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A redox-assisted molecular assembly of molybdenum oxide amine composite nanobelts

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ABSTRACT

In this paper, the nanobelts of molybdenum oxide amine composite were successfully synthesized via a redox-assisted molecular assembly route under the hydrothermal conditions. The synthesized nanobelts were characterized by XRD, SEM, TEM, TG and FT-IR measurements. The thickness of nanobelts is found to be ca. 20–30 nm and their lengths are up to several tens of micrometers. Based on a series of the experimental results, a possible model, redox-intercalation-exfoliation, was suggested for the formation of nanobelts of molybdenum oxide amine composite.

1. Introduction

Recently, the intercalated organic–inorganic hybrid nanomaterials have attracted great attention because of their unique microstructure and potential applications in catalysts, batteries, chemical sensors and field-effect transistors [1–4]. A large number of organic surfactants can be introduced into interspaces of the layered inorganic materials by an intercalation route, and the intercalated organic–inorganic hybrid materials were formed. These materials could be exfoliated to form nanosheets, nanowires, nanobelts and nanotubes under the hydrothermal conditions. For instance, amines have been successfully intercalated into interspaces of the layered inorganic materials, and one-dimensional (1D) organic–inorganic nanocomposites were obtained [5,6]. As is well known, amines are splendid guest molecules and can be easily intercalated into the interspaces of the layers of inorganic materials, resulting in some cations or water located in the interspaces being replaced.

Molybdenum oxides and their derivatives are particularly interesting due to their physical and chemical properties as well as potential applications in display devices, smart windows, and storage batteries [7]. So far, the reports on the intercalation between molybdenum oxides and surfactants have been described. Tagaya et al. [8] investigated the intercalation between amines and MoO_3. Using alkylamines. Jing et al. [9] obtained layered MoO_3-alkylamine composite. Under the hydrothermal conditions, hexadecylamine was successfully intercalated into MoO_3 by Krumeich and coworkers [10]. Using layered yellow molybdic acid and amines as starting materials, nanorods-, disks-, and scrolls-like MoO_3 were formed [11]. More recently, a new synthetic route, elicitation by the redox-assisted assembly, was developed to synthesis of 1D transition metal compositions [12,13]. Herein, we report the synthesis of MoOx–amine composite nanobelts using a redox-assisted assembly route. Furthermore, the effects of reaction conditions on structures and morphologies of products were investigated. Based on the experimental results, a possible model for the formation of MoOx–amine composite nanobelts is proposed.

2. Experimental

The synthesis involved a redox reaction between $MoCl_3$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ in the presence of surfactants, including octylamine (OA), dodecylamine (DDA) and hexadecylamine (HDA). The typical procedure is as follows: $MoCl_3$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were dissolved into distilled water with vigorous stirring. After 24 h, the alkylamine was introduced into the mixed solution and stirred for 1 h; the mixture was transferred into a Teflon-lined autoclave, kept at 170 °C for 7 days. The mass of $MoCl_3$ was all kept at 0.08 g and the molar ratio of $MoCl_3$, 1/7 $(NH_4)_6Mo_7O_{24}$ and amine was kept at 1:1:4. The obtained precipitate was separated by centrifugation, and washed with distilled water and ethanol for several times. Finally, the obtained MoOx–amine composite specimens were dried at ambient temperature for 36 h.

The X-ray diffraction (XRD) patterns of all products were recorded on a PANalytical X'Pert spectrometer using the Co Kα radiation (λ = 1.788 Å), and the data would be changed to Cu Kα data. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were taken on a Philip-XL30 instrument and a FEI F20 S-TIN (200 kV) instrument, respectively. Thermo gravimetric (TG) analysis was carried out on a Perkin Elmer thermo gravimetric analyzer with the heating rate of

