# **Electronic Supplementary Information**

# Flowerlike WSe<sub>2</sub> and WS<sub>2</sub> Microspheres: One-pot Synthesis, Formation Mechanism and Application in Heavy Metal Ion Sequestration

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## Chemicals and Materials

Analytical grade W(CO)<sub>6</sub> (99%) was purchased from Strem Chemicals Inc. Mo(CO)<sub>6</sub> (98%), S (99.98%), Se (99.99%) and Te (99.8%) were purchased from Sigma-Aldrich. Anhydrous p-xylene (99%, Merck) was used as the solvent. Pb(NO<sub>3</sub>)<sub>2</sub>, HgCl<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O, Na<sub>2</sub>HAsO<sub>4</sub>•7H<sub>2</sub>O, and NaAsO<sub>2</sub> were purchased from Merck and used to prepare different heavy metal ion solutions. Milli-Q water (18.2 MΩ·cm) was used for solution preparation. All the chemicals were used as received without further purification.

# Synthesis of flowerlike WSe<sub>2</sub> microspheres

The flowerlike WSe<sub>2</sub> microspheres were synthesized by a facile solvothermal method. In a typical procedure, white W(CO)<sub>6</sub> (5.28 g,15 mmol) powder and grey Se (2.29 g, 29 mmol) powder were mixed in anhydrous p-xylene (100 mL) under vigorous magnetic stirring for 30 min. W(CO)<sub>6</sub> was slightly dissolved in p-xylene, while Se was not dissolved in p-xylene. Then the solution was transferred to a Teflon-lined stainless steel autoclave with an inner volume of 200 mL and heated to 250 °C for 24 h, followed by natural cooling to room temperature. The product was collected by centrifugation, washed with acetone three times to remove possible residues (W(CO)<sub>6</sub> could be easily dissolved in acetone.) and dried in a vacuum oven at 60 °C overnight. In a typical batch synthesis, around 4.7 g of WSe<sub>2</sub> was produced with a high yield of 95 %.

## Synthesis of WS<sub>2</sub> microspheres

The WS<sub>2</sub> microspheres were synthesized by a similar solvothermal method. In a typical procedure,  $W(CO)_6$  (5.28 g, 15 mmol) and S (0.93 g, 29 mmol) were mixed in anhydrous p-xylene (100 mL) under vigorous magnetic stirring for 30 min. Sulfur was slightly dissolved in p-xylene. Then the solution was transferred to a Teflon-lined stainless steel autoclave with an inner volume of 200 mL and heated to 250 °C for 24 h, followed by natural cooling to room temperature. The product was collected by centrifugation, washed with acetone three times to remove possible residues and dried in a vacuum oven at 60 °C overnight. In a typical batch synthesis, 3.3 g of WS<sub>2</sub> was produced with a high yield of 92 %.

#### Attempted synthesis of WTe<sub>2</sub> materials

In order to synthesize  $WTe_2$ , Te was employed instead of Se as the starting material. Other synthetic conditions remained identical.

### *Heating of* $W(CO)_6$ *in p*-*xylene*

In order to confirm whether  $W(CO)_6$  would be dissociated or decomposed into a W intermediate under the solvothermal condition, white  $W(CO)_6$  powder (5.28 g, 15 mmol) was added into anhydrous p-xylene (100 mL) under vigorous magnetic stirring for 30 min. Then the slurry solution was transferred to a Teflon-lined stainless steel autoclave with an inner volume of 200 mL and heated to varying temperatures ranging from 100 to 250 °C for 24 h, followed by natural cooling to room temperature. The product was collected by centrifugation, washed with p-xylene three times and dried in a vacuum oven at 60 °C overnight. The product remained white small crystalline grains.

#### Adsorption experiments

All the adsorption experiments were carried out at room temperature by the batch method. The initial pH of the Pb<sup>2+</sup> and Hg<sup>2+</sup> solutions was not adjusted and fell within the range of 4-5, which avoided possible self-precipitation that occurs at pH > 6 especially at high initial concentrations. The stock solutions (*ca.* 1000 mg L<sup>-1</sup>) of each heavy metal: As(V), As(III), Cr(VI), Pb<sup>2+</sup>, Hg<sup>2+</sup> and Cd<sup>2+</sup> were prepared and then diluted to various concentrations. In a typical procedure, 0.01 g of flowerlike WSe<sub>2</sub> was added to 20 mL of heavy metal ion solution with different initial concentrations ranging from 50 mg L<sup>-1</sup> to 1000 mg L<sup>-1</sup>, and shaken at a rate of 800 rpm for 12 h. The WSe<sub>2</sub> was then separated by centrifugation and the initial and equilibrium concentrations of heavy metal ions in the remaining solution were then measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The adsorption capacity of the adsorbent was calculated based on the following equation:

#### $Q_e = (C_0 - C_e) * V/m$

where  $C_0 \text{ (mg } L^{-1)}$  and  $C_e \text{ (mg } L^{-1)}$  represent the initial and equilibrium concentrations of heavy metal ions, respectively. V (L) is the volume of the arsenic solution and m (g) is the mass of adsorbent. The flowerlike WSe<sub>2</sub> and WS<sub>2</sub> microspheres did not show any uptake capacities for As(V), As(II) and Cd<sup>2+</sup>.

