CdS QDs dispersed in cyclohexane is displayed in Fig. 1(a). Next to

FIG. 1. (a) Raman spectra of CdSe/CdS QDs in cyclohexane solution. Peaks from the CdSe core and the CdS shell can be seen at 210 cm^{-1} and 292 cm^{-1} , respectively. The solvent cyclohexane has peaks at 382 and 425 cm^{-1} . Position of the CdSe (b) and CdS (c) LO-like modes depending on time passed during silica synthesis. Time = 0 corresponds to the time of TEOS precursor injection. Note that a break has been introduced in the time axis at 10 h to highlight early hours of the synthesis. (d) FWHM of the CdS shell phonon fit during the course of synthesis.

the LO-like Raman modes of the CdSe core (210.3 cm^{-1}) and the CdS shell (292.3 cm^{-1}), characteristic Raman bands of cyclohexane are visible at 382.5 and 425.2 cm^{-1} , which remain unchanged during the whole synthesis, as verified by neon calibration. In line with previous studies, both the CdSe and the CdS modes are redshifted relative to their bulk position (room temperature bulk phonon frequencies $\omega_{\text{CdSe, bulk}} = 210\text{ cm}^{-1}$, $\omega_{\text{CdS, bulk}} = 302\text{ cm}^{-1}$),³⁴ albeit their exact frequencies depend on the geometry of the chosen QDs.²⁶ The developing silica shell is merely visible as a broad background within the low frequency region of the acquired spectra, as it is an amorphous material. Note that both frequencies and intensities discussed within this work were obtained from Lorentzian fits to the spectra, after normalization to the unaffected intensities of the cyclohexane modes.

In Figs. 1(b) and 1(c), the frequencies of the CdSe core and CdS shell LO-like Raman modes (sample QD A) are given as a function of the reaction time. Here, the start of the measurement time ($t = 0\text{ h}$) corresponds to the moment the silica precursor was injected. During the reaction, the CdSe mode only shows a small shift of $\approx 0.5\text{ cm}^{-1}$ towards higher frequencies, while the CdS mode exhibits a much larger increase in frequency of $\approx 2.2\text{ cm}^{-1}$ towards the CdS bulk frequency. This indicates that the silica shell mainly influences the CdS shell structure but keeps the lattice of the CdSe core intact. Furthermore, if the growing silica shell were to only interact with residual organic ligands, it would be difficult to imagine how this could affect the structure of the QDs' surface so strongly. Hence, we presume that the observed shifts of the CdS Raman modes upon silica overgrowth point towards a strong interaction between the CdS outer surface and silica.

While the frequency of the CdS shell shifts by more than 2 cm^{-1} , the full width at half maximum (FWHM) of the signal is only marginally changed from 20 cm^{-1} to 19.5 cm^{-1} , as can be seen in Fig. 1(d). As any intrinsic heterogeneity would inevitably broaden the phonon lineshape, the absence of any

such effect demonstrates that the silica overgrowth does not lead to a mere formation of structural defects.

The observed shifting of the Raman modes can be explained by different models. First of all, the initial shift in frequency can be attributed to strained growth caused by the CdSe/CdS core/shell lattice mismatch.^{25,26,35} In an elastic spring model based on those different lattice constants, the minimization of the overall strain leads to tensile strain in the CdS shell, which decreases for increasing shell thickness. This results in an initial redshift of the CdS phonon that relaxes back to the bulk phonon frequency with increasing shell thickness. The experimentally observed blueshift of the CdS phonon towards the bulk frequency during silica encapsulation could thus simply reflect a relaxation of tensile strain. Second, based on *ab initio* calculations for CdSe/CdS QDs and similar systems, it has been argued that the initial redshift of the CdS phonon is mainly due to surface undercoordination.³⁶ This is a pure surface effect, caused by the breaking of the lattice periodicity at the QD surface, which will be more pronounced for larger surface-to-volume ratios, i.e., thinner shells.³⁶ An improved coordination of surface atoms due to silica overgrowth would then also yield a blueshift of the CdS frequency.

