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ARTICLE

Colloidal WSe₂ Nanocrystals as Anodes for Lithium-Ion BatteriesPengshang Zhou,^{ab,†} Gearoid Collins,^{c,†} Zeger Hens,^{ab} Kevin M. Ryan,^c Hugh Geaney^{c*} and Shalini Singh^{abc*}Received 00th January 20xx,
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Transition metal dichalcogenides (TMDs) are increasingly of interest in the field of lithium ion batteries due to their unique structure. However, previous preparation methods have mainly focused on their growth from substrates or by exfoliation of the bulk materials. Considering colloidal synthesis has many advantages including precision control of morphology and crystal phases, there is significant scope for exploring this avenue for active material formation. Therefore, in this work, we explore the applicability of colloidal TMDs using WSe₂ nanocrystals for Li ion battery anodes. By employing colloidal hot-injection protocol, we first synthesize 2D nanosheets in 2H and 1T' crystal phases. After detailed structural and surface characterization, we investigate the performance of these nanosheets as anode materials. We find that 2H nanosheets outperformed 1T' nanosheets exhibiting a higher specific capacity of 498 mAh g⁻¹ with an overall capacity retention of 83.28%. Furthermore, to explore the role of morphology on battery performance 3D interconnected nanoflowers in 2H crystal phase were also investigated as an anode material. A noteworthy specific capacity of 982 mAh g⁻¹ after 100 cycles was exhibited by these nanoflowers. The anode materials are characterized prior to cycling and after 1, 25, and 100 charge/discharge cycles, by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), to track the effects of cycling on the material.

Introduction

Transition metal dichalcogenides (TMDs), with the formula MX₂ (M=Mo, W; X=S, Se) have been extensively researched over the past decade for use in catalysis, photovoltaics, transistors, batteries, photodetectors and memory devices.^{1–5} TMDs are layered van der Waals solids characterized by strong covalent bonding in-plane and weak van der Waals forces between the layers. As a consequence, bulk TMDs can be exfoliated into few- or single-layered nanostructures. The individual layers of bulk TMDs (MX₂) are composed of an atomic layer comprising a transition metal (M – Mo, W etc.) sandwiched atomic layer between two chalcogen (X – Se, S etc.) atomic layers. MX₂ are known to primarily form crystals in two phases depending on the atomic stacking configurations: a trigonal prismatic (2H) phase and an octahedral (1T) phase. For instance, six Se atoms coordinate to each W atom prismatically to form a thermodynamically stable 2H-WSe₂ phase, whereas when six Se atoms coordinate octahedrally around one W atom, they form metastable 1T phase or 1T' phase (distorted octahedral) WSe₂. These phases show completely different electronic properties: 2H-WSe₂ is semiconducting, while 1T or 1T'-WSe₂ is metallic in nature.

TMDs nanomaterials have become interesting candidate Li ion battery (LIB) anode materials owing to their good chemical stability,

low cost, high theoretical capacities along with the large interlayer spacing which promote reversible Li ions movement and insertion/extraction.^{6–10} TMDs also present additional avenues for property tuning to enhance battery performance. For example, interlayer spacing engineering of TMDs has been shown to provide sufficient space for ultrafast Li ion intercalation.⁷ Vikraman *et al.* investigated the performance of mixed phase (1T and 2H) MoSe₂ as LIB anode material where they found that phase engineering led to impressive high rate specific capacity (843 mAh/g) with robust cycling stability.¹¹ Additionally, combining TMDs with other higher conductive materials, e.g. carbon nanomaterials can increase the conductivity of the anode materials thereby, further improving the efficiency of the electrochemical energy storage device.^{12–14} For instance, Kim *et al.* has reported that employing WS₂ nanoparticles anchored on graphene sheets as LIB anodes exhibits a reversible capacity of 371.9 mAh/g with 62% capacity retention after 500 cycles.¹⁴ Recently, in the case of MoSe₂@graphite, reversible discharge capacities of 909 mAh/g at 100 mA/g were reported.¹²

