Organic assisted hydrothermal route to MoO₂/HDA composite microspheres and their characterization

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Abstract

Synthesis of molybdenum oxide/hexadecylamine (MoO₂/HDA) microspheres in aqueous solution has been investigated systematically by varying the concentration of the precursor, surfactant and reducing agent, as well as the reaction temperature and duration. To understand this, the nature of the solid has been probed by PXRD, FTIR, UV–visible and SEM equipped with an EDS. The PXRD patterns of as-prepared products reveal that MoO₂ microspheres are of monoclinic structure. The bands at 985 and 952 cm^{−1} reflect the $\nu(\text{Mo}-\text{O})$ stretch vibration of terminal $-\text{Mo}^{\text{VI}}=\text{O}_t$ and $-\text{Mo}^{\text{IV}}=\text{O}_t$ groups. UV–vis spectrum of calcined sample exhibits maximum absorption at 358 nm. SEM images reveal that the average diameters of the MoO₂ microspheres are in the range 1–3 μm . The reduction of the precursor yields a metastable poorly crystalline oxide of lower valence molybdenum, which is crystallized to $\alpha\text{-MoO}_3$ on calcination to 400 °C.

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1. Introduction

Nanoscale/nanostructural materials with different morphologies have simulated great interest due to their importance in basic scientific research and potential technology applications [1,2]. The ability to control and manipulate the physical and chemical properties of materials, as we desire is one of the challenging issues in chemistry and materials science. Bulk inorganic crystals possess their own characteristics and innate properties, such as color and melting point, however at the nanometer scale, these properties can be tailored as desired [3]. Current technology relies heavily on composite materials, but in most cases, the sizes of the individual components have been micrometers or larger [4]. Transition metal oxides comprise a large family of materials exhibiting a variety of interesting properties that are attractive for applications in lithium ion batteries, catalysis, electrochemical materials, sensors, etc [5]. Nonstoichiometric oxides are of particular interest because of their unique electronic characteristics. For, e.g. molybdenum oxides (MoO_{3-x}) can be a semiconductor [direct band gap between 2.9 and 3.15 eV], conductor or superconductor depending on its oxidation states [6]. Molybdenum is an important refractory material; it has very high melting point, high electrical conductivity and toughness [7]. Its oxides mainly include MoO₂ and MoO₃, which

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have many advanced applications as catalysts, sensors, photochromic and electrochromic materials and recording materials [8]. MoO_2 has a distorted rutile structure, whereas $\alpha\text{-MoO}_3$ forms a unique layer structure composed of distorted $[\text{MoO}_6]$ octahedra [9]. Molybdenum oxide is important as a catalytic material particularly in methanol oxidation and NO reduction [10]. Molybdenum oxides with average valence of less than six are excellent catalysts for the partial oxidation of alkenes [11]. Their catalytic properties can be controlled by varying the surface structures of oxides or change the valence state of molybdenum atoms [12]. MoO_2 is a good precursor for the synthesis of many other important materials such as Mo, MoO_3 and MoO_{3-x} [13].

Inorganic syntheses using organic surfactants are successfully applied for the preparation of various nano/microstructural materials [14,15]. Recently, Rao and co-workers developed a method using carbon nanotubes as template for growth of MoO_3 nanorods. By further reduction in an H_2 atmosphere at 500°C for 48 h, MoO_3 nanorods can change to MoO_2 nanorods [16]. Well-aligned MoO_2 nanowires were prepared on silicon substrates without using any catalyst [13]. Li et al. prepared MoO_2 nanowires reductively from an alkaline MoO_4^{2-} solution on to highly oriented pyrolytic graphite surfaces [17]. Porous molybdenum dioxide nanofibers and nanospheres were prepared by redox method using MoO_3 with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in aqueous terephthalic acid medium [12]. Manthiram and co-workers have investigated the reduction of Na_2MoO_4 with NaBH_4 and similarly, the reduction of K_2MoO_4 with KBH_4 to synthesize MoO_2 [18]. The instability of the metastable dioxides with low oxidation valence states makes their synthesis difficult in solutions [19,20]. Thus further studies are necessary and challenging for synthesis of lower valent molybdenum oxides through the solution phase route. Among the existing technologies currently employed for the production of nanostructured powders, the hydrothermal technology presents many benefits, including a high degree of chemical homogeneity achieved on the molecular scale, use of mild temperatures and pressures, production of nanocrystalline powders in a single step, and elimination of high-temperature calcinations. A wide range of crystalline, single and multicomponent oxide materials can be produced by hydrothermal technology and it is also possible to synthesize transition metal compounds with unusual oxidation states, low-temperature phases, and metastable compounds [21]. Hydrothermal technology was used to control the phase behavior and morphology of nano/nanostructured materials.

