Effects of surfactants on morphology in synthesis of α-Mn$_2$O$_3$ nanostructures

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ABSTRACT

Cubic and chain-like structure of α-Mn$_2$O$_3$ with a high surface area was prepared by air oxidation of manganese chloride through sol process by adding hexamine and mercaptosuccinic acid as wetting agent, respectively. The as-synthesized products were characterized with X-ray powder diffraction (XRD), Energy Dispersive X-ray spectroscopy (EDX), transmission electron microscope (TEM), and selected area electron diffraction (SAED). The possible formation mechanism of α-Mn$_2$O$_3$ cubic and chain-like nanostructures has been proposed and discussed.

1. Introduction

Nanostructural materials have been actively studied by many researchers due to the scientific interests and potential applications [1,2] as well. Among the transition metals, manganese exhibits many oxidation state and form different oxides (MnO, Mn$_2$O$_3$, Mn$_3$O$_4$, Mn$_5$O$_8$, and MnO$_2$). Manganese oxides are non-toxic, abundant, cost effective, and having a wide range of technical applications, viz. catalysis for completely oxidizing various volatile organic substances [3–5], molecular adsorption [6], ion exchange, biosensor, high density magnetic storage media [7], electrochemical supercapacitor [8], an oxygen storage component (OSC) for a three-way catalyst [9], and promising cathode material for lithium batteries [10]. Manganese sesquioxide are used for preparing soft magnetic materials such as manganese zinc ferrite [11].

Until now, numerous processes have been developed for the synthesis of inorganic nanostructures, in that, chemical routes have proved to be more effective and versatile [12]. A wide variety of morphological forms of manganese sesquioxide (Mn$_2$O$_3$), ranging from one- to three-dimensional structures such as rods, wires, cubes, octahedra, and hollow spheres have been synthesized through various methods [13–17]. However, the morphology controlled synthesis of manganese sesquioxide nanostructures, particularly those with novel and attractive morphologies is difficult and it remains a great challenge. Manganese sesquioxide nanoparticles with various morphologies and different crystallographic structures are obtained by various researchers. Recently α-Mn$_2$O$_3$ nanoparticle was prepared by Thota et al. [18] through sol–gel method using manganese acetate tetrahydrate and oxalic acid as a precursor and ethanol

as a solvent. Liu et al. [19] have obtained different manganese sesquioxide nanostructure using heat treatment of manganese alkoxide precursor, which was synthesized from the reaction of manganese acetate with ethylene glycol. Cao et al. [20] have reported various manganese sesquioxide hollow nanostructures prepared by oxidation of manganese carbonate using potassium permanganate as oxidizer. Tsang et al. [21] investigated the reduction of potassium permanganate with potassium borohydride in aqueous solutions to obtain binary and ternary manganese oxides. Ahmad et al. [22] have reported the synthesis of various manganese oxides via thermal decomposition of manganese oxalate obtained using manganese acetate as precursor and cetyl trimethyl ammonium bromide (CTAB) as surfactant. Chen et al. [13] have reported a hydrothermal cleavage-decomposition mechanism which was used to synthesize a single-crystal α-Mn$_2$O$_3$ nanorod at 160 °C for 16 h using potassium permanganate, as manganese source and cetyl trimethyl ammonium bromide as reducing reagent. Herein, α-Mn$_2$O$_3$ bixbyite cubic and chain-like nanostructures have been successfully synthesized through sol process by air oxidation of manganese chloride as precursor, hexamine and mercaptosuccinic acid as wetting agent, respectively. The influences of different reaction conditions on the morphology and crystalline structure of final products and its formation mechanism have been proposed and discussed.

2. Experimental

2.1. Materials

All the chemical reagents are analytical grade and they are used as received without further purification. Millipore water is used throughout the experiment. Manganese (II) chloride (MnCl$_2$·4H$_2$O),

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hexamine and sodium hydroxide (NaOH) were purchased from Sisco Research Laboratories (SRL), Mumbai. Mercaptosuccinic acid was purchased from Alfa Ascer India, and ethanol (absolute 99.9%) was purchased from Hayman Limited, England.

2.2. Methods

The well known sol process method was carried out to synthesize manganese sesquioxide nanostructure. An aqueous solution of 30 ml containing 0.05 M manganese (II) chloride ($MnCl_2 \cdot 4 \, H_2O$) and 0.01 M hexamine was stirred at room temperature for 15 min. 30 ml solution containing 0.05 M sodium hydroxide (NaOH) was added drop wise under continuous stirring. The colorless solution turned initially to light brown and finally to dark brown, which indicates the formation of manganese oxide nanostructure. The stir was continued up to 2 h. After the particles were washed with ethanol, the same procedure was repeated with same concentration using mercaptosuccinic acid.