As a member of the TMDs class of layered nanomaterials, tungsten diselenide (WSe₂) has a layered structure with a larger interlayer distance (0.65 nm) than graphite (0.355 nm), efficiently promoting Li ion diffusion. The density of WSe₂ is 9.32 g cm⁻³, offering significant potential for high volumetric energy densities. This is a critical consideration when factoring in applications with limited battery space (e.g. electric vehicles).^{9–10} To date, research into nanostructured WSe₂ anodes has been quite limited, with the best performing anodes realized by Chen and co-workers, reaching 530 mAh g⁻¹ after 30 cycles.¹⁵ Similarly, Yang *et al.* demonstrated the highly stable performance of WSe₂ nanoplatelets, showing stable cycling of around 200 mAh g⁻¹ over 1500 cycles.⁹ It is worth mentioning that much of the reported work to date relies on

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preparation of TMDs from chemical vapor deposition (CVD) or hydrothermal reactions.¹⁵ The former approach requires high temperature and pressure which elevates the manufacturing cost, while the latter approach yields materials of low chemical stability, with poor crystallinity and structural defects.

Colloidal synthesis approaches offer a promising route to facilitate the production of TMDs nanocrystals (NCs) with controlled dimension and morphology with the capability of phase engineering for targeted energy applications.¹⁶⁻¹⁹ For instance, Sokolikova *et al.* reported scalable colloidal synthesis of WSe₂ NCs in 1T' phase which showed enhanced electrocatalytic performance for hydrogen evolution compared to other metallic TMDs nanomaterials.¹⁸ Henckel *et al.* reported the direct influence of surface ligand coverage of colloidal WSe₂ NCs on their hydrogen reduction ability.²⁰ While the research on the exploitation of colloidal TMDs is mainly focused on electrocatalytic applications, there are barely any reports on the applicability of colloidal TMDs NCs for battery applications.¹⁷

In this study, we investigate colloiddally prepared TMDs NCs (WSe₂) as LIB anode material. First, we synthesize few-layers WSe₂ nanosheets in 2H and 1T' crystal phases by using colloidal hot injection protocols. These WSe₂ samples of similar morphology yet different crystal phases were compared electrochemically. The specific capacity of 2H nanosheets was 498 mAh g⁻¹ after 100 cycles with a capacity retention of 83.28 %. In comparison 1T' nanosheets exhibited a poor initial capacity of 156 mAh g⁻¹, which dropped to 102 mAh g⁻¹ after 100 cycles. We further synthesized 2H WSe₂ NCs in the form of 3D interconnected nanoflowers and used this sample to investigate the role of morphology on performance. We found that the overall discharge capacity of the 2H nanoflowers is highest among all three samples given a final capacity of 982 mAh g⁻¹ after 100 cycles. We further carried post-mortem SEM and XRD analysis of the anode materials to gain insights into the electrochemical reactions involved. As such, this work constitutes a next step towards the exploration of colloiddally synthesised TMDs NCs for energy storage applications.

Experimental

Materials.

Tungsten hexcarbonyl (W(CO)₆, 99.99% trace metals basis), Trioctylphosphine oxide (TOPO, reagentplus, 99%), and diphenyl diselenide (Ph₂Se₂, 98%) were bought from Sigma Aldrich. Selenium powder and oleic acid (90 %) were provided by Alfa Aesar. Oleylamine (90%) was purchased from Acros Organics. Squalane (98%) was obtained from VMR. Toluene, methanol and ethanol were supplied by Fiers. All solvents were used as received. Cu foil (9 μm thick) was provided by Pi-Kem. Carboxymethyl cellulose sodium salt (CMC, ≥1900 mPa.s) and Super P Conductive Carbon Black (CB) were purchased from VWR and MTI Corporation, respectively. Battery grade 1.0 M LiPF₆ in EC:DEC (50:50 v/v) and vinylene carbonate (VC, 97 %) were purchased from Sigma Aldrich.

Preparation of semiconducting WSe₂ nanoflowers.

The nanoflower sample was synthesized using colloidal hot-injection method. In a typical process, 0.2 mmol W(CO)₆ and 8 mL oleic acid were added into a 25 ml three-neck flask, the mixture was vacuumed at room temperature for 1h and at 80 °C for 20 min. Meanwhile, Se

precursor was prepared by dispersing 0.8 mmol Se into 2 mL oleic acid in a vial. After degassing, the mixture was heated to 330 °C under a nitrogen flow, at which point the Se precursor was injected into the flask. The flask was cooled down to room temperature after 1h reaction. 5 mL ethanol was added into the flask and the suspension was centrifuged. The precipitate was washed several times with toluene and ethanol.