#### Characterization

The products were characterized by scanning electron microscopy (SEM, FEI 400F) equipped with the Energy Dispersive X-ray Spectroscopy detector (EDX, Oxford INCA), transmission electron microscopy (TEM) and high resolution TEM (HRTEM, FEI Tecnai F20), powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer with Cu Kα radiation at 40 kV and 40 mA), and X-ray photoelectron spectroscopy (XPS, ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation). The concentration of all the heavy metal ions was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 730-ES Simultaneous Axial ICP-OES).

#### In situ synchrotron-radiation X-ray diffraction characterization

The *in situ* synchrotron-radiation X-ray diffraction (SR-XRD) experiments were conducted at the Australian Synchrotron Powder Diffraction beamline, using monochromatic X-rays with a wavelength of 0.689 Å (18 keV). **Scheme S1** shows the configuration of the setup. W(CO)<sub>6</sub> and Se or S were mixed with a molar ratio of 1:2 and loaded into the capillary micro-reactor made of a fused quartz glass capillary (1 mm in outer diameter and 0.1 mm in wall thickness). Then p-xylene was injected into the capillary and mixed with the powder. The micro-reactor was then sealed into a custom-made stainless steel holder. External N<sub>2</sub> pressure was applied to the micro-reactor through a pressure line during the solvothermal synthesis to prevent boiling of the solvent. The loaded micro-reactor was fixed at the beam center and was heated to 250 °C at a rate of 20 °C min<sup>-1</sup> for WS<sub>2</sub> and 10 °C min<sup>-1</sup> for WS<sub>2</sub> by a hot air blower. The temperature was calibrated using a KNO<sub>3</sub> temperature standard and was monitored by a K-type thermocouple 3.5 mm beneath the micro-reactor. The sealed micro-reactor was oscillated continuously during the measurement. The in *situ* SR-XRD diffraction patterns were collected every 1.4-1.5 minutes by a position sensitive MYTHEN detector. The synthesis was terminated when no noticeable change in diffraction patterns could be observed.



Scheme S1 Schematic of the experimental setup for *in situ* SR-XRD at the Australian Synchrotron. The colour of the micro-reactor represents the temperature distribution; temperatures from high to low are red, orange, yellow, green, purple, blue, and black; only the red zone is monitored by the detector. Reproduced with permission from *Chem. Mater.* 2015, 27, 3471-3482. Copyright 2015, American Chemical Society.



Fig. S1 XRD pattern (a) and EDX spectrum (b) of the as-synthesized flowerlike WSe<sub>2</sub> sample.



Fig. S2 High resolution XPS W 4f peak (a) and Se 3d peak (b) of the flowerlike WSe<sub>2</sub> microspheres.



Fig. S3 XRD pattern (a) and EDX spectrum (b) of the as-synthesized WS<sub>2</sub> sample.



Fig. S4 High resolution XPS W 4f peak (a) and S 2p peak (b) of the WS<sub>2</sub> microspheres.



**Fig. S5** SEM images of the WSe<sub>2</sub> products synthesized at various reaction temperatures, (a) 100 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C for 24 h; (e) XRD patterns of the Se precursor and products synthesized at various temperatures for 24 h.

Below 200 °C, the products were the mixture of grey Se and white  $W(CO)_6$ .  $W(CO)_6$  was dissolved in acetone and removed during the rinsing process and only Se remained eventually. At 200 °C, some of Se was converted to WSe<sub>2</sub> with poor crystallinity and small lateral size of the nanosheets, and a small amount of Se remained. At 250 °C, all of Se was converted to WSe<sub>2</sub> with high crystallinity and uniform flowerlike structure. This temperature-dependent process is likely related to the melting point of Se (221 °C). Se reacted with W(CO)<sub>6</sub> at temperatures close to or higher than 221 °C.



Fig. S6 SEM images of commercial (a) W(CO)<sub>6</sub> and (b) Se precursors and (c) their XRD patterns.



