



Cite this: *Chem. Commun.*, 2016, 52, 4481

Received 21st January 2016,
Accepted 25th February 2016

DOI: 10.1039/c6cc00577b

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Flowerlike WSe₂ and WS₂ microspheres: one-pot synthesis, formation mechanism and application in heavy metal ion sequestration†

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Flowerlike WSe₂ and WS₂ microspheres were synthesized by a facile and scalable one-pot solvothermal method. Their formation mechanism followed the reaction between dissolved W(CO)₆ and dissolved S or melted Se without complete decomposition of W(CO)₆ into tungsten. As novel efficient sorbents, WSe₂ and WS₂ demonstrated outstanding uptake capacities for Pb²⁺ and Hg²⁺.

Layered transition metal dichalcogenides (TMDs), MX₂ where M is a transition metal (such as Mo, W, and Nb) and X is a chalcogen (S, Se and Te), have received intensive research interest due to their unique electronic, optical, mechanical and chemical properties.¹ Among them, WSe₂ and WS₂ have been extensively studied for a variety of applications including valleytronics,² batteries,³ electrocatalysis,⁴ photocatalysis,⁵ bioimaging labels,⁶ and electronic devices.⁷ WSe₂ and WS₂ have a layered structure in the form of Se–W–Se or S–W–S with a W atomic layer sandwiched by two hexagonal chalcogen atomic layers.^{4a,b} The interlayers are coupled by weak van der Waals forces and the intralayer W–Se/S bonding is covalent.¹ Most reports focus on the fabrication of nanosheets/nanotubes of WSe₂ and WS₂ by chemical vapor deposition (CVD), electrochemical exfoliation and hot-injection approaches.^{2–7} These methods require high temperature, expensive precursors or toxic H₂S/H₂Se, and harsh conditions that give low yields. The growth mechanisms of TMDs have been rarely described, although the formation mechanisms of similar lamellar bismuth chalcogenide materials have been explored.^{1e,f} Moreover, there are few reports on the construction of three-dimensional (3D)

hierarchical nanosheet-assembled flowerlike architectures of WSe₂, although 3D flowerlike MoS₂ and metal oxides or hydroxides such as FeOOH and AlOOH have been widely studied.⁸ WS₂ nanoflowers were produced by using CVD with low yields.⁹ Hierarchical nanosheets assembled into flowerlike structures normally show superior performance in batteries and water treatment.^{8,10} Therefore, it is highly desirable to develop hierarchical WSe₂ and WS₂ using a facile, cost-effective and scalable approach.

As a new class of heavy metal ion scavenger, metal chalcogenides have been used in heavy metal ion sequestration for water treatment, including ZnS, K₂xMn_xSn_{3–x}S₆, (NH₄)₄In₁₂Se₂₀, H₂xMn_xSn_{3–x}S₆ and H_xNa_yIn_z,¹¹ due to the strong affinity of the chalcogen to heavy metal ions. In this study, flowerlike WSe₂ and WS₂ microspheres consisting of their corresponding nanosheets were synthesized by a simple, low-cost and high-yield one-pot template-free solvothermal approach. Their growth mechanism was elucidated by *in situ* synchrotron radiation X-ray diffraction (SR-XRD). WSe₂ and WS₂ were used in heavy metal ion sequestration for the first time and showed exceptional uptake capacities for Pb²⁺ and Hg²⁺, making them ideal candidates for heavy metal remediation in practical water purification.