Preparation of metallic WSe₂ nanosheets.

The procedure was the same as the one for the nanoflowers sample except that oleylamine was used instead of oleic acid. The purification process was the same.

Preparation of semiconducting WSe₂ nanosheets.

0.1 mmol W(CO)₆, 0.4 mL oleic acid, 2.4 mL oleylamine, 2g TOPO were added into a flask with 4 mL squalane. The mixture was first degassed at room temperature for 30 min and then at 120 °C for another 30 min under stirring to make sure to get rid of any residual traces of oxygen and moisture. After degassing, the flask was filled with nitrogen and heated up to 330 °C for the injection of Se precursor (herein, the Se precursor was prepared by dissolving Ph₂Se₂ in 2 mL oleylamine). The reaction mixture was kept at 330 °C for 1h before it was cooled down. When the temperature went down to 80 °C, 8 mL toluene was added into the flask to prevent TOPO from solidifying. 12 mL of methanol was used to precipitate the samples followed by centrifugation. The precipitate was washed with toluene and methanol several times before it was used for further characterization.

Characterization Techniques.

Bright field transmission electron microscopy (TEM) images were obtained by using a Cs-corrected JEOL 2200-FS TEM operated at an acceleration voltage of 200 kV. X-ray diffraction (XRD) characterization was performed with a Thermo Scientific ARM X-ray diffractometer with the Cu Kα line as primary source. X-ray photoelectron spectroscopy (XPS) was recorded on S-Probe Monochromatized XPS spectrometer using Monochromatized Al Kα source. A Bruker Dimension Edge with a NCHV probe with tapping mode was used to carry out the Atomic Force microscopy (AFM) measurements. Raman spectra was collected using a KAISER dispersive RXNI spectrometer, the excitation wavelength is 532 nm. Scanning electron microscopy (SEM) was carried out using a Hitachi SU-70 system with accelerating voltage of 7 kV. Cells were disassembled under argon and the anodes were soaked in acetonitrile for 6 h before being successively dipped in 0.1 mM acetic acid, deionized water and ethanol. This process removes the SEI layer from the anode along with any residual electrolyte on the surface. X-ray diffraction (XRD) of the anodes was carried out on the different anode types using the X'Pert PRO MRD with a Cu Kα (λ = 1.5418 Å) source and an X'celerator detector. To analyse the charge behaviour of these materials, XRD was taken of the lithiated anodes. This was achieved, through low current charging to 0.01 V. Afterwards, the cells were disassembled, and the electrodes were taped to a glass slide using Scotch tape to remove contact with the atmosphere.

Electrochemical Testing.

WSe₂ anodes were processed using a conventional slurry processing technique. Formulated slurries consisted of 80 wt% as-synthesised WSe₂ powder, 10 wt% carboxymethyl cellulose (CMC) and 10 wt%

carbon black (CB). Initially, carbon black was dispersed in a 1.5 wt% CMC in H₂O solution with constant mixing. To ensure homogeneity of the mixture enough time of 6 h was given for the CB to disperse in the solvent. The WSe₂ powder was then added to the solvent mixture incrementally and with constant stirring. Prior to casting, the slurry mixture was left stir overnight. Planar Cu foil with a thickness of 9 μ m (purchased from Pi-Kem) was employed as the anode current collector. Using a heated vacuum doctor blade, slurries were cast on Cu foil with a blade height of 0.25 mm and dried for 12 h at 120 $^{\circ}$ C. Prior to cell assembly, anodes with an area of 0.64 cm² and an average loading of 0.98 ± 0.11 mg cm⁻² were punched out and stored under argon. Anodes were tested in a two-electrode Swagelok configuration vs metallic Li. A typical electrolyte solution of 1 M LiPF₆ in EC-DEC (1:1 v/v) + 3 wt% VC was used throughout testing. Using a BioLogic MPG-2 multichannel potentiostat, the electrochemical performance of these materials was tested through galvanostatic cycling between a 0.01-3 V vs Li/Li⁺. Initially, 100 mA g⁻¹ constant current cycling was employed to determine the specific capacities of the different anode types.