**Fig. S7** SEM image of the WS<sub>2</sub> products synthesized at various reaction temperatures, (a) 100 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C for 24 h; XRD patterns (e) of the W(CO)<sub>6</sub> and Se precursors and

products synthesized at various temperatures for 24 h. Insets of (b), (c) and (d) are high-magnification SEM images.

At 100 °C, white W(CO)<sub>6</sub> remained after reaction and could be easily dissolved in acetone and removed during the rinsing process. At 150 °C, smooth WS<sub>2</sub> microspheres formed. As the temperature rose, curly nanosheets grew on the surface of WS<sub>2</sub> microspheres and the crystallinity also improved. As sulfur has a low melting point (115 °C), WS<sub>2</sub> could form at relatively low temperature (i.e. 150 °C) in spite of poor crystallinity.



**Fig. S8** SEM images of the WSe<sub>2</sub> products synthesized at 250 °C for various reaction times: (a) 1 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h and (f) 24 h; and (g) the corresponding XRD patterns.

 $WSe_2$  evolved from smooth microspheres (1 h  $WSe_2$  composition, confirmed by EDX) to coarse microspheres (3-9 h) and finally flowerlike structure with well-defined nanosheets. The nanosheets

initially formed on the surface of smooth microspheres and further grew to the flowerlike structure assembled by nanosheets with large lateral sizes. No tungsten intermediate from the decomposition of  $W(CO)_6$  was observed.





**Fig. S9** SEM images of the WS<sub>2</sub> products synthesized at 250 °C for various reaction times: (a) 1 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h and (f) 24 h; and (g) the corresponding XRD patterns. Insets are corresponding high-magnification SEM images.

The WS<sub>2</sub> structure was developed from smooth microspheres to coarse microspheres (3-9 h) and finally uniform microspheres with clear nanosheets on the surface. The nanosheets initially formed on the surface of smooth microspheres and the lateral sizes of those nanosheets grew as the reaction time increased. However, the lateral size of the final WS<sub>2</sub> nanosheets was smaller than that of WSe<sub>2</sub> nanosheets. No tungsten intermediate from the decomposition of W(CO)<sub>6</sub> was observed.



**Fig. S10** XRD patterns of the samples after the solvothermal reaction at varying temperature, in which only  $W(CO)_6$  (15 mmol) was heated in p-xylene (100 mL) in the absence of Se or S. For reference, the standard JCPDS card of  $W(CO)_6$  (40-0752) was also given.

It was found that the product remained  $W(CO)_6$  even after the solvothermal reaction at 250 °C in pxylene. In this experiment, evidence for the formation of W, which had been previously proposed to be produced through the complete dissociation of  $W(CO)_6$ ,<sup>1</sup> was not found. No discernible phases of any impurities or W intermediate were detected in the XRD results.



**Fig. S11** SEM images (a), (b), TEM image (c) and XRD pattern (d) of the WSe<sub>2</sub> sample synthesized by heating the mixture of  $W(CO)_6$  and Se powders in the Teflon-lined autoclave at 250 °C for 24 h without addition of p-xylene solvent.

Irregular WSe<sub>2</sub> agglomerates with poor crystallinity were obtained. This demonstrates that the pxylene that could generate high pressure at 250 °C played a critical role in the formation of assembly of WSe<sub>2</sub> nanosheets.



**Fig. S12** (a) Time-resolved *in situ* SR-XRD patterns showing the evolution from W(CO)<sub>6</sub> and S precursors to WS<sub>2</sub>, (b) temperature ramp (10 °C min<sup>-1</sup>), (c) and (d) characteristic SR-XRD patterns of the *in situ* products at the noted reaction time.

Note that the reaction rate in the micro-reactor is always much higher than the bulk reaction rate in the autoclave. The shift of 2-Theta angles of  $W(CO)_6$  towards the lower angles is due to expansion of d spacing of  $W(CO)_6$  under heating. The diffraction peaks of WS<sub>2</sub> were broad and thus not very sharp in (a). The characteristic peaks of WS<sub>2</sub> were relatively clear in (d). The S peaks disappeared at 83 °C (< m. p. 115 °C) and  $W(CO)_6$  peaks vanished at 116 °C (< decomposition temperature 170 °C). After that, WS<sub>2</sub> was formed and crystallized upon heating, indicating that WS<sub>2</sub> was produced possibly through a straightforward one-step reaction:

 $W(CO)_6 + 2S \rightarrow WS_2 + 6CO$ ,

or a modified two-step reaction:

 $W(CO)_6 \rightarrow W(CO)_{6-n} + nCO (n < 6)$  (partial dissociation)

 $W(CO)_{6\text{-}n} + 2S \rightarrow WS_2 + (6\text{-}n)CO$ 

Both of these reaction mechanisms are different from the two-step reaction mechanism previously proposed in the literature reported as follows:<sup>1</sup>

 $W(CO)_6 \rightarrow W + 6CO;$ 

 $W + 2S \rightarrow WS_2.$ 



**Fig. S13** SEM images (a) and (b) and XRD pattern (c) of the product from the reaction between  $W(CO)_6$  and Te in the solvent of p-xylene at 250 °C for 24 h in the Telfon-lined autoclave.