WSe₂ and WS₂ were prepared in high yields (>3 g) by a solvothermal method from the reaction of W(CO)₆ and Se or S powders in *p*-xylene (see details in ESI†). Fig. 1 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the flowerlike WSe₂. The WSe₂ sample displays a hierarchical flowerlike micro/nanostructure (Fig. 1). The flowerlike WSe₂ is composed of many self-assembled petals that are curly nanosheets (Fig. 1c). These WSe₂ nanosheets are 5 nm in thickness and 300 nm in width, and are assembled together to form 3D WSe₂ flowers with diameters ranging from 500 nm to 1 μm. Fig. 1d demonstrates that the thin WSe₂ nanosheets consist of a few layers (<10 layers) stacking together and the interlayer spacing of the nanosheets is 0.689 nm, corresponding to the (002) plane of the hexagonal WSe₂, with slight expansion due to the strain from the layer curvature.^{3b} The lattice spacing of 0.285 nm corresponds to the (100) plane of the 2H–WSe₂ phase. The X-ray diffraction

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc00577b



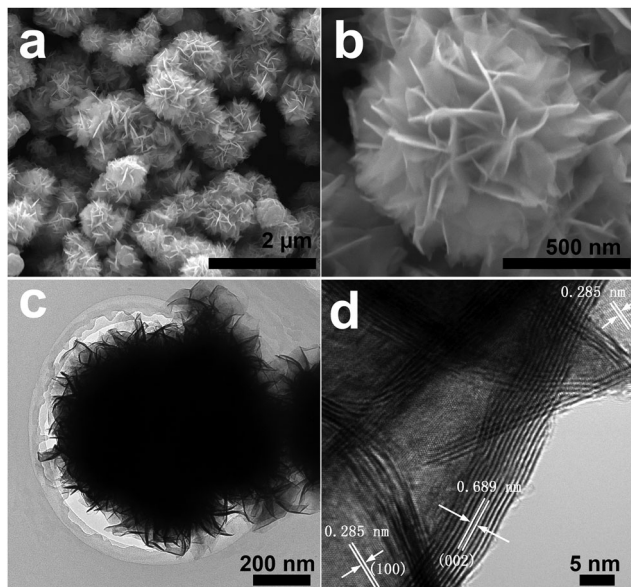


Fig. 1 SEM images (a and b) and TEM images (c and d) of the WSe₂ microspheres.

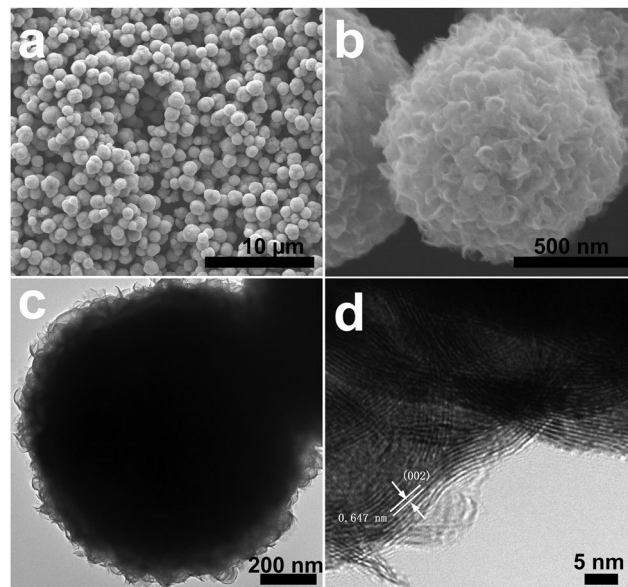


Fig. 2 SEM images (a and b) and TEM images (c and d) of the WS₂ microspheres.

(XRD) pattern (Fig. S1a, ESI[†]) is indexed to the hexagonal 2H-WSe₂ structure (JCPDS Card No. 38-1388). The energy dispersive X-ray (EDX) spectroscopy confirms the composition of WSe₂ with a W/Se atomic ratio of 0.51 (Fig. S1b, ESI[†]), in good agreement with the result (W/Se atomic ratio = 0.54) from inductively coupled plasma optical emission spectroscopy (ICP-OES). The X-ray photoelectron spectroscopy (XPS, Fig. S2, ESI[†]) shows that the W 4f_{7/2} (31.9 eV) and W 4f_{5/2} (34.0 eV) peaks are consistent with previous studies of WSe₂ samples.^{4a,12} The small peaks at 35.6 eV and 37.8 eV are assigned to W 4f_{7/2} and W 4f_{5/2} from WO₃, likely due to oxidation because of exposure to air during sample preparation and transfer for XPS characterization, and were observed in previous WSe₂ reports.^{4a,12} The Se 3d peak was located at 54.4 eV which could be deconvoluted into 3d_{5/2} and 3d_{3/2} peaks.