Results and discussion

Fig. 1 (a) Low-resolution TEM image of NS-2H. Inset: High-resolution TEM image. (b) AFM image of NS-2H. Inset: The height profile of the white line in b. (c) Low-resolution TEM image of NS-1T'. Inset: High-resolution TEM image. (d) AFM image of NS-1T'. Inset: The height profile of the white line in d.

We synthesized few-layer thick WSe₂ nanosheets by utilizing colloidal hot-injection synthesis approach. The nanosheets are formed by ligand-assisted reaction between W and Se precursors at high temperature. Details on the reaction mechanism is given in Supporting information, section S1. By varying the composition of the ligand mixture and the Se precursor used in the synthesis (see experimental details), nanosheets in 2H and 1T' crystal structures were formed. For ease of reading, these different polymorphs of nanosheets (NS) samples are referred to as NS-2H and NS-1T'. Fig. 1(a and inset) show the low and high resolution TEM images of the NS-2H with lateral size of $\sim$ 75 nm. The red square in Fig. 1a (inset)

indicates the few-layer character. We further employed AFM to analyse the thickness of the obtained nanosheets. Fig. 1b shows a typical AFM image of the nanosheets. Analysing 100 nanosheets in such AFM images, we find that the average thickness of NS-2H is 2.8 nm. For WSe₂, this value typically corresponds to the thickness of 3-4 layers. Furthermore, the X-ray diffraction (XRD) spectra of NS-2H (Supporting information, section S2) illustrate the diffraction peaks which match well with 2H WSe₂ (JCPDS card no. 381388).

The TEM images of NS-1T' samples as shown in Fig. 1c, display irregular nanosheets of smaller lateral size compared to the NS-2H samples. The average size of these nanosheets was around 20 nm. The HRTEM image (Fig. 1c inset) and the height profile of AFM image (Fig. 1d) reveal that the NS-1T' samples are also composed of 4-6 layers, similar to the 2H analogues. Furthermore, the XRD spectra of the NS-1T' sample consists of broad peaks with most of the intensity lost in the background (supporting information, Section S2). This is a

Fig. 2 (a, b) High-resolution W XPS spectra of NS-2H and NS-1T', respectively. (c, d) Raman spectra and UV-vis spectra of the as-prepared NS-2H and NS-1T' nanosheets. The dashed lines in c indicate the peak positions.

common issue in the colloidal 1T' structure occurring due the low-crystallinity of the synthesized samples.^{18, 21}

A detailed analysis of the fitting of XPS spectra is shown in Fig. 2a and Section S3 (supporting information). The signals at 32.32 eV and 34.42 eV in Fig. 2a correspond to W⁴⁺ 4f_{7/2} and W⁴⁺ 4f_{5/2} of 2H phase,²² with the small peaks of W⁶⁺ occurring at higher energies (35.64 eV and 37.94 eV) indicating the edge oxidation of the nanosheets.^{18, 20} The deconvolution of the Se XPS spectra (Section S2, supporting information) exhibits the Se 3d_{5/2} and Se 3d_{3/2} signals corresponding to an oxidation state of -2, in good agreement with the peaks of Se 3d that have been reported in 2H WSe₂.²³ This further demonstrates the successful synthesis of pure phase 2H nanosheets. Fig. 2b displays the high-resolution W XPS for the NS-1T' sample. Here, the dominant features at 31.7 eV and 33.8 eV in the W 4f

Fig. 3 Electrochemical cycling of NS-1T' (red) vs NS-2H (blue) vs Li/Li⁺. Charge/discharge capacity profiles for the (a) 1st cycle and (b) 2nd cycle. Differential capacity plots of the (c) 1st and (d) 2nd cycle. Constant current ageing and coulombic efficiencies of (e) NS-1T' and (f) NS-2H. All cells were cycled galvanostatically at a current density of 100 mA g⁻¹ over a potential range of 0.01–3 V vs Li/Li⁺.