Herein, we report on a simple method that has successfully realized the shape-controlled growth of MoO_2/HDA composite. Large-scale MoO_2/HDA microspheres have been yielded with the use of surfactant. In order to understand the habits of MoO_2/HDA microspheres; the effects of temperature, duration, reducing agent, surfactant, and concentration of the starting solution on their morphology have been investigated.

2. Experimental

2.1. Preparation

The synthesis of microspheres MoO_2/HDA composite was performed by hydrothermal method. Solution of HDA (0.248 g/25 mL) in ethanol was added to an aqueous solution of ammonium molybdate (1.235 g/25 mL) taken in a beaker under vigorous stirring. The solution mixture was placed into a PTFE-lined stainless steel autoclave with a capacity of 30 mL. The autoclave was then sealed, heated at 180°C for 24 h and subsequently cooled to room temperature. The black powdery MoO_2/HDA composite powder was retrieved from the solution by filtration, washed with distilled water followed by ethanol to remove ions possibly in the end product and finally dried in air.

2.2. Characterization

Powder X-ray diffraction (PXRD) data were recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized $\text{Cu K}\alpha$ radiation [$\lambda = 1.541 \text{ \AA}$]. The Fourier transform infrared spectra (FTIR) of the samples were collected using Nicolet FTIR spectrometer. The absorption spectra of the samples were measured on a UV-3101 Shimadzu visible spectrometer. Scanning electron micrograph (SEM) images were taken with JEOL [JSM – 840 A] scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

The PXRD pattern (Fig. 1a) of as prepared MoO_2/HDA composite reveals that the products are poorly crystalline monoclinic MoO_2 (JCPDS: 78-1072, space group $P2_1/c$) with lattice constants: $a = 5.61 \text{ \AA}$, $b = 4.86 \text{ \AA}$, $c = 5.54 \text{ \AA}$ and

Fig. 1. Powder X-ray diffraction patterns of (a) MoO_2/HDA composite prepared at 180°C for 24 h using 25 mL ethyl alcohol, (b) MoO_3/HDA composite prepared at 180°C for 24 h using 37.5 mL ethyl alcohol, (c) Calcined at 300°C for 3 h and (d) Calcined at 500°C for 3 h.

$\beta = 119.37^\circ$ [22]. Upon calcinations to $300^\circ\text{C}/3\text{ h}$ an obvious phase transformation from monoclinic MoO_2 to orthorhombic $\alpha\text{-MoO}_3$ is taken place and the resultant product is a mixture of these phases (Fig. 1c). However, on increase in calcination temperature to 500°C , a single phase orthorhombic $\alpha\text{-MoO}_3$ is formed as observed in Fig. 1d. All the diffraction peaks could be readily indexed to the orthorhombic phase of $\alpha\text{-MoO}_3$ (space group $Pbnm$) with the lattice parameters $a = 3.96\text{ \AA}$, $b = 13.86\text{ \AA}$, $c = 3.7\text{ \AA}$ (JCPDS: 5-0508). MoO_2/HDA composite is generated via reductions following the shape of the templates or assembling into spherical particles. The reaction temperature is not high enough to allow the crystallization of the Mo-O species, resulting in the formation of metastable poorly crystalline MoO_2 , which could convert into crystalline $\alpha\text{-MoO}_3$ through calcinations.

Chemical analysis using EDS indicates the presence of only Mo and O, no other elements existed as observed in Fig. 2. However, it is difficult to determine the Mo/O ratio of the microspheres quantitatively due to the uncertainty of intensity of the EDS detection for lighter elements. Considering the above EDS findings in conjunction with the XRD results shown earlier, we can confirm that the microspheres are MoO_2 .