A similar solvothermal approach using sulfur powder instead of selenium produced a WS₂ sample. The product is composed of microspheres with an average diameter of 1 μm (Fig. 2a). The WS₂ microsphere is comprised of curly nanosheets (Fig. 2b and c), yet with smaller width (several tens of nanometers) compared to that of the WSe₂ nanosheets. The WS₂ nanosheets consist of 5–10 layers and the interlayer distance is 0.647 nm corresponding to the (002) plane of the hexagonal WS₂ (Fig. 2d). The XRD pattern (Fig. S3a, ESI[†]) can be assigned to the hexagonal 2H-WS₂ structure (JCPDS Card No. 84-1398), yet with a small shift in (002) peak towards low angle, which is probably caused by the layer curvature.^{3b} Both the EDX spectroscopy (Fig. S3b, ESI[†]) and ICP-OES results show the presence of W and S in the WS₂ microspheres with a W/S atomic ratio close to 0.5. The XPS spectra (Fig. S4, ESI[†]) display the W 4f_{7/2}, W 4f_{5/2} and W 5p_{5/2} peaks as well as S 2p peak consistent with previous reported WS₂ samples, corroborating that the sample is pure WS₂ without oxidation.^{4b,c,5b}

These results demonstrate that the solvothermal method is efficient in producing nanosheet self-assembled 3D WSe₂ and WS₂

micro/nanostructures in high yields. The presence of nanosheets in this architecture enhances the surface-to-volume ratio and offers more accessible interfaces for sequestration, while the entire microstructure enables fast and easy sedimentation and separation from water.^{8a–c}

In order to unravel the growth mechanism of flowerlike WSe₂ and WS₂ microspheres, the synthesis conditions, including temperature and reaction time, were varied and the samples were characterized by SEM and *ex situ* XRD.

For WSe₂, the optimal temperature is 250 °C, which is above the melting point (m.p.) of Se (221 °C). Below 250 °C, there was residual Se in the product (Fig. S5 & S6, ESI[†]). WS₂ microspheres formed at 150 °C and crystallized upon rising temperature and the morphology evolved from irregular microspheres with smooth surfaces to relatively uniform microspheres with a well-defined nanosheet assembly (Fig. S7, ESI[†]). At 250 °C, the smooth WSe₂ microspheres gradually developed into coarse spheres with improved crystallinity and eventually crystalline flowerlike WSe₂ formed (Fig. S8, ESI[†]), as the reaction time was prolonged. A similar process also occurred in the growth of WS₂ microspheres except that the lateral size of the WS₂ nanosheets was smaller than that of the WSe₂ nanosheets (Fig. S9, ESI[†]). Therefore, for both WSe₂ and WS₂, smooth microspheres initially formed and then the nanosheets were developed and crystallized on the surface of microspheres under the solvothermal conditions. Duphil *et al.* reported an ambient solution method to produce merely amorphous WSe₂ and WS₂ irregular nanoparticles using W(CO)₆, Se and S in *p*-xylene.¹³ Pol *et al.* previously reported a high-temperature solid reaction between W(CO)₆ and Se to prepare WSe₂ nanoparticles.¹⁴ They both proposed a two-step reaction mechanism involving first the complete decomposition of W(CO)₆ into W and subsequent reaction of W with Se/S without giving direct evidence. In the absence of Se or S, W(CO)₆ was heated at varying temperatures in *p*-xylene in a Teflon-lined autoclave. The resultant products



