Hydrothermal Synthesis and Characterization of Single-Molecular-Layer MoS_2 and $MoSe_2$

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Single-molecular-layer (SML) MoS_2 and $MoSe_2$ were synthesized by a hydrothermal method at 150–180 °C. XPS, XRD, ICP, and TEM were used to characterize the samples, and BET study indicated that the SML MoS_2 has very large surface area. And it was found that the SML MoS_2 has strong ability to catalytically decompose hydrazine monohydrate, just like platinum black.

Layered transition metal dichalcogenides ME_2 (M = Nb, Ta, Mo, W; E = S, Se) are composed of E–M–E layers and the layers are bound to each other only by van der Waals forces. Intercalating and subsequently exfoliating these dichalcogenides yield the corresponding single-molecular-layer forms of them.[1–4] Among the single layer transition metal dichalcogenides, SML MoS_2 has been extensively studied. The typical characteristic of SML MoS_2 is that the diffraction originated from layer-stacking (002) absolutely disappears in the X-ray diffraction pattern (XRD), and XRD is the most effective method to identify SML MoS_2.[3,5] According to Chianelli et al., SML MoS_2 has an XRD pattern different from those of the amorphous and poorly crystalline MoS_2.[5,6] SML MoS_2 provides a typical material for studies of physical and chemical properties of two-dimensional, ultra thin film (<1 nm). In addition to the intrinsic interest in the properties of this matter, it appears that SML MoS_2 may have useful applications, particularly in catalysis,[7] in the formation of new inclusion solids[8,9] and in the preparation of large area films made by stacking single layers on a substrate. SML MoS_2 is usually synthesized by the exfoliation method.[3] However, this method is oxygen sensitive and most of the operations must be carried out in a dry and inert atmosphere. Recently, Afanasiev et al. reported that SML MoS_2 could be synthesized at low temperature under normal pressure, but the single layer must be stabilized by a surfactant.[10] In their another work, they report XRD pattern quite like the XRD pattern of SML MoS_2, but the sulfur content in their samples is too high.[11] Although $MoSe_2$ is isostructural with MoS_2, SML $MoSe_2$ is not reported still now. Here, we report a hydrothermal method to produce SML MoS_2 and $MoSe_2$.

A typical preparation procedure is as follows. Ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$], 1 g, elemental sulfur, 0.35 g (or elemental selenium, 0.89 g), and 8 mL of hydrazine monohydrate (86%) were put in Teflon-lined stainless steel autoclaves of capacity 25 mL. Distilled water was used to fill the autoclaves to 80% of the total volume. The autoclaves were maintained at 150–180 °C for 48 h and then were cooled naturally. The resulting dark-gray powders were filtered and washed with distilled water, diluted hydrochloric acid and ethanol, successively. The final products were dried in a vacuum at 40 °C for 3 h. The samples of the so-prepared MoS_2 and $MoSe_2$ were denoted as **M1** and **M2**, respectively.

X-ray photoelectron spectra (XPS) of the samples were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer with an exciting source Mg Kα (1253.6 eV). The C 1s binding energy of carbon contamination occurs at 284.8 eV. The binding energies of Mo ($3d_{5/2}$) and Mo ($3d_{3/2}$) in the sample of **M1** were 228.3 and 231.2 eV, respectively, and those for **M2** were the same as **M1**. The binding energies of S ($2p_{3/2}$) and S ($2p_{1/2}$) in the sample of **M1** were 161.7 and 162.7 eV, respectively. The binding energy of Se (3d) in the sample of **M2** is 53.9 eV, which is characteristic binding energy of Se^{2-}. All of these binding energies are consistent with the values of MoS_2 and $MoSe_2$ reported in literatures.[12,13] Analysis of the Mo (3d) and S (2p) or Se (3d) peak intensities gave S/Mo or Se/Mo atomic ratio of 2.05 to 2.1. Chemical analysis[14] of **M1** gave S/Mo atomic ratio of 1.97 to 2.14, which is in agreement with the XPS measurements. The chemical composition of **M2** was determined by ICP–AES (inductively coupled plasma–atomic emission spectra), which gave Se/Mo atomic ratio of 1.98 to 2.12. Thus, **M1** and **M2** should be MoS_2 and $MoSe_2$ and the sulfur content in **M1** was lower than that of the samples prepared by Afanasiev et al.[11] XRD patterns of the samples were recorded with a MAX 18 AHF X-ray diffractometer (MAC Science Co., Ltd.). Figure 1 is the XRD pattern of sample **M1**, which shows only a broad weak envelope beginning at about $2\theta = 30^{\circ}$ and continuing out above 60°. The two maxima approximately locate at the 100 and 110 positions of bulk 2H-MoS_2.[15] The missing of the 002 diffraction and the appearing of 110 diffraction indicate that the SML MoS_2 is aggregates of S–Mo–S single layers and stacking of them has not taken place.[5,6] This XRD pattern is in good agreement with that of previously reported SML MoS_2,[3,10] which indicates that **M1** is SML MoS_2. The XRD pattern of sample **M2** was almost the same as that of sample **M1** except that the two maxima moved a little to the lower angles. So, **M2** should be SML $MoSe_2$.