The IR spectra (Fig. 3) of as-prepared MoO_2/HDA composite and its calcined forms show several bands due to $\nu(\text{Mo-O})$ and $\delta(\text{Mo-O})$ vibrations. The band at 985 cm^{-1} (Fig. 3 b and c) reflects the $\nu(\text{Mo-O})$ stretch vibration of terminal $-\text{Mo}^{\text{VI}}=\text{O}_t$ groups. The band at 869 cm^{-1} corresponds to $\nu_s(\text{Mo-O})$ vibrations of μ_3 and μ_2 bonded oxygen

Fig. 2. Energy dispersive X-ray spectrum of MoO_2/HDA composite microspheres.

Fig. 3. FTIR spectra of (a) MoO_2/HDA composite prepared at 180°C for 24 h, (b) Calcined at 300°C for 3 h and (c) Calcined at 500°C for 3 h.

Mo-O-Mo and $\text{Mo}_2\text{-O-Mo}$ fragments within the (a,b) and (b,c) planes of the $\alpha\text{-MoO}_3$ lattice. The bands below 700 cm^{-1} are due to $\nu_{\text{as}}(\text{Mo-O})$ and $\delta(\text{Mo-O})$ vibrations. We assign the band at 952 cm^{-1} to the $\nu(\text{Mo-O})$ vibrations of terminal $-\text{Mo}^{\text{IV}}=\text{O}_t$ groups. The frequency of the $\nu(\text{Mo}^{\text{IV}}=\text{O}_t)$ vibration is shifted 33 cm^{-1} to lower wavenumbers compared to its value in crystalline MoO_3 , due to the presence of reduced Mo centers. Significant spectral changes within the region due to Mo-O vibrations ($600\text{--}1000\text{ cm}^{-1}$) reveal that the terminal $\text{Mo}=\text{O}_t$ groups at 952 cm^{-1} are the first to disappear under calcination [23]. Orthorhombic $\alpha\text{-MoO}_3$ may be interpreted as a layered structure built up by two layers of chains of MoO_4 tetrahedral running along the c -axis. The structure may alternatively be described as being built by heavily distorted octahedra. However, both descriptions—the four fold or six fold Mo coordination are each idealized. The peaks around 2920 , 2840 and 1400 cm^{-1} could be assigned to $\nu_{\text{as}}(\text{C-H})$, $\nu_{\text{s}}(\text{C-H})$, $\delta(\text{CH}_2)$, vibration modes of $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_2$ (Fig. 3a) [24] in MoO_2/HDA nanocomposite. The peaks at 1610 and 3500 cm^{-1} respectively are assigned to the bending modes of coordinated water molecules and OH stretching of hydroxyl group.

UV-vis spectroscopy is extremely sensitive to oxygen vacancies in MoO_{3-x} ($0 < x < 1$) and has been used to determine the concentration of oxygen in MoO_{3-x} . The optical properties of molybdenum oxide strongly change as a function of oxygen concentration. UV-visible spectrum (Fig. 4b) of $\alpha\text{-MoO}_3$ obtained by calcining MoO_2/HDA composite at 500°C for 3 h exhibits a strong absorption around 362 nm corresponding to a band gap of 3.42 eV . It is known that bulk MoO_3 (3.15 eV) has absorption at 393 nm in the UV-vis spectrum and is obviously larger than the calcined MoO_3 (362 nm). Compared to the bulk MoO_3 , the observed blue shift in $\alpha\text{-MoO}_3$ microspheres can be directly correlated to an increasing oxygen/metal ratio of the molybdenum oxide besides size effect [25].

Fig. 4. UV-vis spectra of (a) $\alpha\text{-MoO}_3$ obtained by calcining at 500°C for 3 h and (b) MoO_2/HDA composite prepared at 180°C for 24 h.

Fig. 5. SEM images of the MoO_3/HDA composite prepared at (a) 150 °C for 24 h, (b) 180 °C for 24 h and (c) 200 °C for 24 h.