correspond to the respective levels of 1T' WSe₂.^{18, 24} The additional signals can be attributed to a minor contribution from 2H WSe₂ and partially oxidized WSe₂. The Se 3d core region (as shown in supporting information section S3) is dominated by the peaks (53.78 eV and 54.58 eV) that are attributed to 1T' WSe₂. Fig. 2c shows the Raman spectra of NS-2H and NS-1T' samples. For NS-2H sample, only one peak around 250 cm⁻¹ is shown, arising from the overlap of the E_{2g}¹ and A_{1g} mode.²⁵ Moreover, the Raman spectra of NS-1T' sample displays peaks at 158 cm⁻¹, 238 cm⁻¹, and 248 cm⁻¹ which indicates the 1T' crystal phase composition in the nanosheets sample. Fig. 2d shows the UV-vis absorption of the samples. In the absorption spectra of NS-2H sample, the peak located at 754 nm arises from direct gap transitions at the Brillouin zone K point.^{26–27} This peak shows a red-shift compared with the monolayer sample where this exciton peak is around 743 nm,²⁸ indicating that the sample consists of few-layer WSe₂ nanosheets,²⁸ which is in line with the TEM and AFM results. Contrary to this, the NS-1T' sample displays a broad and feature-less absorbance spectrum which is characteristic of the metallic 1T' crystal phase of WSe₂.

For the fabrication of battery anode, the colloidal nanosheets samples (NS-2H and NS-1T') were purified by successive precipitation and re-dispersion and dried in an oven overnight. Further, these samples were incorporated into electrode slurries and cast on Cu foil (see experimental details).

Galvanostatic charge/discharge tests compared the electrochemical behaviour of the different anodes composed of similar nanosheet morphologies but different crystal structures (NS-2H vs NS-1T'). The cyclability of WSe₂ in Li-ion cells is governed by a reversible conversion reaction as follows,^{9, 29}

Typically, lithiation of TMDs materials (WS₂, MoS₂, WSe₂) is governed by a two-step intercalation-conversion process.^{30–32} During charge, Li ions intercalate into WSe₂ forming intermediary Li_xWSe₂, which

undergoes conversion, liberating lithium selenide with elemental tungsten embedded in the matrix.^{15, 29, 33} Delithiation converts W and Li₂Se into the intermediary Li_xWSe₂ structure, from which Li ions deintercalated. Fig. 3a,b illustrate the 1st cycle and 2nd cycle voltage profiles of NS-1T' and NS-2H, respectively. Differences in the differential capacity plots (DCPs) of NS-2H and NS-1T' highlight the dependence of electrochemical performance on crystal structure as lithiation into NS-1T' is greatly impeded, reflected by the absence of any distinguishable lithiation/delithiation peaks (Fig. 3c,d). Analogously, voltage profiles for NS-1T' exhibit no discernible kinks or plateaus, reflective of this poor lithiation/delithiation behaviour (Fig. 3a,b). In fact, no characteristic WSe₂ lithiation/delithiation peaks are observed for NS-1T' suggesting the low capacity may come completely from pseudocapacitive contributions, through rapid surficial reactions of the W redox couple.^{34–35} NS-1T' exhibits a low initial capacity of 156 mAh g⁻¹, dropping to 102 mAh g⁻¹ after 100 cycles (Fig. 3e). Conversely, NS-2H exhibits charge-discharge behaviour characteristic to tungsten diselenide.^{29, 33} The DCP of NS-2H exhibits a distinct peak in the cathodic scan at 2.0 V and the anodic profile at 2.1 V (Fig. 3d), corresponding respectively to Li intercalation/deintercalation to/from WSe₂. NS-2H delivers stable high capacity, reaching 498 mAh g⁻¹ after 100 cycles.

