A Novel Molten-Salt Method to Produce Nanocrystalline WS_2

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Nanocrystalline WS_2 was prepared by the reaction of elemental sulfur and sodium tungstate (or calcium tungstate) in an aluminum chloride molten-salt. XPS, XRD and TEM indicated that the product was 2H-WS_2 nanoparticles with size of 20–50 nm and irregular morphology.

Tungsten disulfide, which is anisotropic material with trigonal prismatic structure formed by stacking sandwiches consisting of a layer of tungsten atoms between two layers of sulfur atoms, has stimulated considerable interest as lubricant, battery cathode, and catalyst.[1–3] Traditionally, WS_2 powders have been prepared by the elemental reaction at high temperature or by thermal decomposition reaction of ammonium tetrathiotungstate [$(NH_4)_2WS_4$].[4] Metathesis reactions between tungsten halides and alkali-metal sulfides or covalent sulfating agents in organic solvents to produce finely dispersed amorphous products at moderate temperature have been explored.[5,6] Recently, nanotubes and inorganic fullerene-like structures of WS_2, which were produced by vapor phase reaction or the reaction of $W(CO)_6$ with H_2S in a microwave plasma, have attracted much attention.[7–9]

Molten-salt route is a useful method to prepare some materials and it has been used to synthesize some sulfides-like MoS_2 and $Rb_4Zr_3Te_{16}$.[10,11] In this paper, a novel molten-salt method was reported to prepare nanocrystalline WS_2 at 350–400 °C by using sodium tungstate and elemental sulfur as reactants with $AlCl_3$ as molten-salt.

A typical procedure is as following. All reagents were of 99.9% purity from Shanghai Chemistry Co. and were used without further purification. Sodium tungstate, 6.6 g, elemental sulfur, 2.0 g, and aluminum chloride ($AlCl_3$), 8.0 g, were ground together into fine powder in a dry glove box. The mixture was put into a stainless steel autoclave with the capacity of 25 mL. The autoclave was maintained at 350-400 °C for 48 h, then was cooled to room temperature naturally. The raw product was dug out and dissolved into concentrated sodium hydroxide solution. The solution was heated to 80 °C and stirred for 4 h. Then it was filtered and washed with distilled water, ethanol, CS_2 and ethanol again. The final product was dried in a vacuum at 80 °C for 2 h.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an exciting sources Mg Kα = 1253.6 eV in high vacuum (5×10^{-9} Pa). The binding energy of W ($4f_{5/2}$) and W ($4f_{7/2}$) are 32.75 and 34.85 eV. And that of S ($2p_{3/2}$) and S ($2p_{1/2}$) are 161.75 and 163.25 eV the same as that for conventional WS_2.[12] The binding energy of S (2s) at 226.40 eV is characteristic of S^{2-}. Analysis of the W (4f) and S (2p) peak intensities gave a S/W atomic ratio of 2.00 to 2.08. XPS measurements also indicated that trace amount of Al^{3+} existed in the samples.

X-ray powder diffraction (XRD) patterns were recorded with a MAX 18 AHF X-ray diffractometer (MAC Science Co. Ltd) with Cu Kα_1 radiation (λ = 1.54056 Å). Figure 1 shows the XRD pattern of the so-prepared sample. All of the peaks can be indexed as 2H-WS_2.[13] No peaks of other phase and impurities were detected. According to the Scherrer Formula, the broadening of these diffraction peaks indicates that the obtained sample is made up of small particles. But to layered compounds, the accurate particle size can not be obtained from this formula.

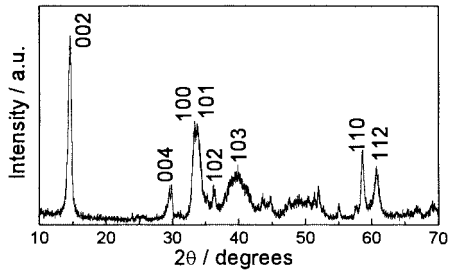

Figure 1. XRD pattern of nanocrystalline 2H-WS_2.

Transmission electron microscopy (TEM) was performed on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 KV. Figure 2 shows the morphology of the so prepared samples. It shows that the particle size is about 20-50 nm and the particles have an irregular morphology.

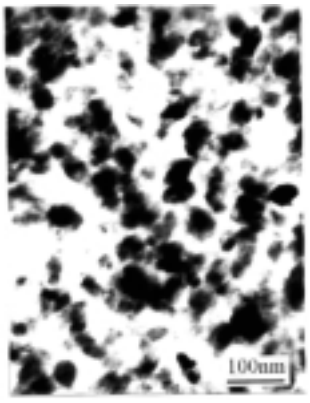

Figure 2. TEM image of nanocrystalline WS_2.

This process is a complicated reaction, the exact mechanism need further research. However, it was found that $AlCl_3$ was involved in the reaction and aluminum oxide was the main by-product. Besides acting as molten salt, $AlCl_3$ stript oxygen from sodium tungstate and made the reaction easy between W

and S. This point is important in this process and the reaction could not take place if $AlCl_3$ was substituted by solvents. And other ordinary molten salts can not be used in the reaction in this temperature range, such as $ZnCl_2$, $SnCl_2$ and $NaNO_2$. In fact, the reason that we chose $AlCl_3$ as the molten salt was that it has low melting temperature and strong oxygen affinity. It was found that calcium tungstate could be used to synthesize nanocrystalline WS_2, too. This method may be used to synthesize other transition metal sulfides from AMO_x (A = Li, Na, K, Ca; M = V, Nb, Ta, etc). When temperature was below 300 °C, the yield of WS_2 would drop significantly. It was found that the reaction was mainly controlled by temperature.

In conclusion, nanocrystalline WS_2 was synthesized by the reaction of elemental sulfur and sodium tungstate (or calcium tungstate) in an aluminum chloride molten-salt at 350–400 °C. XPS and XRD measurements indicated that the so-prepared sample was nanocrystalline 2H-WS_2. TEM revealed that the nanoparticles were mainly 20–50 nm large and with an irregular morphology. It was thought that this method might be used to prepare some special metal sulfides.

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