Fig. 5a–c shows the SEM images of the MoO_3/HDA composite microspheres prepared at 150–200 °C for 24 h. From the images, it is clear that large-scale spherical particles with an average diameter of about 1–2 μm (Fig. 5b) have been obtained only at high temperature. The spheres have smooth surfaces as indicated by a high magnification SEM image. Spheres are the most basic and symmetric motif among shaped nano/microcrystals. The SEM image of the calcined (300 °C for 3 h) sample (Fig. 6a) of MoO_3/HDA composite clearly reveals that these rods are aligned perpendicularly to the spherical surfaces. Further calcinations (500 °C for 3 h) lead to the formation of agglomerated spheres and flakes like structures (Fig. 6b). The presence of small amount of an additives such as cetyl trimethyl ammonium bromide (CTAB)/sodium lauryl sulphate (SLS)/citric acid/ethylene diamine does not affect the structure

Fig. 6. SEM images of the sample (prepared at 180 °C for 24 h) calcined at (a) 300 °C for 3 h and (b) 500 °C for 3 h.

Fig. 7. SEM images of the MoO_2/HDA composite prepared at 180°C for 24 h with different concentration of ammonium molybdate with hexadecyl amine (a) 1:0.5 and (b) 1:2.

of microspheres. The influence of the concentration of HDA on the morphology of MoO_2/HDA composite microspheres was also examined. It was possible to prepare MoO_2/HDA composite microspheres over a wider concentration range of HDA (Fig. 7a and b). With the increase of molar ratio (1:2), the product becomes less agglomerated.

The morphology (Fig. 8a and b) of the products changes significantly by changing hydrothermal duration, i.e. spheres are formed only when treatment time is maintained for 24 h. An attempt is made to know the effect of surfactants other than HDA, i.e. CTAB and SLS on the morphology (Fig. 9a and b) of the products made at 180°C for

Fig. 8. SEM images of the MoO_2/HDA composite prepared at 180°C for (a) 12 h and (b) 48 h.

Fig. 9. SEM images of the MoO_2/HDA composite prepared at 180°C for 24 h using (a) Cetyl trimethyl ammonium bromide and (b) Sodium lauryl sulphate as surfactant.

Fig. 10. SEM image of the MoO_3/HDA composite prepared at 180°C for 24 h by changing ratio of precursor concentrations to 0.1.

24 h. It reveals that the presence of an appropriate amount of suitable surfactant (HDA) is crucial for the formation of self assembled pattern of microspheres. A decrease of the precursor concentration resulted in a decrease in the average size of MoO_3/HDA composite spheres (Fig. 10). The average diameter of the particles reduces from $1\text{--}3$ to $0.3\text{--}1\ \mu\text{m}$ by changing the precursor to surfactant mol ratio to 0.1. Fig. 11a–c shows SEM images of MoO_3/HDA composite prepared using ethylene glycol, methanol and acetone as solvents. Here, ethyl alcohol acts as a good reducing agent during the formation of MoO_3/HDA composite microspheres. Increase in the volume of ethyl alcohol to 37.5 mL leads to the formation of $\text{MoO}_3/\text{amine}$ crystals at 180°C for 24 h (Fig. 1b).

Fig. 11. SEM images of the MoO_3/HDA composite prepared at 180°C for 24 h using (a) Ethylene glycol, (b) Methanol and (c) Acetone as reducing agents/solvents.

According to the classical Einstein–Stokes equation, $D = kT/6\pi\eta r$, the diffusion coefficient (D) of a solute of radius (r) in a solvent is in reciprocal to the viscosity of the solution (η) [26]. In our experiment as the water to ethanol ratio increases from 1:1 to 1:3 by keeping total volume (50 mL) as constant, viscosity of the solution increases significantly and slows down the mass transfer reaction [27]. Under this condition, molybdenum retains its original oxidation state.

4. Conclusion

Micrometer-sized MoO_2/HDA composite spheres have been successfully fabricated by a surfactant-assisted hydrothermal process. The influence of the conditions on the synthesis and morphologies of MoO_2/HDA composite spheres was studied systematically. The reactant molar ratio, hydrothermal reaction time and temperature represent the most important factors for the morphology evolution. The crystallinity of the obtained spheres could be improved by annealing them in air at high temperatures. On air annealing, the monoclinic MoO_2/HDA composite transforms into crystalline orthorhombic $\alpha\text{-MoO}_3$ phase. While, the MoO_2/HDA composite spheres obtained at $180^\circ\text{C}/24\text{ h}$ are poorly crystalline and a post-growth thermal treatment (in air) above 300°C is necessary for crystallization.

