A universal strategy for the synthesis of porous two-dimensional transition metal oxide nanosheets based on chemical topology transformation

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ABSTRACT Two-dimensional (2D) transition metal oxides (TMOs) have attracted much attention for various applications, owing to the abundance of active sites, rapid ion transmission speed, and short carrier migration distance. However, the current preparation strategies are usually limited to producing intrinsically layered compounds or sacrificing template. Here, we report a universal strategy for preparing ultrathin porous 2D TMO nanosheets by chemical topological transformation of the corresponding transition metal selenides. We observed that the as-prepared 2D TMO nanosheets not only perfectly inherit the transition metal selenides' 2D topological structure, but also possess numerous pore structures formed as a way to release the structural stress associated with lattice growth. As a proof of concept, ultrathin porous WO₃, MoO₃, and Co₃O₄ nanosheets were successfully prepared based on the *in-situ* oxidation of the corresponding ultrathin WSe₂, MoSe₂, and Co_{0.85}Se, respectively. The outstanding sensing properties and photodetector performance displayed by the as-prepared porous 2D WO₃ nanosheets further indicate the promising prospects of topology transformation for the preparation of porous 2D TMO nanosheets.

Keywords: topology transformation, two-dimensional nanosheets, porous, transition metal oxide

INTRODUCTION

Graphene discovered in 2004 [1] has sparked a worldwide

boom in research on two-dimensional (2D) materials as a result of graphene's unique physical, chemical, and electrical properties. Many ultrathin materials with graphene-like structures, such as transition metal oxides (TMOs) [2], transition metal chalcogenides [3], graphitic carbon nitride [4], and layered double hydroxides [5], have attracted widespread attention and spurred a range of research efforts. Ultrathin 2D nanosheets usually have a lateral dimension of 100 nm or larger and a thickness of only a few nm [6]; in addition to having a large specific surface area, ultra-high carrier mobility, good electrical conductivity, and excellent mechanical properties, research results also indicate that 2D materials can confine electrons in a 2D space, which affords surprising performance in many applications [7]. In recent years, the continuous development of the semiconductor industry has meant that higher performance and economic benefit requirements now exist for functional materials; in this context, TMOs have attracted increasing attention as a class of compounds comprising elements that are extremely abundant on earth. Besides the economic advantages derived from the abundance of transition metals on earth, 2D TMOs are also considered functional materials with very high application potential due to their unique mixed valence, rich redox combinations, rapid ion transmission speed, short carrier migration distance, and high-temperature stability. Results from published studies indicate that 2D TMOs display ideal performances in the

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fields of sensors [8–9], catalysis [10], and electrochemical energy storage [11]. These excellent performance and broad application prospects have thus encouraged researchers to develop new strategies for the preparation of 2D TMO nanosheets [12]. However, developing efficient methods to prepare 2D TMOs remains a challenging research goal.

Generally, the preparation strategies of 2D TMO nanosheets can be divided into two categories: “top-down” and “bottom-up.” The peeling method is a typical top-down preparation strategy. The principle on which it is based is to overcome the weak van der Waals forces between the layers of the multilayer material to achieve nanosheet separation. For instance, Ji *et al.* [13] prepared ultrathin MoO_3 nanosheets with a thickness of 10 nm by affecting the intercalation of dimethyl sulfoxide and the ultrasonic grinding of MoO_3 samples of higher thickness. Zhao *et al.* [14] also prepared several ultrathin CrO and ZrO nanosheets by heating and stripping the corresponding metal chloride precursor. However, the accurate control of the thickness and number of TMO layers is very difficult to achieve by implementing the heating and stripping approach, and this method is only suitable for peeling intrinsically layered materials. As for the bottom-up synthesis methods, the template-based method has been proven to be a promising strategy for the preparation of ultrathin 2D TMOs. Peng *et al.* [15] reported a universal strategy for the preparation of 2D TMOs that relies on graphene oxide (GO) as a template by which a variety of porous 2D TMO nanosheets were successfully prepared by removing the GO template. Similarly, Zhao *et al.* [16] and Sun *et al.* [17] prepared 2D TMOs using GO and a polymer as templates, respectively. Although the template-based method can be utilized to efficiently prepare intrinsically non-layered 2D TMOs, the implementation of the template preparation procedure and the post-treatment to remove the template not only make the synthesis process complex, but also may cause the nanostructures to be destroyed. Notably, chemical vapor deposition and physical vapor deposition have also been proven to afford the controllable synthesis of high-quality 2D TMO nanosheets. However, the low productivity and the high energy consumption associated with the implementation of these strategies have drawn criticism [18]. Therefore, considering the disadvantages and inherent limitations of existing 2D TMO preparation methods, the development of new and more widely applicable preparation strategies of 2D TMO remains a research goal of high significance.