It is also interesting to analyse the effect of morphology of these layered TMDs on their performance as electrode materials. For this, we synthesised colloidal 2H WSe₂ with a flower-like morphology by injecting Se powder in a mixture of W(CO)₆ and OA at 330 °C. For simplification, we name it as NF-2H. The TEM image in Fig. 4a shows the diameter of the nanoflower is around 200 nm. The HRTEM image indicates that the nanoflowers are produced by few-layer nanosheets that protrude from a central core. AFM image of the sample (Supporting information, section S4) was analysed to determine the average thickness of the sample. The height profile reveals the thickness of the nanoflower layers to be in the range of

2.4-4.9 nm, which correspond to 4-7 layers respectively. The high-

Fig. 4 (a) Low-resolution TEM image of NF-2H. Insert: High-resolution TEM image. (b) High-resolution W XPS spectra of NF-2H (c) Raman spectra of NF-2H sample (d) UV-vis spectra of the as-prepared NF-2H sample.

resolution W XPS profile shows two intense peaks (indicated in blue line) at 32.42 eV and 34.52 eV corresponding to 2H WSe₂. Signals located at higher energies are attributed to W(VI) and W 5p. These nanoflowers samples also show contribution from 1T' phase. The contribution of 1T' phase in this sample can also be seen in the Raman spectra (shown in Fig. 4c) and Se XPS analysis (Section S5, supporting information). Here, the broad peak at 257 cm⁻¹ arises from the phonon-frequency of the in-plane E_{2g}¹ and A_{1g} vibration modes of 2H polymorph of WSe₂. The small shoulder appearing at the onset of the 2H vibration peaks (238 cm⁻¹) is attributed to the presence of 1T' phase in the nanoflower structure. However, the dominant phase in this nanoflower sample is the 2H polymorph, which can be corroborated by the presence of distinct excitonic features in the absorbance spectrum of NF-2H sample (see Fig. 4d). The XRD spectra of this sample further confirms the domination of 2H crystal phase (Section S6, supporting information).

The dependence of electrochemical performance of WSe₂ on nanostructural morphology was analysed through comparative electrochemical analysis of two 2H polymorphs of WSe₂ (NS-2H and NF-2H). Electrochemical analysis of NS-2H and NF-2H suggests a strong dependence of cell performance on structural morphology (Fig. 5). For chemically identical anodes, each anode has a distinct electrochemical behaviour with the capacity, stability and Coulombic efficiency dependent on the morphology of the active material. In terms of specific capacity and capacity retention, NF-2H outperforms NS-2H with capacity continually trending upwards, with the initial 694.8 mAh g⁻¹ rising to 982 mAh g⁻¹ after 100 cycles (Fig. 5a). The charge capacity and corresponding Coulombic efficiency (CE) of NF-2H are presented in Supporting Information Section S7. The initial charge and discharge capacities of NF-2H are 1226.2 and 694.8 mAh g⁻¹, respectively, with an initial Coulombic efficiency of 56.7 %. High initial irreversible capacity loss and low CE are primarily attributed to Li consumption and electrolyte degradation associated with forming

the solid electrolyte interphase (SEI) on the high surface area nanocrystals.^{6, 36-37} After initial capacity stabilisation, NF-2H demonstrates excellent reversibility, reaching near 100 % CE after 20 cycles, with an average CE of 99.84 %. NS-2H on the other hand, exhibits a characteristic ageing profile, delivering an initial capacity of 591 mAh g⁻¹, falling to 498 mAh g⁻¹ after 100 cycles (Fig. 5a).

Fig. 5 Electrochemical performance of NF-2H (black) and NS-2H (blue) vs Li/Li⁺. (a) Constant current discharge capacity of NF-2H vs NS-2H and different capacity plots of the (b) 1st, (c) 2nd, (d) 25th and (e) 100th cycle. Both cells were cycled at a current density of 100 mA g⁻¹.

DCPs helped correlate electrochemical performance differences of these polymorphs to the evolution of the lithiation/delithiation redox peaks (Fig. 5b-e). During the 1st cycle, both cells exhibit a distinct peak at 0.67 V in the cathodic scan, attributable to Li_xWSe₂ conversion to metallic W and Li₂Se (Fig. 5b).²⁹ NS-2H exhibits an additional peak at 0.89 V during the first charge cycle, which attenuates completely for subsequent cycles, indicative of high irreversible loss of active Li and reflected by a low initial CE of 41.14 %. During first cycle delithiation, both samples exhibit a major peak at 2.21 V with NF-2H possessing a minor secondary peak at 1.75 V. This major peak at 2.21 V is representative of delithiation of the Li_xWSe₂ intermediate and conversion back to WSe₂.^{15, 29, 33} During the second cycle, three distinct cathodic peaks (1.52 V, 1.94 V and 2.01 V) govern lithiation of NF-2H whereas only one peak is evident for NS-2H lithiation (Fig. 5c). Similarly, in the anodic scan, an extra peak at 1.75 V further contributes to the high capacity of NF-2H. Extending this to 25 cycles, a minor anodic peak appears at 1.06 V for NF-2H (Fig. 5d). After 100 cycles, both anodes exhibit slightly differing lithiation behaviour. NF-2H exhibits a number of cathodic and anodic peaks with a prominent lithiation peak emerging at 0.67 V (Fig. 5e).