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References

- [1] X.Y. Chen, Z.J. Zhang, X.X. Li, C.W. Shi, X.L. Li, Chem. Phys. Lett. 418 (2006) 105.
- [2] G.T. Chandrappa, Nathalie Steunou, Jacques Livage, Nature 416 (2002) 702.
- [3] Y.W. Jun, J.S. Choi, J.W. Cheon, Angew. Chem. Int. Ed. 45 (2006) 3414.
- [4] W.H. Suh, A.R. Jang, Y.H. Suh, K.S. Suslick, Adv. Mater. 18 (2006) 1832.
- [5] Y. Zhao, J.G. Liu, Y. Zhou, Z.J. Zhang, Y.H. Xu, H. Naramoto, S. Yamamoto, J. Phys. Condens. Mat. 15 (2003) L547.
- [6] K.Q. Hong, M.H. Xie, H.S. Wu, Nanotechnology 17 (2006) 4830.
- [7] I.V. Malikov, G.M. Mikhailov, J. Appl. Phys. 82 (1997) 5555.
- [8] S.L. Zhang, F.M. d'Heurle, Appl. Phys. Lett. 76 (2000) 1831.
- [9] E.M. McCarron Jr, J. Chem. Soc. Chem. Commun. (1986) 336.
- [10] A.K. Santra, B.K. Min, D.W. Goodman, Surf. Sci. 513 (2002) 441.
- [11] T. Ressler, J. Wienold, R.E. Jentoft, O. Timpe, T. Neisius, Solid State Commun. 119 (2001) 169.
- [12] S.T. Wang, Y.G. Zhang, W.Z. Wang, G.L. Li, X.C. Ma, X.B. Li, Z.D. Zhang, Y.T. Qian, J. Crystal Growth 290 (2006) 96.
- [13] J. Zhou, N.S. Xu, S.Z. Deng, Jun Chen, J.C. She, Chem. Phys. Lett. 382 (2003) 443.
- [14] F. Krumeich, H.J. Muhr, M. Neiderberger, F. Bieri, B. Schndler, R. Nesper, J. Am. Chem. Soc. 121 (1999) 8324.
- [15] O. Durupthy, M. Jaber, N. Steunou, J. Maquet, G.T. Chandrappa, J. Livage, Chem. Mater. 17 (2005) 6395.
- [16] B.C. Satishkumar, A. Govindaraj, M. Nath, C.N.R. Rao, J. Mater. Chem. 10 (2000) 2115.
- [17] Q. Li, J.T. Newberg, E.C. Walter, J.C. Hemminger, R.M. Penner, Nano Lett. 4 (2004) 277.
- [18] C.F. Tsang, A. Manthiram, J. Mater. Chem. 7 (1997) 1003.
- [19] Y. Feldman, G.L. Frey, M. Homyonfer, V. Lyakhovitskaya, L. Margulis, H. Cohen, G. Hodes, J.L. Hutchison, R. Tenne, J. Am. Chem. Soc. 118 (1996) 5362.
- [20] C. Tsang, A. Dananjay, J. Kim, A. Manthiram, Inorg. Chem. 35 (1996) 504.
- [21] A. Dias, V.S.T. Ciminelli, Chem. Mater. 15 (2003) 1344.
- [22] G. Wang, Y. Ji, L. Zhang, Y. Zhu, P.I. Gouma, M. Dudley, Chem. Mater. 19 (2007) 979.
- [23] Th. Weber, J.C. Muijsers, J.H.M.C. van Wolput, C.P.J. Verhagen, J.W. Niemantsverdriet, J. Phys. Chem. 100 (1996) 14144.
- [24] G.T. Chandrappa, J. Livage, Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 36 (2006) 23.
- [25] M. Dieterle, G. Weinberg, G. Mestl, Phys. Chem. Chem. Phys. 4 (2002) 812.
- [26] P. Berge, M. Dubois, Phys. Rev. Lett. 27 (1971) 1125.
- [27] C. Sun, H. Li, H. Zhang, Z. Wang, L. Chen, Nanotechnology 16 (2005) 1454.