In this work, considering that, by implementing the

chemical topological transformation approach, the maintenance and “inheritance” of the precursor’s topological structure during the preparation of the target product can be achieved in the absence of an auxiliary template; while the topology transformation of transition metal selenide (TMSe) nanosheets to TMO nanosheets at the 2D scale has been rarely mentioned, we demonstrated for the first time a universal strategy for the preparation of porous 2D TMO nanosheets based on the chemical topological transformation approach. By oxidizing the corresponding ultrathin TMSe nanosheets at a specific temperature determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (Fig. S1), we were able to successfully prepare several porous 2D TMO nanosheets, including WO_3 , MoO_3 , and Co_3O_4 , by implementing the chemical topological transformation approach. Transmission electron microscopy (TEM) evidence indicated the synthesized TMO nanosheets display a rich and evenly distributed porosity. In addition, taking WO_3 nanosheets as an example, atomic force microscopy (AFM) data indicated that the thickness of the nanosheets of this TMO is only 4–5 nm, a value that is highly consistent with the thickness of the nanosheets of the WSe_2 precursor [19]. The explanation of the observation that the prepared TMO nanosheets can perfectly maintain the topological morphology of the utilized precursor may be that the precursor prepared by the hydrothermal method has a relatively loose structure, which provides a suitable 2D space for the breakage of W–Se bonds and the formation of W–O bonds, and the formation of a uniform pore structure benefits from the need for stress release during lattice growth. On the one hand, the generation of these pores offsets the tendency of the 2D TMO nanosheets to crack and undergo granulation, thus ensuring the integrity of the 2D structure of the TMO nanosheets. On the other hand, studies have shown that a porous structure often implies the presence of highly reactive exposed edges [10,20–21]; thus, the abundance of pores in the prepared TMO nanosheets will lead to a large specific surface area and a significantly increased number of active sites; moreover, compared with non-porous WO_3 nanosheets, density functional theory (DFT) calculations confirmed that more charge is transferred in W atoms in porous WO_3 nanosheets, so that the nanosheets could have superior performance in many electronic applications. In fact, we found that porous 2D WO_3 exhibited excellent performance in both gas sensing and light excitation, which makes us confident about the application prospects of such porous 2D TMO nanosheets.

EXPERIMENTATION

Material synthesis

All chemicals were used as purchased without further processing. The preparation of ultrathin porous TMO nanosheets can be divided into two steps: the synthesis of ultrathin selenide nanosheets and the *in-situ* oxidation of the said nanosheets in an oxygen atmosphere. We synthesized ultrathin and dense selenide nanosheets implementing the hydrothermal method according to literature directions [22–24]; we then completed the inheritance of the 2D morphology from TMSe to TMO, performing an *in-situ* oxidation.

Preparation of ultrathin porous WO₃ nanosheets

Dimethylformamide (50 mL, analytical reagent (AR)) were poured into a three-necked flask along with 8 mmol of Se (99%) powder and 0.2 g of NaBH₄ (99%). After 10 min of magnetic stirring, 4 mmol of Na₂WO₄·2H₂O was added to the above solution under stirring, and the mixture thus obtained was further stirred for 1 h. The mixed solution was then transferred to a 100-mL Teflon-lined autoclave, which was placed in a muffle furnace for hydrothermal processing at 240°C for 48 h. The precipitate thus produced was collected and washed five times with deionized water and ethanol alternately, and the obtained powder was dried at 60°C for 10 h. Finally, porous 2D WO₃ nanosheets were obtained by *in-situ* oxidizing the collected WSe₂ nanosheets in a tube furnace under an oxygen atmosphere at 450°C for 3 h.

Preparation of ultrathin porous MoO₃ nanosheets

Se powder (0.3158 g) and 0.3 g of NaBH₄ were poured into a beaker containing 30 mL of deionized water. Upon dissolution of the Se powder after 10 min of magnetic stirring, 0.4839 g of Na₂MoO₄·2H₂O and 30 mL of ethanol (AR) were quickly added to the above-mentioned solution under magnetic stirring. Subsequently, the prepared precursor solution was transferred to a 100-mL high-pressure reaction kettle, which was kept in a muffle furnace at 200°C for 24 h. After the mixture was naturally cooled to room temperature, the black MoSe₂ powder was collected by washing followed by centrifugation; it was then calcined in a tube furnace at 400°C for 3 h under an oxygen atmosphere. Finally, porous 2D MoO₃ nanosheets were obtained.