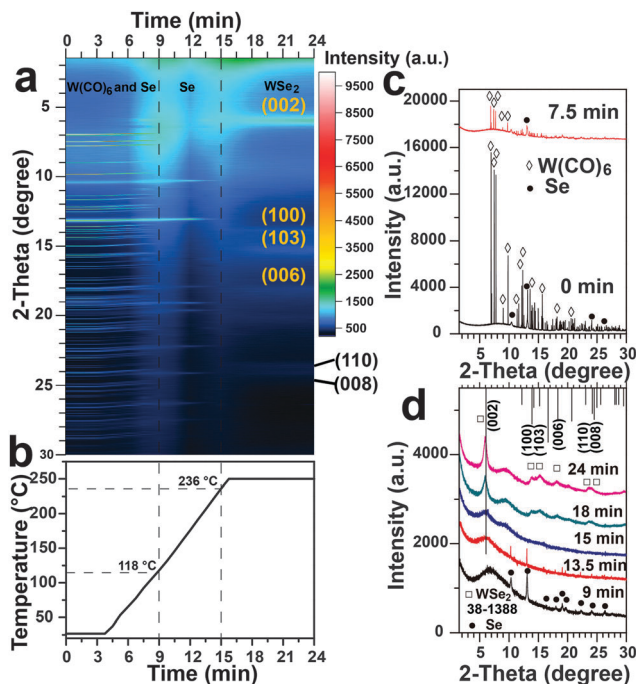


Fig. 3 (a) Time-resolved *in situ* SR-XRD patterns showing evolution from $W(CO)_6$ and Se precursors to WSe_2 , (b) temperature ramp rate ($20\text{ }^{\circ}\text{C min}^{-1}$), (c) and (d) characteristic SR-XRD patterns of *in situ* products at the noted reaction time. Note that the reaction rate in the micro-reactor is much faster than that of the bulk solvothermal reaction in the autoclave.

remained in the phase of $W(CO)_6$ (Fig. S10, ESI[†]), with no evidence of a W intermediate.

To track the phase evolution as a function of reaction time, time-resolved *in situ* SR-XRD experiments were performed. The *in situ* SR-XRD is able to provide valuable real-time phase evolution during the reaction,^{1e,15} as illustrated in Scheme S1, ESI[†]. The *in situ* SR-XRD patterns of WSe_2 (Fig. 3) demonstrate that the solvothermal process involves dissolution of $W(CO)_6$, melting of Se and growth of flowerlike WSe_2 . The *in situ* SR-XRD patterns (Fig. 2a) of the starting precursors are readily indexed to the orthorhombic phase of $W(CO)_6$ (JCPDS Card No. 40-0752) and hexagonal Se (JCPDS Card No. 06-0362), consistent with *ex situ* XRD patterns (Fig. S6, ESI[†]).

Upon heating in *p*-xylene, the peaks of $W(CO)_6$ continuously decreased in intensity and vanished after about 9 min at $118\text{ }^{\circ}\text{C}$ (Fig. 3b–d). This temperature was much lower than the decomposition/melting point of $W(CO)_6$ ($\sim 170\text{ }^{\circ}\text{C}$) indicating that $W(CO)_6$ was neither melted nor completely decomposed into elemental tungsten. $W(CO)_6$ was likely dissolved in *p*-xylene. The peaks of the Se precursor remained until the temperature reached $236\text{ }^{\circ}\text{C}$ (above the melting point of Se, $221\text{ }^{\circ}\text{C}$), when the Se precursor peak disappeared instantly. WSe_2 formed rapidly after the melting of Se. The elemental W intermediate arising from the decomposition of $W(CO)_6$ proposed in the early literature was not detected.^{13,14} The formation mechanism determined from the *in situ* SR-XRD result agrees with the aforementioned *ex situ* SEM and XRD characterization. The heating rate governs the rate of Se melting and hence the whole reaction rate. Therefore, the reaction temperature

plays a critical role in the formation of WSe_2 . Since evidence for the formation of W was not found in either *ex situ* or *in situ* experiments, we do not deem that the reaction between dissolved $W(CO)_6$ and melted Se in *p*-xylene in this case followed the two-step process as proposed in the literature.^{13,14} The reaction mechanism might be a straightforward one-step reaction, or a modified two-step process initially involving the partial dissociation of $W(CO)_6$ into $W(CO)_{6-x}$,¹⁶ and the subsequent oxidation by Se/S atoms. The underlying mechanism will be investigated in the future through advanced *in situ* techniques (*e.g.* mass spectrometry). Besides, agglomerate WSe_2 with poor crystallinity (Fig. S11, ESI[†]) was obtained when $W(CO)_6$ reacted with Se without *p*-xylene, highlighting the importance of the *p*-xylene solvent in inducing the formation of flowerlike structures.