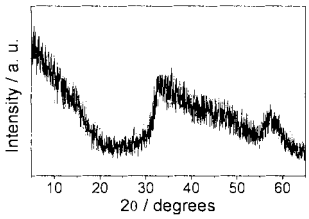

Figure 1. XRD pattern of the as-prepared SML MoS_2.

As the strong electron beam and high vacuum easily caused the monolayers to stack,[10,16] transmission electron microscope (TEM) is not a good instrument to identify and study pure SML MoS_2. But as an effective measure to observe morphology, the present samples were still observed by a Hitachi H-800 transmission electron microscope. Of course,

what was observed in TEM probably was stacked structure of single layers. TEM image (Figure 2a) shows sample **M1** has crimpled rag-like morphology. And it was found that when the concentration of the reactants was decreased, the area of thin sheets became large and the degree of crimple decreased (Figure 2b). The morphology of **M2** is similar to that of **M1**, and the same trend as that of **M1** was also observed with the decrease of the concentration of the reactants. Electron diffraction pattern of the samples can not be obtained, which is consistent with the result of XRD. The surface areas of sample **M1** and **M2** were determined by low-temperature nitrogen adsorption (BET). The surface area of **M1** was 180–240 m^2/g, which is larger than that reported by Afanasiev et al.[10,11] **M2** had a relatively small surface area (70 m^2/g) compared with **M1**.

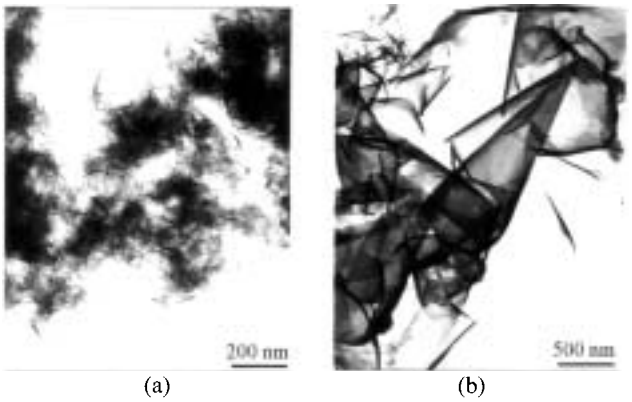

Figure 2. TEM images of the as-prepared SML MoS_2 (a) prepared in normal concerntration, (b) in low concerntration.

It was found that freshly prepared SML MoS_2 (dried in air) could react with concentrated hydrazine monohydrate (86%) violently with the evolution of a large amount of ammonium. Sometimes the heat released was so large that the SML MoS_2 became glowing red. But if the SML MoS_2 had been boiled in water for more than one hour, the reaction would be weak or even, there would be no reaction. This is the first report about the phenomenon for MoS_2 and the phenomenon has been observed for platinum black by A. Purgotti and L. Zanichelli.[17] According to their report, this process is a catalytic decomposition of hydrazine monohydrate and the adsorbed oxygen induces the catalytic process. This phenomenon showed that the as-prepared SML MoS_2 have phenomenological similar catalytic ability at this point to platinum black. Considering MoS_2 is a widely used catalyst,[18] an in-depth study of the catalytic properties of the SML MoS_2 is necessary and valuable, and it may be a kind of potential powerful catalyst at some aspects. Yet, the SML $MoSe_2$ reacted with hydrazine monohydrate weakly.

In conclusion, SML MoS_2 and $MoSe_2$ were synthesized by a hydrothermal method at 150–180 °C and characterized by XPS, XRD, ICP and TEM. BET study indicated that the SML MoS_2 has very large surface area and the SML $MoSe_2$ has relatively small surface area. The SML MoS_2 was found to have strong ability to catalytically decompose hydrazine monohydrate just like platinum black, which indicates that the SML MoS_2 may be a potential powerful catalyst.

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