Preparation of ultrathin porous Co₃O₄ nanosheets

Ultrathin porous cobalt oxide nanosheets were also obtained by calcining cobalt selenide nanosheets that was

prepared by implementing the hydrothermal method. In detail, 0.0866 g of Na₂SeO₃ and 0.1455 g of Co(NO₃)₂·6H₂O were transferred to a three-necked flask containing 18 mL of deionized water. After stirring, the mixture thus obtained for 20 min, and 2 mL of hydrazine hydrate were added to a three-necked flask under nitrogen atmosphere. The obtained mixture was then transferred to an autoclave with Teflon lining for hydrothermal processing conducted at 160°C for 24 h. Once the reactor was allowed to cool to room temperature, the black ultrathin cobalt selenide nanosheets could be obtained by repeated centrifugation and ethanol washing. Finally, the porous 2D Co₃O₄ nanosheets were collected after calcining the dried cobalt selenide nanosheets in an oxygen atmosphere at 600°C for 4 h.

Characterization

X-ray diffraction (XRD, Philips X' Pert diffractometer) with a Cu K α light source was used to determine the phase of the sample. Field emission scanning electron microscopy (FESEM, FEI Sirion200) and TEM (FEI Tecnai G2 F20) were employed to investigate the morphology of the sample. Energy-dispersive X-ray spectroscopy (EDS, ULTIM MAX 100) was used to determine the elemental content of WO₃ nanosheets. AFM (SPM9700, Shimadzu, Japan) was employed to determine the thickness of the nanosheets, and X-ray photoelectron spectroscopy (XPS, Kratos XSAM800 spectrometer) was used to analyze the molecular structure and atomic valence of the sample. Thermogravimetric differential scanning calorimetry (TG–DSC) was used to determine the minimum oxidation temperature for the prepared TMSe nanosheets.

Gas sensor measurements and photodetector measurements

The micro-dropping method was implemented to evenly distribute the WSe₂ nanosheets dispersed in ethanol with ultrasound onto the electrode substrate. The prepared electrode substrate was dried at 80°C for 10 min to remove the ethanol and placed in a tube furnace, which was calcined under an oxygen atmosphere at 450°C for 3 h, thereby preparing a WO₃ device that could be used for hydrogen sulfide (H₂S) gas sensing. Gas sensing relied on a high-throughput test platform built independently by our laboratory. The prepared device was inserted into the testing chamber, and a heating voltage was applied. We controlled the concentration of the H₂S gas by adjusting the ratio of H₂S gas to dry air. Next, according to the response value formula, $S = R_a/R_g - 1$, where S is the

response value, R_a is the resistance value of the device in the air background, and R_g is the response resistance value of the device to H_2S gas. Finally, the response of gas sensing was calculated by analyzing the resistance signal recorded by a computer. The above-mentioned device can also be used for photodetector testing. By applying to or removing from the device containing porous 2D WO_3 nanosheets, the uniform optical radiation (400 nm peak, 5.20 mW cm^{-2}), and photoelectric response data were collected with the high-throughput test platform independently developed by our laboratory.

RESULTS AND DISCUSSION

The two-step method for preparing ultrathin porous 2D TMO nanosheets is roughly depicted in Fig. 1. During the oxidation of ultrathin TMSe nanosheets prepared *via* the hydrothermal method in an oxygen atmosphere at a specific temperature, Se atoms in TMSe nanosheets will undergo complete oxidation to generate the corresponding stable oxide SeO_2 . This compound is in the gas phase at high temperature, and it will stay in the tube furnace with the oxygen flow. Taking the oxidation process of WSe_2 as an example, the said reaction course is represented by the following equation [25]:

In order to confirm that WSe_2 had been oxidized completely, we performed EDS experiments on the as-prepared porous 2D WO_3 nanosheets. As can be evinced from Fig. S1d, the content of Se atoms in the product WO_3 is 0, and the atomic ratio of O to W is 76.69/23.31, which is close to the theoretical stoichiometric ratio of

3/1.

As the *in-situ* oxidation of Se centers proceeds, the TMO lattice continues to grow. Since the WSe_2 precursor is sufficiently thin (about 5 nm), the lattice growth process of WO_3 is limited to the 2D space, thereby thwarting the tendency of TMO nanosheets to form granular structures, and a large number of micropores form on the surface of the nanosheet as a way to release the huge surface stress associated with maintaining the original 2D morphology of the TMSe nanosheets. Through this topology transformation strategy, we successfully prepared several ultrathin porous TMO nanosheets, such as WO_3 , MoO_3 , and Co_3O_4 . Details on these types of nanosheets refer to the Supplementary information.

