Hydrothermal Synthesis of Fine MoS_2 Crystals from Na_2MoO_4 and KSCN

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A fine crystal MoS_2 has been synthesized by hydrothermal method in a clean and efficient system consisting of Na_2MoO_4 and KSCN in a short time (24 h). The product is characterized by XRD and TEM, and the ED pattern reveals a hexagonal crystal. The mechanism of this reaction is also put forward. Thus this method provides us a new routine to synthesize other transition metal sulfides.

Molybdenum disulfide, as one of the most important transition metal sulfides, has intensive applications as solid state lubricants,[1] hydrodesulfurization catalysts,[2] nonaqueous lithium batteries,[3] intercalation hosts,[4] and so on. Besides its natural state (molybdenite), there have been a large number of preparation methods for MoS_2. For example, high-temperature solid state reaction between molybdenum and sulfur powders,[5] thermal decomposition[6] or hydrogen processing[7,8] of ammonium tetrathiomolybdate and molybdenum trisulfides, frit reaction in molten potassium thiocyanate,[9] hydrothermal method,[10–13] sputter deposition,[14] chemical vapor deposition (CVD),[15,16] anode discharge electrolysis,[17] and so on. Among these methods, reactions can easily take place under relatively lower temperature (100–300 °C) by hydrothermal method. However, the product MoS_2 always comes out to be in poor crystals;[12,13] otherwise, it will take extremely long time (30 days) to get better crystals.[11] What's more, the MoS_2 getting from frit reaction in molten potassium thiocyanate[9] at a temperature of 350 °C also has poor crystals. In this communication, we report the hydrothermal reaction between sodium molybdate and potassium thiocyanate, by which we first get MoS_2 powders in fine crystals in a short time (24 h) and in a clean dissolvent (deionized water). Also, the mechanism of the reaction is discussed.

The preparation procedure is as follows. All the reagents used were of analytical grade purity. 1.21 g (0.005 mol) sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), 1.22 g (0.0125 mol) potassium thiocyanate (KSCN) were put into a Teflon-lined autoclave of 100 mL capacity. Then the autoclave was filled with deionized water up to 60% of the total capacity. The autoclave was sealed into a stainless steel tank and kept at 260 °C for 24 h, and then cooled to room temperature on standing. A dark gray laminar powder with silvery luster was collected and washed with deionized water for several times to remove the residue of the reactants. The final product was dried at 40 °C for 12 h.

The product was examined by X-ray diffraction (XRD) using a Bruker D8-advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). All the reflections shown in Figure 1 can be indexed as hexagonal 2H-MoS_2 [space group $P6_3/mmc$(194)]. After refinement, the cell constants ($a = 3.159 \pm 0.002$ Å, $c = 12.30 \pm 0.01$ Å) are close to the reported data ($a_0 = 3.1616$ Å and $c_0 = 12.2985$ Å] in the JCPDS cards (37-1492). The XRD pattern shows that the sample had a fairly good crystallization compared to other MoS_2 products synthesized by hydrothermal methods previously,[10–12] especially the reflection of the (008) plane, which has never been observed by others using this method. However, it was found that temperature was a controlling factor of the reaction. Good MoS_2 crystals were yielded at the temperature of 260 °C, but if the temperature was dropped under 240 °C, a large number of impurities were found in the product.

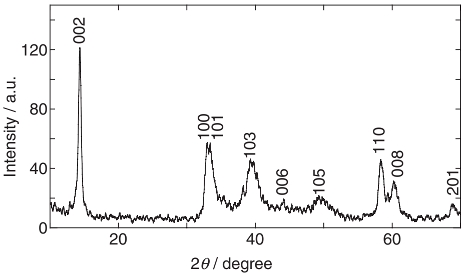

Figure 1. XRD pattern of the prepared 2H-MoS_2.

