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Short communication

Low-temperature synthesis of pure rock-salt structure manganese sulfide using a single-source molecular precursor

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ABSTRACT

Pure rock-salt structure manganese sulfide (α-MnS) powders were synthesized via solvothermal decomposition of an easily obtained single-source molecular precursor (manganese *N,N′*-diethyl dithiocarbamate: Mn-DDTC) in 80 vol.% hydrazine hydrate aqueous solution at 90–120 °C for 24 h. The as-obtained products were characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), chemical analysis, scanning electron microscope (SEM), and UV–vis absorption spectra. Furthermore, the control experiments with multiple-source precursors revealed that the single-source molecular precursor, Mn-DDTC played an important role in synthesizing phase-pure MnS under the present solvothermal conditions.

1. Introduction

MnS is a wide bandgap VIIB–VIA semiconductor that has potential uses as a window/buffer material in solar cells and short wavelength optoelectronic devices, or as luminescence and dilute magnetic semiconductor materials, etc. It usually crystallizes into three different polymorphs [1–13]: the stable green α-MnS with rock-salt type structure, and the two pink metastable structures, β-MnS (sphalerite type) and γ-MnS (wurtzite type). Both tetrahedrally coordinated β and γ forms can only exist in a low-temperature range, and will transform into octahedrally coordinated stable α form at 100–400 °C or at high pressure [1–7]. The preparation of thermally stable α-MnS is generally desirable for practical applications in the above-mentioned purposes. Nevertheless, the low-temperature synthesis of pure and well-crystallized α-MnS seems to be somewhat difficult, because it is hard to see some literatures reporting the successful synthesis of α-MnS at temperatures ≤120 °C so far.

Recently, the solvothermal method has opened a fruitful way for the mild synthesis of advanced inorganic materials that are difficult or impossible to obtain by high temperature solid-state reactions [1–11]. The choice of appropriate precursors played a key role in the solvothermal method [1–11], because the precursors with different composition, structure, solubility, thermal stability, etc., have different reactivity and transport behavior, which influence the subsequent crystal growth of the product from solution [1–11]. The single-source molecular precursor (i.e., a precursor compound which contains all elements of the final material within a single-molecule [14]) was proven to be an excellent candidate for solvothermal synthesis of novel chalcogenide nanomaterials [14–18]. The main advantage of utilizing single-source molecular precursors is to induce the unusual crystal growth selectivity or metastable phase formation of the resultant products [16–18], which were sometimes unattainable with multiple-source precursors. Therefore, we attempt for the first time the solvothermal synthesis of α-MnS crystallites using an easily obtained, cheap single-source molecular precursor (Mn-DDTC, which can be prepared directly from the precipitation reaction of manganese acetate and sodium diethyldithiocarbamate in distilled water under the ambient condition. Sodium diethyldithiocarbamate (*the commercial price is 30.7 Chinese Yuan per 100 g at present*) is cheaper than thioacetamide (*the commercial price is 35 Chinese Yuan per 25 g at present*), which is one of the most used sulfide sources in the laboratory). By the proposed single-source precursor solvothermal method, pure α-MnS powders are successfully synthesized in 80 vol.% hydrazine hydrate aqueous solution at 90–120 °C, which can not be obtained with multiple-source precursors under the same condition. The as-obtained products are characterized by powder XRD, FTIR, XPS, chemical analysis, SEM, and UV–vis absorption spectra.

2. Experimental

All the chemical reagents used in our experiments are of analytical grade. The single-source molecular precursor, Mn-DDTC, was prepared directly from the precipitation reaction of manganese

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acetate and sodium diethyldithiocarbamate in distilled water under the ambient condition.

In a typical procedure for the solvothermal synthesis of α-MnS, 1.0 g of Mn-DDTC powders was put into a Teflon-lined stainless steel autoclave of 50 ml capacity, to which 40 ml of 80 vol.% hydrazine hydrate aqueous solution was added. The autoclave was sealed and maintained at 90–120 °C for 24 h, then allowed to cool to room temperature naturally. The as-formed green precipitates were filtered, washed with distilled water and ethanol for several times (*during the filtration, the top surface of the products was always covered with liquids to prevent its oxidation in air*), and dried in vacuum at 60 °C.

