Supporting Information

Synthesis of Highly Ordered Mesoporous Crystalline WS₂ and MoS₂ *via* a High-Temperature Reductive Sulfuration Route

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Figure S1. Schematic diagram of the synthesis apparatus

Figure S2. Small-angle XRD pattern (left) and nitrogen sorption isotherms (right) of mesoporous 70-SBA-15 prepared by a low-temperature (70°C) hydrothermal treatment. Inset is the corresponding pore-size distribution curves.

Figure S3. Nitrogen sorption isotherms and corresponding pore size distribution curves (inset) of ordered cubic mesoporous WS₂ and MoS₂ casted from the mesoporous silica KIT-6 template *via* a high temperature (600°C) reductive sulfuration method.

Table S1. Theoretic volume yields* of metal oxides from salt precursors.

Precursor	Product	Volume yield (%)	Precursor	Product	Volume yield (%)
Mg(NO ₃) ₂ ·6H ₂ O	MgO ^{1, 2}	6.2	Ni(NO ₃) ₂ ·6H ₂ O	NiO ⁶	7.1
Al(NO ₃) ₃ ·9H ₂ O	Al ₂ O ₃ ³	5.9	Cu(NO ₃) ₂ ·3H ₂ O	CuO ¹⁰	12.1
Cr(NO ₃) ₃ ·9H ₂ O	Cr ₂ O ₃ ⁴⁻⁶	6.6	Zn(NO ₃) ₂ ·6H ₂ O	ZnO ¹¹	10.1
Mn(NO ₃) ₂ ·6H ₂ O	MnO ₂ ⁶⁻⁸	10.7	In(NO ₃) ₃ ·4.5H ₂ O	In ₂ O ₃ ^{6, 14}	11.9
Fe(NO ₃) ₃ ·9H ₂ O	Fe ₂ O ₃ ^{6, 9}	6.3	Co(NO ₃) ₂ ·6H ₂ O	Co ₃ O ₄ ^{4, 6, 12-14}	8.5

* It summarizes the typical precursors which have been used in the literatures (ref. 1-14, see below) to prepare metal oxide replicas using nanocasting method. The volume yields are calculated based on the molecular weight and density of the precursors and products. The higher the yield is, the larger the particle size of the replicas is, and the closer the morphology is to that of silica templates. A high volume yield of PTA to WS₂ (71%) in our synthesis is a key issue for the final product that can faithfully replicate the morphology from the silica template. This yield is much higher than that from nitrate salt precursors as shown in Table S1. The particle sizes of the metal oxide replicas from these nitrate salt precursors are much smaller than that of the template materials, and their morphologies have weakly correlation to the templates.^{4-6,9,14}

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Calculation process for the comparison of the surface energy between the two crystal orientation

models:

The above geometric scheme shows the orthographic projection views of the two proposed models as shown in Figure 5c and d. The parameters for the description of crystals are marked in the scheme and listed below:

L : length of the mesochannels D : diameter of the mesopore

If the number of dangling bond is larger, the formation energy is higher. Therefore, in order to simplify the comparison, we directly calculate the specific surface area of S-W-S layer edges, because only these edges are covered by dangling bonds. The specific surface areas of these two models can be described respectively as

$$\text{Model A: } S_A = L_A \times \alpha \times D + 2 \times \frac{1}{4} D^2 (\alpha + \sin \alpha) \quad [1]$$

$$\text{Model B: } S_B = L_B \times \pi \times D \quad [2]$$

With the condition that the total mass of the two model is a constant, we obtain

$$V_A = L_A \times \frac{1}{4} D^2 (\alpha + \sin \alpha) \equiv V_B = L_B \times \frac{1}{4} D^2 \times \pi \quad [3]$$

$$\text{Which means } L_A = \frac{\pi}{\alpha + \sin \alpha} \times L_B \quad [4]$$

Then, the S_A/S_B ratio can be calculated by employing Equation [1], [2] and [4] together

$$\frac{S_A}{S_B} = \frac{L_A \times \alpha \times D + \frac{1}{2} D^2 (\alpha + \sin \alpha)}{L_B \times \pi \times D} = \frac{\alpha}{\alpha + \sin \alpha} + \frac{D(\alpha + \sin \alpha)}{L_B \times 2\pi} \quad [5]$$

As shown by equation [5], S_A/S_B is determined by only two factors: α and L_B/D . We calculate S_A/S_B ratio values by tuning α from 90 to 180° and L_B/D from 0.1 to 100. The results are shown in Figure S5.

Figure S5. The map of S_A/S_B ratio values (calculated based on Equation [5])

In the blue region, S_A/S_B is below 1 that means $S_A < S_B$. If S-W-S crystal layers are parallel to the long axis of the mesochannels (Model A), the surface area can be reduced. As a consequence, the crystal model A is more favorable in this region by reason of less dangling bonds. On the contrary, S_A is larger than S_B in other regions. The crystal model B is more favorable.

As shown in Figure S5, when L_B/D is below 1, S_A is always larger than S_B . This results indicating that the crystal model B is more stable in a short cylindrical confined space. If L_B/D exceeds 10, S_A is smaller than S_B in the range covered most α values. In this case, the crystal model A is more stable in a long cylindrical confinement space.

In the present case, the diameter of the mesopores (D) is about 10 nm as shown by the nitrogen sorption results (Table 1), and the total length of the template mesochannels is about 1000 nm as shown by the TEM and SEM images. So, L_B/D is about 100. From the above calculation (Figure S5), it can be concluded that the crystal model A is more favorable than the model B in such an anisotropic

nanospace. This result can explain why S-W-S layers always grow along the long axis of the mesochannels in the products.