The growth process of WS_2 was also explored by the *in situ* SR-XRD (Fig. S12, ESI[†]). Sulfur (m.p. $115\text{ }^{\circ}\text{C}$) and $W(CO)_6$ were dissolved at $83\text{ }^{\circ}\text{C}$ and $116\text{ }^{\circ}\text{C}$, respectively. Then WS_2 was gradually formed and crystallized upon heating. Both precursors vanished below their melting or decomposition point and no W intermediate was detected, consistent with the results of WSe_2 .

The synthesis of WTe_2 at $250\text{ }^{\circ}\text{C}$ with the solvothermal method using $W(CO)_6$ and Te (m.p. $450\text{ }^{\circ}\text{C}$) was attempted. However, the product was only a mixture of Te and TeO_2 with $W(CO)_6$, which was removed by rinsing with acetone (Fig. S13, ESI[†]).

Based on the above *ex situ* and *in situ* experimental results, the growth of WS_2 and WSe_2 began with the dissolution of S and $W(CO)_6$, melting of Se and then both precursors reacted quickly to produce crystalline WS_2 and WSe_2 under the solvothermal condition. The absence of complete dissociation of $W(CO)_6$ into W in this work appears to defy the commonly accepted two-step reaction mechanism.^{13,14} The knowledge gained about the growth mechanism of tungsten sulfide and selenide by the time-resolved *in situ* SR-XRD technique will inspire new studies of various layered transition metal dichalcogenides.

These as-synthesized flowerlike WSe_2 and WS_2 microspheres possess many nanosheets and abundant chalcogen ligands with innate reactivity towards soft heavy metal ions (Hg^{2+} , Pb^{2+} , *etc.*) and structural rigidity. These features are desirable for the sequestration of heavy metal ions from water. The flowerlike WSe_2 and WS_2 microspheres were used to sequester various heavy metal ions, including As(v), As(III), Cd^{2+} , Pb^{2+} and Hg^{2+} , from water. They did not remove As(v), As(III) and Cd^{2+} , whereas they exhibited high uptake capacities for Hg^{2+} and Pb^{2+} . This is due to the innate selectivity of metal chalcogenides for soft heavy metal ions (*i.e.* Hg^{2+} and Pb^{2+}).¹¹ Fig. 4 exhibits the variation in Pb^{2+} and

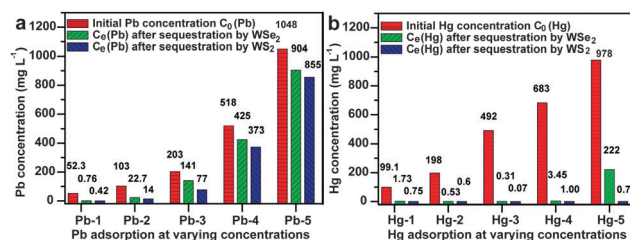


Fig. 4 (a) Pb^{2+} and (b) Hg^{2+} sequestration of WSe_2 and WS_2 in water. The WSe_2 and WS_2 content in the Pb^{2+} and Hg^{2+} aqueous solutions was 0.5 g L^{-1} .