To interpret the observed shift within either of both models, it is important to remember that the overgrown silica is amorphous and thus lacks a lattice constant that could be easily fitted into a strained-growth-model. In fact, an amorphous material is unlikely to form a structure in which it exerts pressure on a substrate—the QD in this case—as such a configuration is energetically unfavorable. Furthermore, as the synthesis is performed at room temperature (20 °C), strain due to different thermal expansion coefficients of the QD and silica can be excluded. It appears, therefore, unlikely that the shift of the CdS Raman mode results from external strain induced by the silica shell. It can, however, be attributed to an improved coordination of surface atoms.^{36,37} This could, for example, reflect the formation of strong, direct bonds between silica and the QD, an interpretation that accounts for the shifts occurring at the earliest stages of silica growth only. Although there is no direct evidence on the nature of this bond, QDs are known to have dangling bonds on their surface,³⁸ thus allowing for the formation of covalent bonds with the silica monomers. Since the reactive species formed during the hydrolysis of TEOS are silanol groups, we assume that a Cd–O–Si bridge is more likely to form with a dangling bond on Cd rather than a Cd–S–Si bond. Although such a reaction step has been proposed as part of the encapsulation process before,^{19,20} the *in situ* Raman investigations thus provide a direct observation of this step for the first time.

To further analyze the time scale and extent of the CdS phonon shifts, we varied the amount of silica precursor per QD, in order to change the rate of the reaction. Here, amounts of $2.86 \cdot 10^5$, $5.51 \cdot 10^5$, and $7.71 \cdot 10^5$ TEOS:QD molar ratios were used, respectively, 13 μ l, 25 μ l, and 35 μ l of TEOS for 0.2 nmol of QDs. To correlate the CdS LO phonon shift with the silica shell thickness, we successively analyzed the three syntheses in separate experiments by TEM (Fig. 2) and by Raman spectroscopy (Fig. 3). For the TEM analysis, we

FIG. 2. (a) Silica shell thickness as determined by TEM-analysis as a function of the synthesis time for different TEOS amounts ($2.86 \cdot 10^5$, $5.51 \cdot 10^5$, and $7.71 \cdot 10^5$ TEOS:QD molar ratio in black, blue, and green, respectively), fitted with a function after Ref. 39, see text. The final size, as well as the speed of the reaction, increases with a higher TEOS concentration. Inset in (a): TEM image of final silica shelled QD. (b) Linear fit of 0–4 hour range (formation of the first silica on the QD) of data given in (a). (c) Slope values from (b) given as a function of TEOS concentration.

stopped the reaction after different time spans, and we can confirm a faster shell growth and a thicker final shell for higher TEOS concentrations, see Fig. 2.

The growth of silica particles in a microemulsion has been described by Osseo-Asare and Arrigada,³⁹ under the assumption that the conversion of TEOS after nucleation can be described by first-order kinetics. This results in a time dependent equation for the average particle size as a function of the TEOS concentration and water-to-surfactant molar ratio. To account for the presence of initial CdSe/CdS seeds, which will influence the initial growth rate, we introduced a time offset to their equation. In this way, a good fit to the TEM data is obtained after 4 h of reaction time. To estimate the

FIG. 3. (a) Raman shift of the CdS mode as a function of the synthesis time for different TEOS amounts per QD surface ($2.86 \cdot 10^5$, $5.51 \cdot 10^5$, and $7.71 \cdot 10^5$ TEOS:QD molar ratio in black, blue, and green, respectively). The final frequency is the same between the different conditions, while the shift rate increases for higher TEOS concentrations. The red vertical markers indicate the time where 90% of the final frequency shift is reached. (b) Raman shift of the three syntheses in dependence of the estimated silica layer thickness determined from linear fits shown in Fig. 2(b). (c) shows the frequency first order shift rates corresponding to the fits in (a) in dependence of the TEOS concentration in the synthesis.

growth rate in the first 4 h of the growth process, we fitted the silica thickness to a linear growth model. Compared to the growth of pure silica particles, the growth rate during this reaction step is reduced. This is of most importance because the strongest shift in the Raman signal appears within this time scale (Fig. 1), indicating a connection between Raman shift and formation of the silica interface. To gather an idea on the initial growth rate of the silica shell, we employ a simple linear fit and find that the speed of silica shell formation is roughly proportional to the fraction of TEOS added in the synthesis (see Fig. 2(c)).