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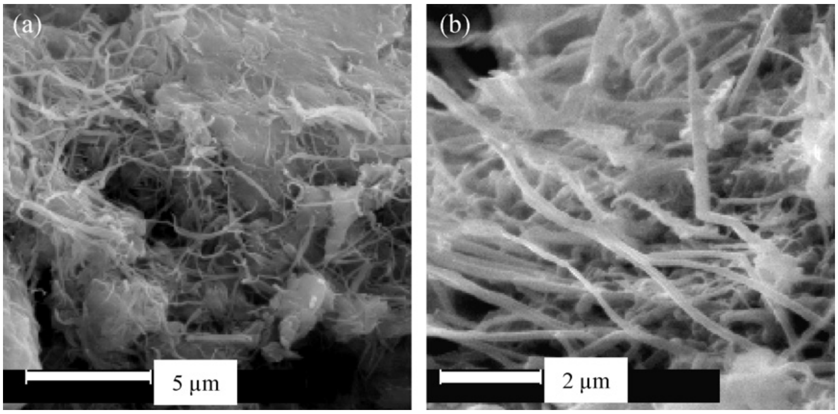

Fig. 1. SEM images of the synthesized MoOx–amine composite nanobelts. (a) Low magnitude image, (b) high magnitude image.

10 °C min^{-1} under N_2 atmosphere at a flow rate of 100 ml min^{-1}. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a PE SPECTRUM2000 using the KBr pellet technique.

3. Results and discussion

Fig. 1 depicts the SEM images of the product synthesized at 170 °C for 7 days using DDA as a surfactant. A large number of nanobelts were formed in the product, and their lengths were up to several tens of micrometers. These nanobelts lie close to each other to form a bundle morphology.

The morphologies of the products can be further confirmed from TEM measurements. As depicted in Fig. 2a, it clearly shows that the products are composed of nanobelts. High magnification image in Fig. 2b shows that the synthesized nanobelts have a crooked morphology, indicating that the products are layered structure. This phenomenon can also be observed in graphite carbon and $NH_4Nb_3O_8$ nanobelts [14]. On the other hand, this also indicates that the nanobelts were obtained from the exfoliation of layered structures. It can be found that the thickness of nanobelts is ca. 20–30 nm, as shown in Fig. 2c. High magnification TEM image of a single nanobelt is depicted in Fig. 2d. It clearly shows that the synthesized nanobelts are lamellar structure, and the nanobelts appear as alternating fringes of dark and bright contrast. The dark fringes represent the molybdenum oxide layers, while the bright fringes represent organic surfactants that were intercalated into the interspaces of molybdenum oxide layers. The distance of layers is found to be ca. 2.6 nm.