The morphologies and structure of the prepared MoS_2 were further examined with transmission electron microscopy [TEM, Hitachi (Tokyo, Japan) H-800]. Figure 2 clearly reveals the laminar structure of the product. The resulting MoS_2 appears to have the general morphologies showed in Figure 2a, with a blanket-like shape and a size of 0.3–1.0 µm in diameter. There are also some regular large hexagonal flakes in the sample showed in Figure 2b, which is the typical morphology of hexagonal crystals. At the top right corner of the each image, are the electron diffraction (ED) patterns of the sample, indicating that the sample is single crystals and of hexagonal lattice. Energy dispersive X-ray analysis (EDX) indicates that only the elements Mo and S are detected (except the peaks arising from Cu grid). The S/Mo ratio was evaluated to be 2.03–2.05 from the intensities of the separated peaks. Combining all the analy-

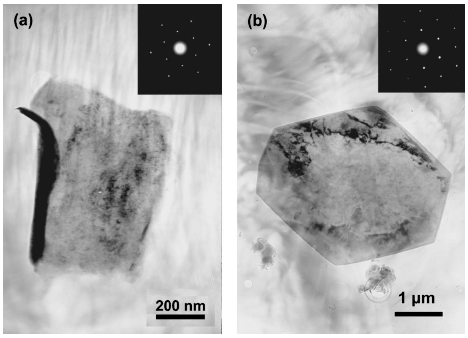

Figure 2. TEM images of the prepared MoS_2, (a) blanket-like morphology (b) hexagonal morphology. The insets are the ED patterns taken on the regions showed in the image.

sis results above, the sample should be MoS_2, and it is distinguished to the other MoS_2 synthesized by hydrothermal method from its sheet morphology, single crystals ED pattern, and fairly good XRD pattern.

In the reaction process, KSCN acts as a reducing reagent as well as a vulcanizer. At the end of the reaction, Ba^{2+} was put into the supernatant and immediately a large amount of white deposition came out. Some of the deposition could not be dissolved in acid. From the phenomenon above, we concluded that there was $SO_4{}^{2-}$ formed in the reaction. And the XRD pattern of the deposition also proved it to be $BaSO_4$. This revealed that a part of S in SCN^- changed into $SO_4{}^{2-}$ and reduced Mo(VI) to Mo(IV), and the other part of S contributed to form MoS_2 with Mo. In the result of the reaction, $CO_3{}^{2-}$ was also found, because of the XRD pattern of $CaCO_3$ formed by depositing the supernatant with Ca^{2+}. What's more, the alkalinous gas sending out after the reaction revealed the existence of NH_3. In addition, no NaCN, KCN, NaOCN or KOCN were detected in the residue by XRD after drying the supernatant. Thus the possible reaction for the synthesis of MoS_2 could be formulated as:

$$4MoO_4{}^{2-} + 9SCN^- + 15H_2O \longrightarrow 4MoS_2 + SO_4{}^{2-} + 3NH_4{}^+ + 9CO_3{}^{2-} + 6NH_3(g)$$

Compared to other hydrothermal synthesis of MoS_2, this reaction has some other merits. In order to dissolve some of the reactant such as elemental sulfur, pyridine or some other organic regents are often used before,[10,13] which can bring pollution to the product and the environment. While in this reaction, deionized water is used as solvent. What's more, sodium molybdate and potassium thiocyanate are both water soluble, so they can react in their ionized state in the solvent, and the reaction takes place more thoroughly, which may contribute to the good yield of MoS_2 crystals.

In conclusion, KSCN is a good reducing reagent and vulcanizer. Under the hydrothermal condition, KSCN can reduce Mo(VI) to Mo(IV), and provide S to form fine MoS_2 crystals. After changing some of the reacting conditions, we also get MoS_2 crystals in different morphology from MoO_3 in this method, and a further work is in progress. Thus, we think that in the existence of KSCN, it could be applicable for preparing other technologically important transition metal sulfides, such as WS_2 and so on.

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