In Fig. 3, the time evolution of the CdS LO Raman features is shown for three different TEOS concentrations. In each synthesis, the Raman modes start at the same initial frequency (same initial QD) and end at the same final frequency. However, the frequency shifts faster and reaches saturation earlier for higher TEOS concentrations in the synthesis. Ordered by increasing TEOS concentrations, 90% of the final frequency change was reached after about 4.4 h, 3.0 h, and 1.8 h, respectively. Translating these early reaction times into a silica shell thickness using the linear growth model, we can plot the Raman shift as a function of the estimated silica shell thickness. As shown in Fig. 3(b), it appears that the Raman shift directly reflects the silica shell thickness, regardless of the TEOS concentration, and thus the silica growth rate. Moreover, this change in Raman shift levels off once the shell thickness exceeds 2 nm. We thus conclude that the Raman shift is determined by the properties of the CdS/silica interface in the early stages of silica shell growth.

The Raman shift can be well described as $\omega(t) = \omega_f - \Delta\omega e^{-kt}$ (see lines in Fig. 3(a)), where ω_f is the final Raman frequency reached during synthesis, $\Delta\omega$ the maximum change in Raman signal, and k the rate of saturation. As could be expected from the initial linear growth regime (see Fig. 2(b)) and the linear dependence of the Raman shift on the shell thickness for thin shells (see Fig. 3(b)), the Raman shift rate k shows an approximately linear dependence on the TEOS concentration (see Fig. 3(c)). Hence *in situ* Raman measurements can be used to estimate the reaction rate and provide a tool to further analyze the influence of each constituent in the reaction on this critical interface. The fact that $\Delta\omega$ remains constant for the three syntheses (Fig. 2(b)) already suggests that the degree of re-coordination of the QD surface during the microemulsion process is independent of the growth rate of the silica shell, at least under the conditions addressed in this study.

Further analysis of the Raman data reveals an additional feature occurring during silica overgrowth. In Figure 4, the Raman intensities of the CdSe and CdS modes are given in the case of the silica synthesis with a medium TEOS concentration. Within the first 6 h of the reaction, the intensity of the CdS mode increases, while that of the CdSe decreases. Note that both intensities saturate on a longer time scale than the frequency change displayed in Fig. 3. The Raman intensity is determined by the strength of electron-phonon coupling, resonance conditions with electronic transitions, and by the strength of the local electric field. Amongst others, these quantities depend on the dielectrical environment. As the local

FIG. 4. Raman intensities, i.e., peak areas obtained from Lorentzian fits for the CdS (a) and CdSe (b) LO-like modes as a function of synthesis time, in each case normalized to the cyclohexane peak (383 cm^{-1}). (c) Raman spectra of the same QD measured with different laser wavelengths, again normalized to cyclohexane according to Trulson *et al.*⁴⁰ For higher excitation energies, the intensity of the CdS mode increases, while that of the CdSe mode decreases.

environment of the QD evolves during the synthesis from a mixture of ligands and cyclohexane ($\epsilon \approx 2.0$)⁴¹ to a micelle in water ($\epsilon = n^2 \approx 1.8$)⁴² and to silica ($\epsilon \approx 2.4$),⁴³ the overall dielectric constant of the environment changes from $\epsilon \approx 2.0$ to ≈ 2.4 . This can have different effects. The screening of the optical field depends, for example, on the local dielectric environment and so do the transition energies between valence- and conduction-band states. Both properties influence the interaction between the QDs and the laser light and thus the intensity of the Raman signals. Unfortunately, the precise effect of dielectric confinement on the optical band gap of QDs is difficult to predict, especially in the case of complex heterostructures.^{44,45} Nevertheless, energy-dependent Raman measurements of the unencapsulated QD given in Fig. 4(c) show that higher intensities for the CdS Raman mode can be found for higher excitation energies. If the transition energies are lowered due to the silica encapsulation, states with stronger Raman coupling could come into resonance with the exciting laser wavelength. This hypothesis of shifting transition energies, induced by a changing dielectric environment, is supported by our experimental observations. It does however not exclude influences of the local field factor modification by silica encapsulation. The fact that the CdSe mode on the other hand displays the opposite behavior both in resonance Raman measurements (Fig. 4(c)), as well as during synthesis (Fig. 4(b)), supports our hypothesis of states shifting towards lower energies.