The continual capacity increase of NF-2H (Fig. 5a) is primarily attributed to the emergence of this broad peak along with minor anodic peaks at 1.06 V and 1.75 V, corresponding to the reversible alloying of Li with elemental Se, through electrochemically-driven precipitation of elemental Se from the WSe₂ matrix.³⁸⁻³⁹ Gradual capacity increases of NF-2H is also suggestive of contributions from surface pseudocapacitance and structural porosity, respectively acting as an additional charge storage mechanism and improving electrolyte diffusion to the active layer.⁴⁰⁻⁴¹ The theoretical capacity (Q_{th}) of MX₂ TMD materials is a contentious topic, with capacity contributions from typical intercalation/conversion along with TM pseudocapacitance and TM Li alloying often pushing experimental capacity well above the calculated Q_{th} (314 mAh g⁻¹ for WSe₂, based on $WSe_2 + 4Li^+ + 4e^- \leftrightarrow W + 2Li_2Se$).⁴²⁻⁴³ Therefore, the high achievable capacity of NF-2H (982 mAh g⁻¹ after 100 cycles) arises due to multiple capacity contributions, including the gradual displacement of electrochemically active metallic Se for alloying reactions with Li⁺ ($Se + 2Li^+ + 2e^- \leftrightarrow Li_2Se$; $Q_{th} = 678 \text{ mAh g}^{-1}$),⁴⁴⁻⁴⁵ enabled by the emergence of a major lithiation peak at 0.67 V, attributed to reversible alloying between Li⁺ and Se, liberated through continual WSe₂ conversion (Fig. 5e). Moreover, the tendency of W to undergo fast redox reactions at the surface further elevates experimental capacity through pseudocapacitance.⁴⁶⁻⁴⁷

For NS-2H, the same peak (0.67 V) shows a much lower intensity, suggesting a lower amount of available Se for Li alloying. No new peaks are realised after 100 cycles with the charge/discharge processes of NS-2H governed by two major peaks at 1.94 V and 2.21 V. NS-2H peaks gradually shrink with each successive cycle, along with the major cathodic peak gradually shifting to lower voltages, indicative of a gradual increase in cell impedance through electrode polarisation. W nanoparticles, are formed during Li_xWSe₂ conversion during low voltage lithiation (0.65 V) show a high degree of reversibility, reflected by the continued formation of WSe₂ during delithiation. The excellent stability of NF-2H cycling is reflected by the stability of the major delithiation peak at 2.21 V vs Li/Li⁺ (Fig. 5b-e). After 100 cycles, the peak corresponding to Li_xWSe conversion to WSe₂ does not exhibit any notable potential shifts or intensity loss, suggesting a continued reformation of the WSe₂ during deep delithiation. However, it is unclear whether the initial TMD material (in terms of morphology, particle size etc.) is being completely retrieved or whether Se extraction is distorting the morphology of WSe₂. Although previous reports of analogous battery chemistries (WS₂/MoS₂) have noted the irreversible decomposition of the TMD,⁴⁸⁻⁵⁵ NF-2H lithiation/delithiation exhibits a continued two-step reversible intercalation/conversion process up to 100 cycles. However, the continued precipitation of metallic Se suggests that although WSe₂ is being reformed during delithiation, it may not be reforming to the same extent or with the morphology.