Hg²⁺ concentrations before and after sequestration by WSe₂ and WS₂ samples at 0.5 g L⁻¹. The WSe₂ and WS₂ were able to reduce the concentration of Pb²⁺ from 52.30 mg L⁻¹ to 0.76 and 0.42 mg L⁻¹ (Fig. 4a), respectively, giving a Pb²⁺ uptake capacity of ca. 103 mg g⁻¹. The highest Pb²⁺ uptake capacities of WSe₂ and WS₂ are 288 and 386 mg g⁻¹ when treating 1048 mg L⁻¹ of lead ions in water, which are substantially higher than those of nanostructured adsorbents with abundant hydroxyl groups reported previously, such as urchin-like FeOOH (80 mg g⁻¹),^{8a} flowerlike zinc silicate (210 mg g⁻¹) and flowerlike AlOOH (124.2 mg g⁻¹) under similar conditions (Table S1, ESI†).^{8c,10} Particularly, WSe₂ and WS₂ show extremely high uptake capacities for Hg²⁺ (Fig. 4b). WSe₂ and WS₂ could decrease the concentration of Hg²⁺ from 978 mg L⁻¹ to 222 mg L⁻¹ and 0.71 mg L⁻¹ resulting in impressive capacities of 1512 mg g⁻¹ and 1954 mg g⁻¹, respectively. Their capacities for Hg²⁺ are significantly higher than those of conventional metal oxide and carbon-based adsorbents (Table S1, ESI†) and those of metal chalcogenides (Table S2, ESI†).¹¹ Flowerlike WSe₂ was characterized after removal of Pb²⁺ and Hg²⁺ (Fig. S14 & S15, ESI†). PbWO₄ polyhedron nanoparticles are embedded in the WSe₂ nanosheets suggesting that Pb²⁺ ions were removed *via* a chemical reaction. When treating Hg²⁺ ions in water, the WSe₂ nanosheets were almost fully covered by Hg₂Cl₂ and Hg₃Se₂Cl₂ nanoparticles, suggesting that WSe₂ is a reducing agent that has high reactivity towards Hg²⁺ leading to the high Hg²⁺ uptake capacity. Likewise, PbWO₄ nanoparticles are immobilized on WS₂ nanosheets (Fig. S16 & S17, ESI†). WS₂ microspheres are enclosed by as-formed Hg₃S₂Cl₂ and Hg₂Cl₂ particles, indicating extremely high reactivity and reducibility of WS₂ towards Hg²⁺ ions, which resulted in such a high Hg²⁺ sequestration capacity. The WS₂ microsphere is superior to the flowerlike WSe₂ in terms of uptake capacities for Pb²⁺ and Hg²⁺, possibly because sulfide has higher reactivity towards Pb²⁺ and Hg²⁺ than selenide. This mechanism is different from the direct cation exchange mechanism of other metal chalcogenides for heavy metal ion sequestration.¹¹

In summary, flowerlike WSe₂ and WS₂ microspheres assembled of nanosheets were synthesized by a facile and high-yield solvothermal method. The *in situ* SR-XRD gave insights into the growth mechanism of the flowerlike WSe₂ and WS₂, which is the reaction between dissolved W(CO)₆ and dissolved S or melted Se without complete decomposition of W(CO)₆ into a W intermediate. Flowerlike WSe₂ and WS₂ microspheres were used for heavy metal ion sequestration and exhibited remarkable uptake capacities for Pb²⁺ (288 mg g⁻¹ for WSe₂ and 386 mg g⁻¹ for WS₂) and Hg²⁺ (1512 mg g⁻¹ for WSe₂ and 1954 mg g⁻¹ for WS₂), showing great potential in heavy metal remediation. The synthesis method and SR-XRD characterization in this work offer novel approaches towards rational design and fabrication of hierarchical transition metal dichalcogenides and understanding of their formation mechanism.

This project received financial support from Joint Research Project funding (GJHZ1224) from the Chinese Academy of Sciences and CSIRO. We acknowledge the Australian Synchrotron for the Powder Diffraction beamline access, and CSIRO Minerals for laboratory *in situ* XRD access. The CSIRO Office of the Chief Executive (OCE) Postdoctoral and Science Leader Schemes are

acknowledged for supporting this work. R. A. C. acknowledges the Australian Research Council for a Future Fellowship (FT0990583).

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