As can be evinced from Fig. 2, SEM and TEM experiments were conducted to determine the morphologies of several TMSe nanosheet precursors. Clearly, these selenide nanosheet precursors all displayed ultrathin and dense sheet morphologies, and the edges of the said sheets were characterized by a degree of curling due to surface tension; notably, these structural features are very similar to those of reduced GO (Figs S2 and S3). TEM was also employed to observe the pore structure and lattice distribution of ultrathin porous TMO nanosheets (Figs S4 and S5). Taking ultrathin porous WO_3 nanosheets as an example, the TEM image in Fig. 2d indicates that the lateral size of the prepared nanosheets can reach several hundred nanometers, and this structural feature is a direct consequence of the size of the nanosheets of the precursor, WSe_2 . The XRD pattern reported in Fig. 2a indicates that WSe_2 nanosheets are completely transformed into orthogonal phase WO_3 (JCPDS No.20-1324)

Figure 1 Schematic diagram of the two-step synthesis of the 2D porous TMO nanosheets.

Figure 2 (a, b) XRD and Raman results of the 2D porous WO_3 nanosheets. (c, f, i) SEM images of the ultrathin WSe_2 , MoSe_2 and $\text{Co}_{0.85}\text{Se}$ precursors. (d, g, j) TEM images of the 2D porous WO_3 , MoO_3 and Co_3O_4 . (e, h, k) High-resolution TEM images and selected area electron diffraction images of the 2D porous WO_3 , MoO_3 and Co_3O_4 .

with lattice constants $a = 7.384$, $b = 7.512$, and $c = 3.846$, after undergoing calcination in an oxygen atmosphere. Notably, Raman spectroscopy measurements can afford the non-destructive detection of defects in 2D materials [26]. Therefore, we compared the Raman spectra of smooth and porous WO_3 nanosheets and found that the Raman peak position of WO_3 nanosheets with a porous

structure exhibits an obvious shift with respect to the positions of their counterparts for smooth WO_3 nanosheets (Fig. 2b). This observation may be related to phonon softening and phonon–electron coupling induced by point defects [27]. In addition, evidence suggests that dense pore structures are evenly distributed on the surface of the WO_3 nanosheets; additionally, results of

Brunner–Emmet–Teller (BET) measurements indicate the specific surface area of the nanosheet to be about $58.9 \text{ m}^2 \text{ g}^{-1}$ (Fig. S6), and the average pore diameter to be 2–4 nm. As can be evinced from Fig. 2c–k, high-resolution TEM evidence supports the data on the average pore diameter obtained by BET; moreover, the selected area electron diffraction patterns indicate that WO_3 and MoO_3 nanosheets prepared by this chemical topology transformation strategy are polycrystalline, while Co_3O_4 nanosheets are composed of single crystals. AFM evidence indicates the thickness of the WO_3 nanosheets is about 4.6 nm (Fig. 3a), which is equivalent to a stack of seven WO_3 monolayers [28]. The 2D ultrathin structure and the abundance of pores in nanosheets will inevitably bring

about a short electron migration channel, a large exposed surface, and a wealth of active sites, which could be very beneficial to the materials' development and application to the manufacture of electronic devices.

XPS was employed to determine the chemical composition and element valence states of the ultrathin porous WO_3 nanosheets (Fig. 3b, c). We found the binding energies of W $5p_{3/2}$, W $4f_{5/2}$, and W $4f_{7/2}$ to be 41.8, 38.0, and 35.9 eV, respectively, which are basically consistent with those reported for W^{6+} [29]. Moreover, it is worth noting that the binding energies of W $4f_{5/2}$ and W $4f_{7/2}$ have increased offsets of 0.2–0.6 eV compared with the standard reference of WO_3 (Table S1), indicating that the charge density around the W atom has decreased with

Figure 3 (a) AFM image and thickness annotation of the 2D porous WO_3 nanosheets. (b, c) Typical XPS spectra of the 2D porous WO_3 nanosheets: O peaks and W peaks. (d, e) Charge density distribution of the porous and non-porous WO_3 nanosheets. (f) Differential charge density diagram between the porous WO_3 nanosheets and the non-porous WO_3 nanosheets.