Electrochemically driven precipitation of elemental Se from the WSe₂ structure behaves as an additional capacity reservoir in NF-2H, increasing capacity through Li-selenium side reactions (Section S8, supporting information).⁵⁶⁻⁵⁷ Post-mortem analysis of cycled WSe₂ found that NF-2H exhibited a striking red discolouration, indicative

of elemental Se precipitation from WSe₂.⁵⁸ Analogously, the electrochemical activity of MoS₂ systems is largely driven by the evolution of elemental sulfur, with the layered transition metal dichalcogenides (TMDs) structure behaving as a sacrificial source for S liberation during the 1st cycle, driving electrochemical activity for subsequent cycles.⁵⁹ The electrochemically driven precipitation of the corresponding chalcogen atom from compositionally different TMDs has been reported for a number of different TMDs systems^{9, 59-60}, suggesting that this chalcogen liberation (S, Se and Te) is characteristic of TMDs systems and independent of the constituent metal group (Mo, W)⁵⁹⁻⁶⁰, showing promise for translation to generalised MX₂ systems. Additionally, surface pseudocapacitance of WSe₂ contributes to the high and increasing capacity of NF-2H. Pseudocapacitance of TMDs anodes is often denoted by a gradual increase in cell capacity, attributed to fast surficial redox reaction of the consistent transition metal atom.^{31, 52, 61-62} Activation of surface redox couple can introduce pseudocapacitive gains that offset faradaic losses of capacity from the bulk.⁶³⁻⁶⁶ Further, electrochemically driven structural porosity may play a role in the increasing capacity of NF-2H. As outlined by Liu *et al.*⁶⁷ pristine electrodes undergo gradual pore formation after successive cycling, increasing contact area and promoting facile diffusion of the electrolyte to the surface for Li ion solvation/desolvation. However, it should be noted that structural porosity may be distorted in the slurry process.

Overall, the electrochemical performance of WSe₂ nanocrystals is dictated by both crystal phase (NS-2H and NS-1T') and nanocrystal morphology (NS-2H vs NF-2H) with NF-2H demonstrating the highest capacity and best stability of tested anodes. Although impressive in half-cell configurations, the increasing and somewhat unpredictable capacity of NF-2H may deplete the finite Li content in a full-cell configuration. NS-2H offers a more reliable capacity retention behaviour, suitable for full-cell analogues. However, the high capacity of NF-2H has not been matched by reported studies^{15, 68-70} and as such capacity could be exploited in future to control the increasing lithiation behaviour. The effects of applied current density (Section S9) and electrolyte composition (Section S10) on the cyclability of NF-2H were analysed. Interestingly, increasing the current density from 100 mA g⁻¹ to 250 mA g⁻¹ saw a loss in this gradual precipitation of electrochemically active Se, with NF-2H demonstrating a typical capacity fade behaviour (Section S9). This behaviour was attributed to insufficient lithiation time of NF-2H at 250 mA g⁻¹, suppressing Se formation over the 1st 100 cycles. Substitution of the traditional carbonate-based electrolyte with an ether-based solvent revealed near identical redox behaviour of NF-2H at 100 mA g⁻¹, with lithiation of both cells governed by a two-step intercalation-conversion process (Section S10).

Conclusions

In summary, we report the synthesis of WSe₂ NCs using a colloidal hot-injection procedure allowing formation of 2H nanosheets, 1T' nanosheets and 2H nanoflower forms. After detailed structural characterization, these NCs were investigated for their performance as anode materials in LIBs. Among the three, we found 1T' nanosheets perform poorly compared to 2H crystal phased nanosheets and nanoflowers. 2H nanosheets exhibited stable high

capacity, reaching 498 mAh g⁻¹ after 100 cycles with a capacity retention of 83.3%. 2H nanoflowers on the other hand demonstrated an excellent reversibility with initial capacity of 694.8 mAh g⁻¹ growing to 982 mAh g⁻¹ after 100 cycles. Further, a detailed post-mortem analysis of these anode samples including DCPs, SEM and XRD showed the electrochemically driven precipitation of elemental Se during the charge and discharge cycles. These findings not only shed light on the structure-dependent LIB performance of TMDs nanocrystals but also suggest that precision tuned colloidal TMDs offer significant advantages to the TMDs obtained from CVD or hydrothermal methods as anode materials for LIB.

Conflicts of interest

There are no conflicts to declare.

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