Both white  $W(CO)_6$  and black powder were observed in the product. Before SEM and XRD characterization, white  $W(CO)_6$  was dissolved in acetone and rinsed away. Therefore, the XRD pattern shows the presence of Te and TeO<sub>2</sub> due to the partial oxidation during the solvothermal reaction. Owing to the reaction temperature remaining below the melting point of Te (450 °C), dissolved  $W(CO)_6$  could not react with Te to generate WTe<sub>2</sub> and eventually white  $W(CO)_6$  separated out after cooling, without decomposition into W.



**Fig. S14** (a) SEM image of the flowerlike WSe<sub>2</sub> after sequestration of 100 mg L<sup>-1</sup> of Pb<sup>2+</sup>; (b) SEM and (c) TEM images of the flowerlike WSe<sub>2</sub> after sequestration of 1000 mg L<sup>-1</sup> of Pb<sup>2+</sup>; (d) SEM image of WSe<sub>2</sub> after sequestration of 100 mg L<sup>-1</sup> of Hg<sup>2+</sup> and (e) SEM and (f) TEM images of WSe<sub>2</sub> after sequestration of 1000 mg L<sup>-1</sup> of Hg<sup>2+</sup>. Inset of (b) is the SEM image with higher magnification.

Polyhedron  $PbWO_4$  nanoparticles were formed through the chemical reaction between  $Pb^{2+}$  and  $WSe_2$  under the weak acidic condition and were immobilized in the nanosheets. After sequestering  $Hg^{2+}$ ,  $WSe_2$  was almost completely covered by Hg-based nanoparticles, indicating extremely high uptake capacity for  $Hg^{2+}$ .



Fig. S15 XRD patterns of the WSe<sub>2</sub> before and after sequestration of  $Pb^{2+}$  (a) and  $Hg^{2+}$  (b).

PbWO<sub>4</sub> formed when sequestering Pb<sup>2+</sup> with WSe<sub>2</sub>, while WSe<sub>2</sub> peaks were still discernible. WSe<sub>2</sub> was almost completely converted to Hg<sub>3</sub>Se<sub>2</sub>Cl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub> and WO<sub>3</sub> when reacting with Hg<sup>2+</sup> under the

acidic condition. The presence of  $Hg_2Cl_2$  demonstrated that part of  $Hg^{2+}$  was reduced and thus  $WO_3$  was formed due to the oxidation of  $W^{4+}$  (WSe<sub>2</sub>). This mechanism for removal of  $Pb^{2+}$  and  $Hg^{2+}$  is different from the direct cation exchange mechanism of metal sulfides including ZnS gel,<sup>2</sup> (NH<sub>4</sub>)<sub>4</sub>In<sub>12</sub>Se<sub>20</sub>,<sup>3</sup> H<sub>2x</sub>Mn<sub>x</sub>Sn<sub>3-x</sub>S<sub>6</sub>,<sup>4</sup> K<sub>2</sub>MnSn<sub>2</sub>S<sub>6</sub>,<sup>5</sup> and H<sub>2.67</sub>Na<sub>0.48</sub>InS<sub>3.07</sub>.<sup>6</sup>



**Fig. S16** SEM images (a), (b) and TEM image (c) of the flowerlike WS<sub>2</sub> after sequestration of 1000 mg L<sup>-1</sup> of Pb<sup>2+</sup>; SEM images (d), (e) and TEM image (f) of the WS<sub>2</sub> after sequestration of 1000 mg L<sup>-1</sup> of Hg<sup>2+</sup>. Inset of (c) is the HRTEM image of the PbWO<sub>4</sub> nanoparticle.

Polyhedron PbWO<sub>4</sub> nanoparticles were embedded in the WS<sub>2</sub> nanosheets on the surface of the microspheres. After sequestrating  $Hg^{2+}$ , WS<sub>2</sub> was almost completely covered by as-formed nanoparticles, indicating extremely high uptake capacity for  $Hg^{2+}$ .



Fig. S17 XRD patterns of the WS<sub>2</sub> before and after sequestering  $Pb^{2+}$  (a) and  $Hg^{2+}$  (b).