respect to the said standard; this observation may descend from an electronic rearrangement caused by the lattice distortion and chemical bond breakage. The intuitive explanation of this process is that, with the breakage of the W–Se bond and the formation of the W–O bond, electrons begin to transfer from the W atom to the O atom, which leads to an increase in chemical state of the W atom. DFT calculations were performed to estimate the value of the differential charge density of porous WO_3 nanosheets and non-porous ideal WO_3 nanosheets. As can be easily evinced from Fig. 3d–f, the charge transfer of W atoms in porous WO_3 nanosheets is significantly enhanced with respect to non-porous WO_3 nanosheets. Compared with the ideal non-porous WO_3 nanosheet, the charge of the six tungsten atoms at the pore edge of a porous WO_3 nanosheet transfers 0.14 more electron than non-porous WO_3 . In addition, the average charge of W atoms in porous WO_3 nanosheets is reduced by 0.05 e with respect to non-porous WO_3 nanosheets (Fig. S7). The calculated value of the Bader charge further supports the enhancement of the charge transfer associated with the presence of pores; notably, this enhancement often

means an increase in reactivity [27,30–31], which is beneficial to the potential applications of the obtained porous materials.

In order to test the application performance of such ultrathin porous TMO nanosheets, we conducted H_2S gas-sensing tests with ultrathin porous WO_3 nanosheets as a typical example. H_2S is well known to be a good electron donor, and we found the resistance of the WO_3 nanosheet sensor to be significantly reduced when the sensor was in contact with H_2S gas; moreover, the said resistance quickly and completely recovered its original value when the flow of H_2S gas was discontinued, which is the typical behavior expected from n-type semiconductors. We compared the responses of WO_3 nanosheets to H_2S gas at a concentration of 2 ppm at different temperatures and found that, as the temperature gradually increased to 160°C , the response value continued to increase and reached a peak at 160°C ; above this temperature, however, the response value gradually decreased as the temperature increased. Therefore, we determined the best working temperature for WO_3 nanosheets to be 160°C . As can be evinced from Fig. 4,

Figure 4 (a) Schematic diagram of the device prepared by dripping-annealing. (b, c) The cycle stability curve and response/recovery curve of the sensor to 2 ppm hydrogen sulfide at 160°C . (d) Photoelectric response/recovery curve of the WO_3 device.

five repeated measurements indicated that the average response value of the device to 2 ppm H₂S gas was 35.55; additionally, the values for the response/recovery times measured in the five tests were basically the same, with the resistance value returning to the baseline value every time. Such gas-sensing performance was observed to be superior to those reported in the literature for H₂S gas sensors [32–35]; these results undoubtedly indicate that the porous 2D WO₃ nanosheets, or other TMO nanosheets, have great potential as gas sensors. Similarly, we also found that the value of the light–dark resistance ratio of WO₃ nanosheets was 317% when used in photo-detectors, and it can not only recover to the baseline stably, but also display an extremely high response/recovery speed, suggesting that WO₃ nanosheets also have the potential to be utilized as optoelectronic devices.

CONCLUSION

In summary, based on a simple topology transformation strategy, we synthesized several kinds of porous 2D TMO nanosheets, such as WO₃, MoO₃, and Co₃O₄, by oxidizing the corresponding TMSe nanosheets. In fact, the use of ultrathin TMSe nanosheets limits the lattice growth process of TMO nanosheets to the 2D space, while the formation of pores affords the means to release the huge stress associated with crystal lattice growth, thereby maintaining a complete 2D morphology and avoiding the fracture and granulation of nanosheets during the oxidation process. We also found that the as-synthesized porous 2D WO₃ nanosheets exhibit excellent H₂S gas sensitivity and photoelectric performance; notably, the performance of this material in other fields is also worth investigating in the future. Furthermore, the range of suitable precursors that can be utilized in the described topology transformation strategy may be extended to include other ultrathin TMSe nanosheets or even other ultrathin transition metal chalcogenide nanosheets.

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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一种基于化学拓扑变换合成多孔二维过渡金属氧化物纳米片的通用策略

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摘要 二维(2D)过渡金属氧化物(TMO)由于其丰富的活性位点,快速的离子传输速率和较短的载流子迁移距离引起了广泛关注。但是,当前的合成策略通常局限于本质分层的化合物或基于牺牲模板的方法。本文中,我们报道了一种通过相应过渡金属硒化物的化学拓扑转移制备超薄二维多孔TMO纳米片的通用策略。值得注意的是,所制备的2D TMO纳米片不仅可以完美地继承过渡金属硒化物的2D拓扑结构,而且由于晶格生长中的应力释放产生了大量的孔洞结构。此外,我们基于原位氧化相应的超薄 WSe_2 , MoSe_2 和 $\text{Co}_{0.85}\text{Se}$ 纳米片,成功制备了多孔超薄 WO_3 , MoO_3 和 Co_3O_4 纳米片。所制备的多孔二维 WO_3 纳米片出色的气敏性能和光探测性能进一步表明了该制备策略具有广阔的应用前景。