Powder XRD patterns were measured on a German Bruker AXS D8 ADVANCE X-ray diffractometer at room temperature. FTIR spectra were recorded on a Bruker Tensor-27 FTIR spectrometer at room temperature with samples in a KBr wafer. XPS measurements were conducted on a Thermo ESCALAB 250 XPS system with Al K_α radiation as the exciting source, where the binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. The manganese content in the bulk products was also determined by EDTA complex titrimetry. SEM images were taken on a Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy attachment. UV–vis absorption spectra were obtained using a Shimadzu UV-2550 spectrophotometer, by dispersing the samples in ethanol at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the products derived from solvothermal decomposition of Mn-DDTC in 80 vol.% hydrazine hydrate aqueous solution at 90–120 °C for 24 h. All of the resultant products displayed the characteristic XRD peaks corresponding to α-MnS (JCPDS card no. 06-0518), and no obvious diffraction peaks arising from the possible impurity phases such as Mn-DDTC, γ-MnS and manganese hydroxide were observed, suggesting the formation of single-phase α-MnS. In addition, the typical FTIR spectrum of the obtained products (Fig. 2(c)) further revealed that they were free of the contaminations from the solvent (Fig. 2(b)) and single-source molecular precursor (Fig. 2(a)). The three obvious peaks centered at around 3426, 1638 and 1386 cm^{-1} in Fig. 2(c) were caused by the adsorbed water and carbon dioxide, because submicron crystallites exhibited a high surface-to-volume ratio.

By contrast, when multiple-source precursors such as stoichiometric manganese acetate or manganese sulfate and sodium sulfide or thioacetamide or thiourea or sodium thiosulfate, instead of Mn-DDTC, were employed as the reactants in the solvothermal synthesis of MnS, keeping the other conditions constant (e.g., 80 vol.% hydrazine hydrate aqueous solution, $T = 100\,°C$ and $t = 24\,h$), the obtained products all contained an impurity of $Mn(OH)_2$ (in some cases, unknown impurities may be included in the resultant products, especially when thiourea was used as the sulfide source) as disclosed by their XRD patterns (not shown here). The inclusion of $Mn(OH)_2$ in the products was likely due to the competing reactions of forming MnS and $Mn(OH)_2$ precipitates in the alkaline hydrazine hydrate aqueous solution, because the solubility constants of α-MnS and $Mn(OH)_2$ in aqueous solution are close (the solubility constants of α-MnS and $Mn(OH)_2$ in aqueous solution are 3×10^{-13} and 1.9×10^{-13}, respectively [19]). The control experiment results clearly indicated that Mn-DDTC, the single-source molecular precursor with pre-established Mn–S chemical bonds, played an important role in preparing pure α-MnS under the current low-temperature solvothermal conditions: Mn-DDTC can be regarded as an inorganic core [MnS] with two capping groups [20], nucleophilic attack by hydrazine hydrate at the thione carbon can lead to the removal of the capping groups, then the [MnS] inorganic cores would combine with each other and grow into larger crystallites during the solvothermal process.

The surface and bulk compositions of the as-prepared product were examined by XPS and chemical analysis, respectively. Fig. 3

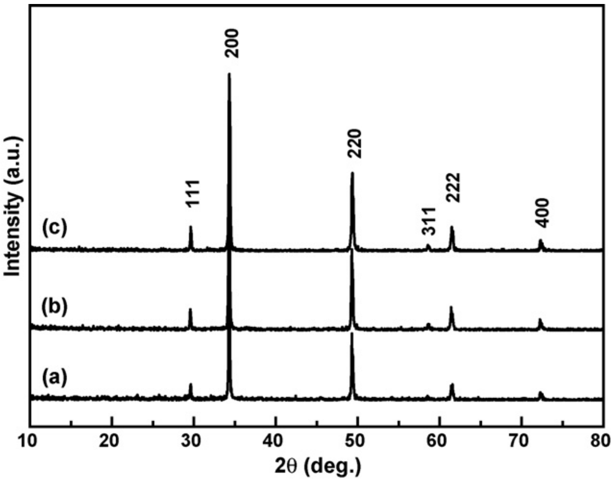

Fig. 1. XRD patterns of the products derived from solvothermal decomposition of Mn-DDTC in 80 vol.% hydrazine hydrate aqueous solution at (a) 90 °C, (b) 100 °C and (c) 120 °C for 24 h.

