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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, K_{2x}Mn_xSn_{3–x}S₆, (NH₄)₄In₁₂Se₂₀, H_{2x}Mn_xSn_{3–x}S₆ and H_xNa_yInS_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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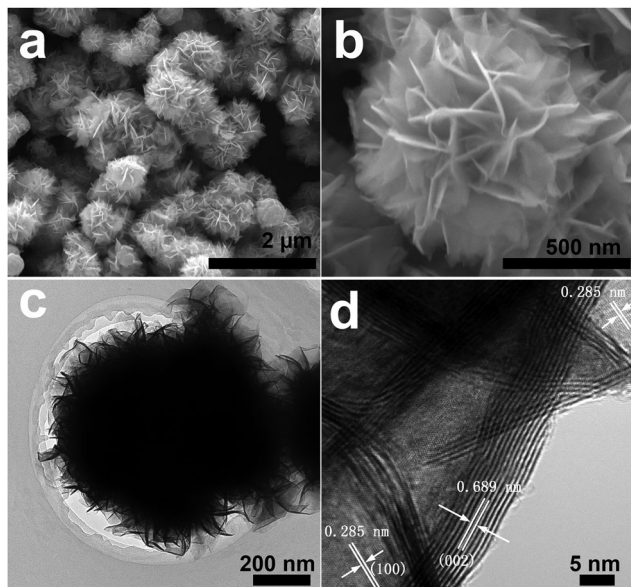


Fig. 1 SEM images (a and b) and TEM images (c and d) of the WSe₂ microspheres.

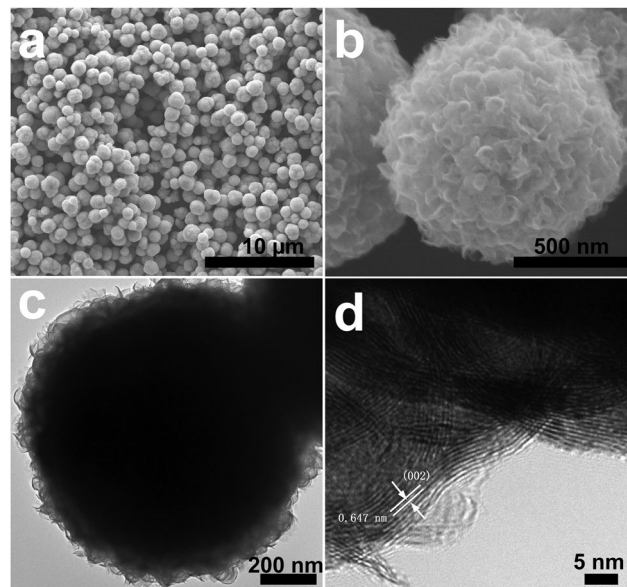


Fig. 2 SEM images (a and b) and TEM images (c and d) of the WS₂ microspheres.

(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

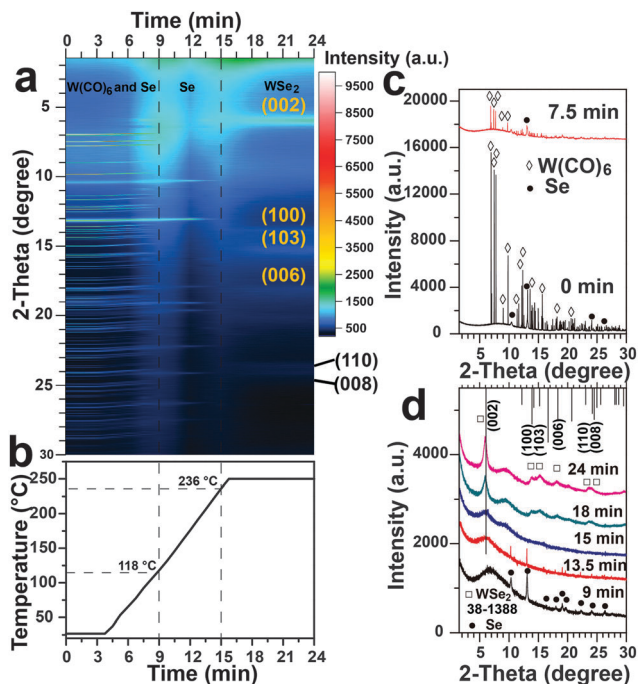


Fig. 3 (a) Time-resolved *in situ* SR-XRD patterns showing evolution from W(CO)₆ and Se precursors to WSe₂, (b) temperature ramp rate (20 °C min⁻¹), (c and d) characteristic SR-XRD patterns of *in situ* products at the noted reaction time. Note that the reaction rate in the micro-reactor is much faster 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,^{16,15} as illustrated in Scheme S1, ESI[†]. The *in situ* SR-XRD patterns of WSe₂ (Fig. 3) demonstrate that the solvothermal process involves dissolution of W(CO)₆, melting of Se and growth of flowerlike WSe₂. 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 °C (Fig. 3b–d). This temperature was much lower than the decomposition/melting point of W(CO)₆ (~170 °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 °C (above the melting point of Se, 221 °C), when the Se precursor peak disappeared instantly. WSe₂ 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 WSe₂. 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 WSe₂ 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 WS₂ was also explored by the *in situ* SR-XRD (Fig. S12, ESI[†]). Sulfur (m.p. 115 °C) and W(CO)₆ were dissolved at 83 °C and 116 °C, respectively. Then WS₂ 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 WSe₂.

The synthesis of WTe₂ at 250 °C with the solvothermal method using W(CO)₆ and Te (m.p. 450 °C) was attempted. However, the product was only a mixture of Te and TeO₂ 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 WS₂ and WSe₂ began with the dissolution of S and W(CO)₆, melting of Se and then both precursors reacted quickly to produce crystalline WS₂ and WSe₂ 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 WSe₂ and WS₂ microspheres possess many nanosheets and abundant chalcogen ligands with innate reactivity towards soft heavy metal ions (Hg²⁺, Pb²⁺, *etc.*) and structural rigidity. These features are desirable for the sequestration of heavy metal ions from water. The flowerlike WSe₂ and WS₂ microspheres were used to sequester various heavy metal ions, including As(v), As(III), Cd²⁺, Pb²⁺ and Hg²⁺, from water. They did not remove As(v), As(III) and Cd²⁺, whereas they exhibited high uptake capacities for Hg²⁺ and Pb²⁺. This is due to the innate selectivity of metal chalcogenides for soft heavy metal ions (*i.e.* Hg²⁺ and Pb²⁺).¹¹ Fig. 4 exhibits the variation in Pb²⁺ and

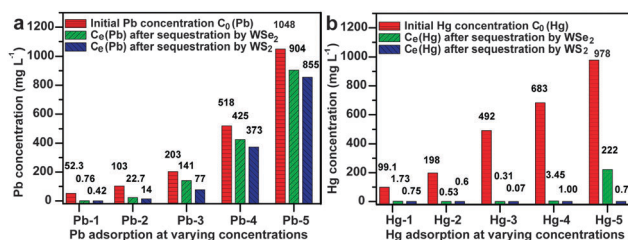


Fig. 4 (a) Pb²⁺ and (b) Hg²⁺ sequestration of WSe₂ and WS₂ in water. The WSe₂ and WS₂ content in the Pb²⁺ and Hg²⁺ aqueous solutions was 0.5 g L⁻¹.

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.

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