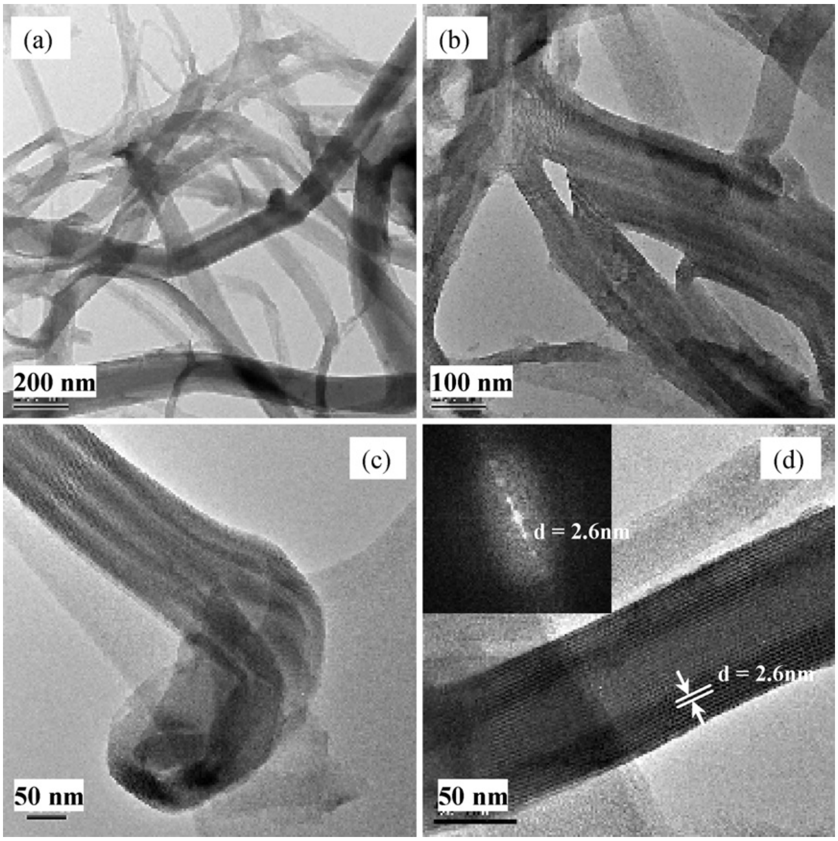

Fig. 2. Representative TEM and HRTEM images of the synthesized MoOx–amine composite nanobelts: (a, b) low-magnification, and (c, d) high magnification (inset, Fourier transforms graph for a single nanobelt).

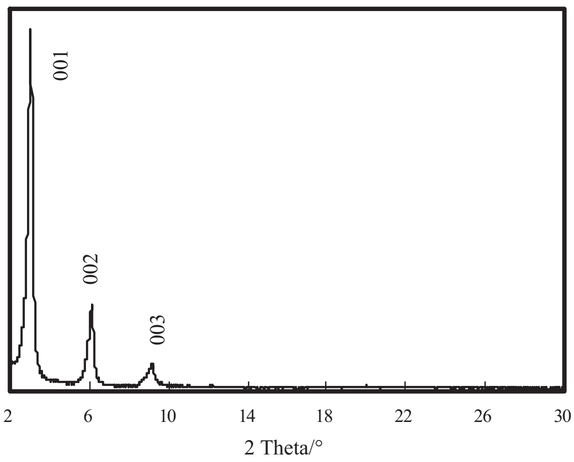

Fig. 3. The XRD pattern of the synthesized MoOx–amine composite nanobelts synthesized at 170 °C for 7 days.

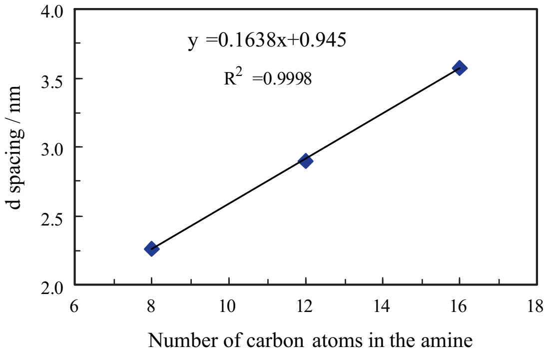

Fig. 4. Experimental plot of interspaces versus the number of carbon atoms in the n-alkyl chain of the amines.

The XRD pattern of the product synthesized at 170 °C for 7 days is shown in Fig. 3. It clearly shows the typical characteristic of a layered compound and *0 0 l* series of reflections with high intensity corresponding to a well-ordered layer structure. This is confirmed by the high magnification TEM image, as depicted in Fig. 2d. On the other hand, the *0 0 l* series also provides the distance of the layers. The peak with the highest intensity, corresponding to the *d* value, reflects the distance between the layers in the product. These results indicate that the intercalated surfactant molecules are located in the interspaces of layers.

The influences of different kinds of amines were also investigated. In the present work, the surfactants of OA, DDA and HAD were used in the hydrothermal reactions, and the results are shown in Fig. 4. It can be found that the *d*-spacing increases with increasing number of carbon atoms in the amines, indicating that the distance of layers can be adjusted by the intercalated amines with different alkyl chain.

Fig. 5 is a TG curve of the product synthesized at 170 °C for 7 days using DDA as a surfactant. It exhibits a weight loss of ca. 8.0% below 200 °C, which is related to dehydration of physical adsorption H_2O. In the range of 200–550 °C, a weight loss of ca. 57.0% was observed, which is believed to correspond to the decomposition of intercalated amine in the interspaces of layers.