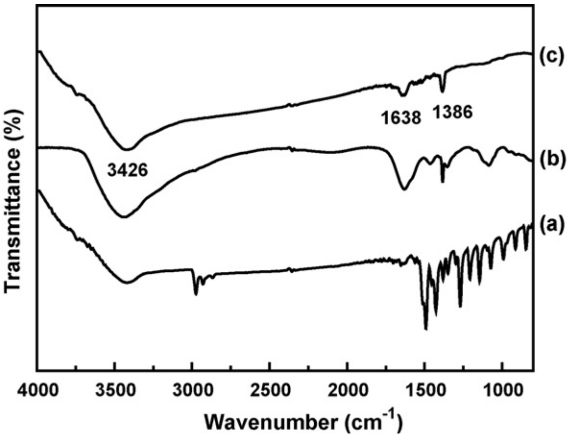

Fig. 2. FTIR spectra of (a) Mn-DDTC, (b) 80 vol.% hydrazine hydrate aqueous solution, and (c) α-MnS powders prepared at 100 °C.

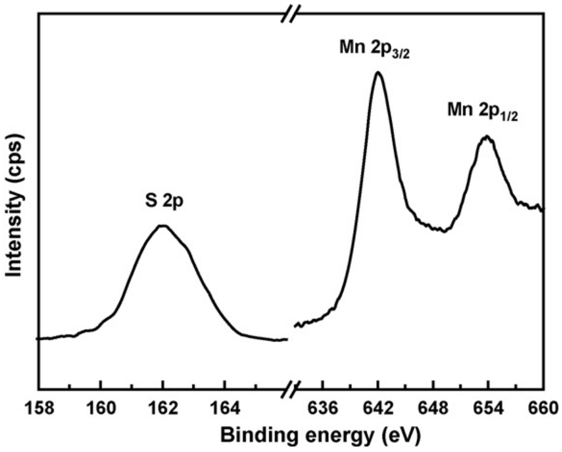

Fig. 3. XPS spectrum of the α-MnS powders prepared at 100 °C.

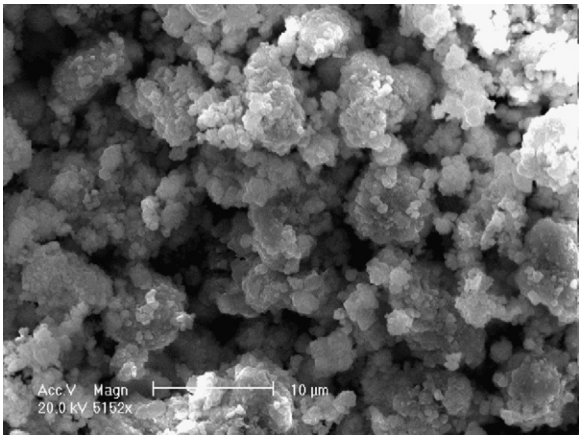

Fig. 4. SEM image of the α-MnS powders prepared at 100 °C.