The effect on the intensity of Raman modes depends on the geometry of the QD, i.e., the core and shell size. In Fig. 5, the *in situ* Raman measurements for two different silica shell syntheses on different QDs are shown. QD A is the configuration used so far, with a CdSe core that has a diameter of 4.0 nm and a total diameter of 7.2 nm, whereas QD B has a 3.6 nm CdSe core and total diameter of 9.1 nm. This leads to lower CdS Raman frequencies for QD A, due to higher strain. The higher CdS surface/volume ratio (QD A: 2.8, QD B: 0.8), results in a higher sensitivity to both strain and surface under-coordination for the uncovered QD A, and thus nicely explains the difference in magnitude of the shift seen

FIG. 5. Raman frequencies of the CdS mode in the course of the silica synthesis for (a) QD A and (b) QD B; Raman intensities (peak area) for the CdS mode during synthesis for (c) QD A and (d) QD B, normalized to solvent intensities to exclude influences of the laser power; Raman spectra of (e) QD A and (f) QD B for different excitation energies, with each spectrum normalized to the solvent as indicated above.

in Figs. 5(a) and 5(b). In Figs. 5(c) and 5(d), the diverging intensity evolutions for QD A and B are shown, and the corresponding energy dependent Raman measurements are given in Figs. 5(e) and 5(f). For QD B (Fig. 5(d)), we find a dip in intensity in the beginning of the synthesis, accompanied by a faster and stronger change in Raman intensity than for QD A (compare Figs. 5(c) and 5(d)). The steep rise in intensity indicates a higher sensitivity to the dielectric environment, which is also supported by the stronger change in intensity upon excitation with higher energies (see Fig. 5(f)). A possible reason for the dip observed in QD B is that at small silica thicknesses (5 nm after 3 h of reaction), the environment is effectively lowered by the introduction of water as the new solvent of the silica coated QD within the micelle. Thus a material with a lower dielectric constant ($\epsilon = 1.8$) is introduced in the environment and is then successively moved further and further away from the QD as the silica shell grows.

IV. CONCLUSION

We have analyzed the Raman signal of CdSe/CdS QDs *in situ* during silica encapsulation. During the reaction, the Raman mode of the CdSe core remains mostly unchanged, indicating that its structure remains mostly unchanged. The Raman mode of the CdS shell on the other hand exhibits a pronounced shift towards the CdS bulk frequency during the initial stage of silica shell growth. We attribute this to the reduced undercoordination of atoms at the CdS surface by the formation of a direct CdS/silica interface. Importantly,

this shift measures the thickness of the early stage silica shell, regardless of the silica growth rate. In addition, also the intensity of the Raman modes changes during silica encapsulation. Since these intensity variations mimic the dependence of the Raman intensity on the excitation energy, this may reflect a variation of transition energies induced by a changing dielectric environment. These observations were made for a limited set of synthesis conditions. Further investigations with varying QD ligands, microemulsion surfactant or pH conditions, for instance, would certainly be of interest for the design of an optimized synthesis towards the production of materials with greater optical properties.

These findings show that Raman spectroscopy allows for the non-destructive, *in situ* monitoring of the critical stages of silica encapsulation of CdSe/CdS QDs. Through frequency shifts or intensity variations of the Raman modes, both structural modifications of the CdS/silica interface and changes in the dielectric environment can be monitored. Clearly, such monitoring enables the silica shell growth process to be studied in more detail and optimized more rapidly than conventional spectroscopic techniques or TEM allows. Moreover, it opens to the prospect of using Raman spectroscopy as a more general *in situ* probe to monitor the formation of colloidal heteronanocrystals that provides information complementary to, for example, absorbance and photoluminescence spectroscopy.

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