Fig. 6 depicts the FT-IR spectra of the product and commercial MoO_3 powder. It can be seen that the commercial MoO_3 powder only exhibits three bands at ca. 563, 863 and 997 cm^{-1}, respectively. The MoOx–amine nanobelts show bands between 490 and 952 cm^{-1}, which can be assigned to the lattice vibration mode of MoO_3 [15,16]. The bands at 2840 and 2970 cm^{-1} can respectively be attributed to the anti-symmetric and symmetric CH_2 stretching vibrations in the amine intercalated product [9], while the band at ca. 1610 cm^{-1} is attributed to –NH bending vibration [11]. These results indicate that the synthesized nanobelts are composed of MoOx and amine, namely, molybdenum oxide amine composite nanobelts.

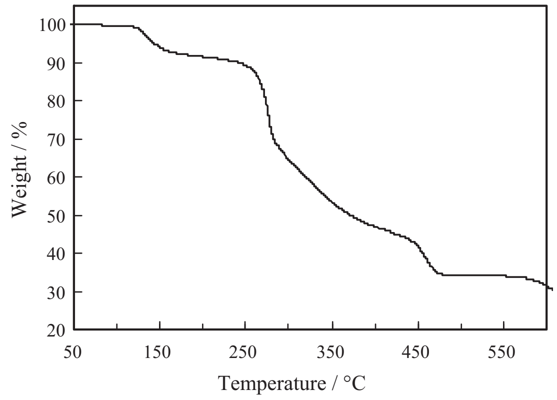

Fig. 5. TG curve of the synthesized MoOx–DDA composite nanobelts.

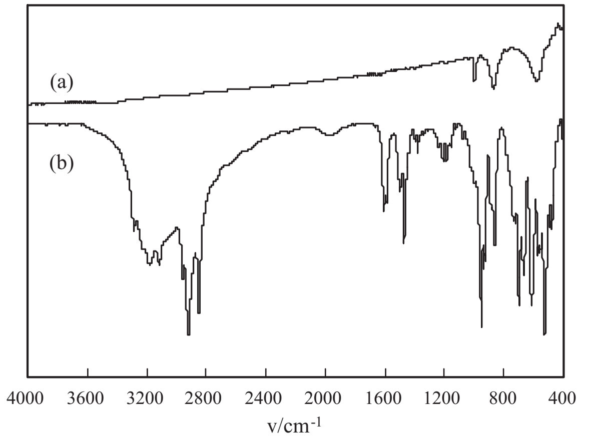

Fig. 6. FTIR spectra of the commercial MoO_3 (a) and the synthesized MoOx–DDA composite nanobelts (b).

In the present work, $MoCl_3$ and $(NH_4)_6Mo_7O_{24}·4H_2O$ were used as precursors and alkylamine was used a structure-directing template. Under the hydrothermal conditions, the nanobelts composed of MoOx and amine have been synthesized. Based on the experimental results of XRD, SEM, TEM, TG, and FT-IR, a possible process of the formation of molybdenum oxide amine composite nanobelts is suggested as the following: (i) the redox reaction between the precursor $MoCl_3$ and $(NH_4)_6Mo_7O_{24}·4H_2O$ was executed and the layered structure MoOx was formed; (ii) surfactant alkylamine was directly intercalated into MoOx layers, forming van der Waals intercalation between the organic molecules and the inorganic oxides during the aging process; (iii) the layered structural MoOx–amine tended to exfoliated and the nanosheets or nanobelts were formed under the hydrothermal conditions. In a word, the formation process might be described as a redox-intercalation-exfoilation model.

4. Conclusion

Nanobelts of molybdenum oxide amine composites have been successfully synthesized using a redox-assisted molecular assembly route under the hydrothermal conditions. The synthesized nanobelts are layered structure and the distance of layer is ca. 2.6 nm. The thickness of nanobelts is found to be ca. 20–30 nm and their lengths are up to several tens of micrometers. Based on a series of the experimental results, a possible model, redox-intercalation-exfoliation, was suggested for the formation of nanobelts of molybdenum oxide amine composite. We believe that the synthetic route of nanobelts has the potential to prepare other 1D nanostructural materials.

Acknowledgments

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