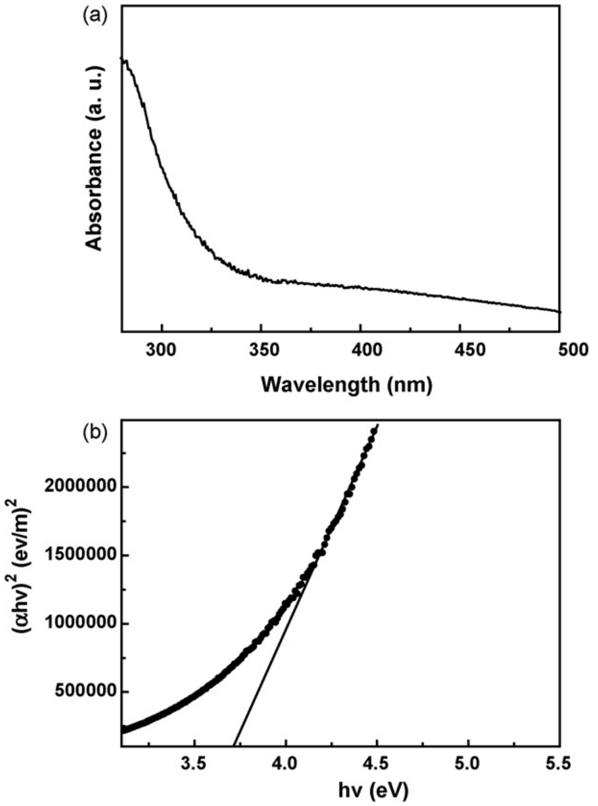

Fig. 5. (a) UV–vis absorption spectrum of the α-MnS powders prepared at 100 °C and (b) the curve of $(\alpha h\nu)^2$ vs. $h\nu$ for the as-prepared α-MnS powders.

shows the XPS spectrum of the α-MnS powders prepared at 100 °C. The binding energies at about 642.0 and 653.9 eV can be assigned to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively; while the binding energy at around 162.0 eV can be assigned to S $2p_{3/2}$. These data were consistent with the corresponding literature values [3], meaning that Mn^{2+} and S^{2-} exist in the sample. Quantification of the Mn and S core areas in Fig. 3 yielded an atomic ratio of Mn to S as 1.04:1 on the sample surface. Moreover, the EDTA complex titrimetry result revealed that the manganese content in the bulk product was 63.18%, which also agreed with the stoichiometry of Mn in MnS. Thus, the above combined analysis results from XRD, FTIR, XPS and chemical analysis indicated the preparation of pure α-MnS powders by the present single-source molecular precursor solvothermal method.

Fig. 4 shows the SEM image of the α-MnS powders prepared at 100 °C. It can be seen that the product comprised submicron crystallites with the size in the range of about 240–715 nm.

Fig. 5(a) shows the UV–vis absorption spectrum of the α-MnS powders prepared at 100 °C. The optical absorption data were analyzed from Eq. (1) in order to determine the bandgap value of direct bandgap semiconductors [12]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the discrete photon energy, B is a constant relative to the material, and E_g is the absorption bandgap. The value of the absorption coefficient can be calculated by Eq. (2) [21]:

$$\alpha = -\frac{1}{t}\ln\frac{I_t}{I_0} = \frac{1}{t}\,\frac{-\log(I_t/I_0)}{\log e} = \frac{1}{t}\,\frac{A}{\log e} \tag{2}$$

in which t is the thickness of the cuvette, I_t and I_0 are the intensities of transmitted light and incident light, respectively, and A is the absorbance, which can be obtained from the absorption spectra. The curve of $(\alpha h\nu)^2$ vs. $h\nu$ was plotted in Fig. 5(b), and the E_g value of the product can be estimated by extrapolating the straight line portion of the plot of $(\alpha h\nu)^2$ vs. $h\nu$ to $\alpha = 0$. The estimated E_g of our product was 3.7 eV, which fell within the range of the bandgap energies reported for α-MnS powders [1–4].

4. Conclusions

Pure α-MnS powders were synthesized via solvothermal decomposition of Mn-DDTC in 80 vol.% hydrazine hydrate aqueous solution at 90–120 °C, and characterized by XRD, FTIR, XPS, chemical analysis, SEM and UV–vis absorption spectra. The control experiments with multiple-source precursors revealed that Mn-DDTC, the single-source molecular precursor with pre-established Mn–S chemical bonds, played a key role in preparing pure α-MnS under the current solvothermal conditions.

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