 $PbWO_4$  was formed after  $WS_2$  sequestered  $Pb^{2+}$  while  $WS_2$  peaks were still discernible.  $WS_2$  was almost completely converted to  $Hg_3S_2Cl_2$ ,  $Hg_2Cl_2$  and  $WO_3$  when reacting with  $Hg^{2+}$  under the acidic condition. The presence of  $Hg_2Cl_2$  demonstrated that part of  $Hg^{2+}$  was reduced and thus  $WO_3$  was formed due to oxidation of  $W^{4+}$  ( $WS_2$ ).

Adsorbent	Concentration range [mg L <sup>-1</sup> ]	Initial pH	Maximum Pb <sup>2+</sup> uptake capacity [mg g <sup>-1</sup> ]	Maximum Hg <sup>2+</sup> uptake capacity [mg g <sup>-1</sup> ]	Reference
Flowerlike WSe <sub>2</sub>	50-1000	4-5 (not adjusted)	288	1512	This work
WS <sub>2</sub> microspheres	50-1000	4-5 (not adjusted)	386	1954	This work
Urchin-like FeOOH	10-1500	Not adjusted	80	N/A	7
Flowerlike zinc silicate	10-1000	Not adjusted	210	N/A	8
Flowerlike AlOOH	10-316 for Pb <sup>2+</sup> 10-266 for Hg <sup>2+</sup>	Not adjusted	124.22	131.23	9
polyacrylamide- grafted chitosan decorated	0-500	5.0	63.67	263.9	10
Fe <sub>3</sub> O <sub>4</sub> Functionalized Fe <sub>2</sub> O <sub>4</sub> @C	10-200	Not adjusted	90.3	83.1	11
$Fe_2O_3/Al_2O_3$ nanofibers	5-50	6	23.75	63.69	12
Carbon nanotubes	0-100	6	N/A	200	13
Chitosan-coated diatomite	10-400	5	N/A	116.2	14
Graphene-Diatom Silica	50-400	6.5	N/A	515	15
Carbon aerogel	0-40	4.5	34.72	35	16, 17
Amine-modified activated carbon	10-100	6	N/A	121	18
FeMnOOH	0-250	7	N/A	0.34	19
Metal organic framework UiO-66- NH <sub>2</sub>	0-200	Not adjusted	232	769	20

Table S1 Comparison of  $Pb^{2+}$  and  $Hg^{2+}$  uptake capacities on metal oxide and carbon-based adsorbents.

Concentration range $[mg L^{-1}]$	Initial pH	Maximum Pb <sup>2+</sup>	Maximum Hg <sup>2+</sup>	Reference
		[mg g <sup>-1</sup> ]	g <sup>-1</sup> ]	
50-1000	4-5 (not adjusted)	288	1512	This work
50-1000	4-5 (not adjusted)	386	1954	This work
1-90	~0	33	31	3
1-70	5	not available	87	4
0.02-350	2.5-9	319	377	5
5-250 for Hg <sup>2+</sup> 1-40 for Pb <sup>2+</sup>	6	189	1386	6
	Concentration range [mg L <sup>-1</sup> ] 50-1000 50-1000 1-90 1-70 0.02-350 5-250 for Hg <sup>2+</sup> 1-40 for Pb <sup>2+</sup>	Concentration  Initial pH    range [mg L <sup>-1</sup> ]	Concentration  Initial pH  Maximum $Pb^{2+}$ range [mg L <sup>-1</sup> ]  uptake  capacity    [mg g <sup>-1</sup> ]  [mg g <sup>-1</sup> ]    50-1000  4-5 (not adjusted)  288    50-1000  4-5 (not adjusted)  386    1-90  ~0  33    1-70  5  not available    0.02-350  2.5-9  319    5-250 for Hg <sup>2+</sup> 6  189    1-40 for Pb <sup>2+</sup> 5  5	Concentration  Initial pH  Maximum $Pb^{2+}$ Maximum $Hg^{2+}$ range [mg L <sup>-1</sup> ]  uptake  capacity  uptake capacity [mg    [mg g <sup>-1</sup> ]  g <sup>-1</sup> ]  g <sup>-1</sup> ]    50-1000  4-5 (not adjusted)  288  1512    50-1000  4-5 (not adjusted)  386  1954    1-90  ~0  33  31    1-70  5  not available  87    0.02-350  2.5-9  319  377    5-250 for Hg <sup>2+</sup> 6  189  1386

Table S2 Comparison of Pb<sup>2+</sup> and Hg<sup>2+</sup> uptake capacities on various metal chalcogenide adsorbents.

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