2.3. Measurements

XRD was done in Seifert JSO Debye-Flex 2002 diffractometer with $CuK\alpha$ radiation ($\lambda = 1.54056 \, \text{Å}$), and the operation voltage and current was maintained at 40 kV and 30 mA, respectively. The XRD data were analyzed using JCPDS files. The surface area of the samples are measured by the Brunauer–Emmett–Teller (BET) method nitrogen adsorption and desorption experiments were carried out at 77 K by using Autosorb-1 analyzer. Morphology and particle size of the products were observed with a Philips CM20 model transmission electron microscope (TEM), operated at an acceleration voltage 200 kV, in which the sample was treated by ultrasonic dispersion in acetone for 10 min and then dropped on carbon coated copper grid. The TEM itself possesses energy dispersive X-ray (EDX) spectroscopy and selected area electron diffraction (SAED) accessories.

3. Results and discussion

The phase and purity of the as-synthesized products are determined by powder X-ray diffraction measurements. The XRD pattern of the product synthesized by using hexamine is shown in Fig. 1a, and using mercaptosuccinic acid is shown in Fig. 1b. From Fig. 1a, it can be observed that all of the diffraction peaks in these spectra can be indexed to a pure cubic phase of α-Mn_2O_3 (bixbyite-c, JCPDS Card File no.78-0390). From this observation, it can be seen that the product is a high crystallinity. Similar results have been reported by Yang et al. [23] by employing thermal decomposition of manganese carbonate. Fig. 1b reveals that the product is in the form of α-Mn_2O_3 (JCPDS Card File no. 41-1442). The sharp and intense peaks in the XRD spectra labeled indicate good crystallinity of the pure α-Mn_2O_3 nanostructure. Similar results have been reported by Li et al. [17] by employing various solvents such as ethanol, 1-butanol, 2-butnol, and acetone. In Fig. 1, the growth of (220) and (332) planes are observed in α-Mn_2O_3 obtained by using mercaptosuccinic acid as surface active material. This observation confirms that mercaptosuccinic acid is capable of accelerating the growth of the material. Similar behavior about mercaptosuccinic acid has been reported by Wang et al. [24] in the preparation of CdTe quantum dots. From XRD data, the average crystallite size (D_c) of prepared α-Mn_2O_3 particles was calculated by using the Debey–Scherrer equation [25]:
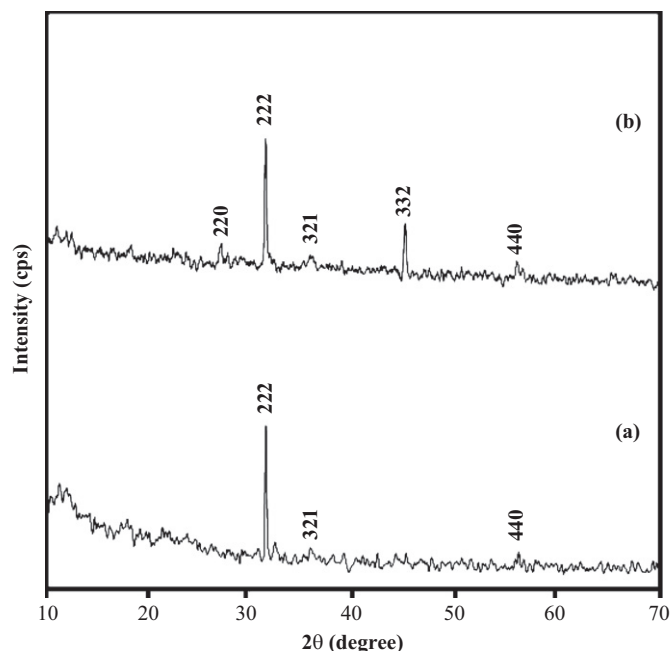
$$D_c = \frac{K\lambda}{\beta \cos\theta}$$

Fig. 1. X-ray diffraction pattern of α-Mn_2O_3 nanostructures prepared by using (a) hexamine and (b) mercaptosuccinic acid.

where β is the breadth of the observed diffraction peak at its half intensity maximum, K is the so-called shape factor, which usually takes a value 0.9 and λ is the wavelength of X-ray source used in XRD. No other phases are detected in the final products. The average particle size using hexamine and mercaptosuccinic acid is 68 and 58 nm, respectively.

The specific surface area of the samples was calculated by the Brunauer–Emmett–Teller (BET) method from nitrogen adsorption. The BET surface area of the products obtained by using hexamine and mercaptosuccinic acid is 122.7 and 138.3 m^2/g, respectively. The α-Mn_2O_3 obtained by using mercaptosuccinic acid having high surface area than the product obtained by using hexamine. This high surface area of the nanostructure may offer application oriented superior properties.

The chemical compositions of the as-prepared products are examined by using EDX in TEM. The EDX analysis of the product obtained by using hexamine reveals that the as-prepared sample contain only Mn and O elements. The as-prepared manganese sesquioxide particles have been found to be of high purity by EDX measurements and the atomic ratio of manganese to oxygen is 37:63. Similar result has been reported by Chandra et al. [26]. The EDX analysis of α-Mn_2O_3 obtained by using mercaptosuccinic acid as a surface active material reveals that the constituents presenting α-Mn_2O_3 nanostructure are Mn and O, with atomic ratio of manganese to oxygen as 33:67.
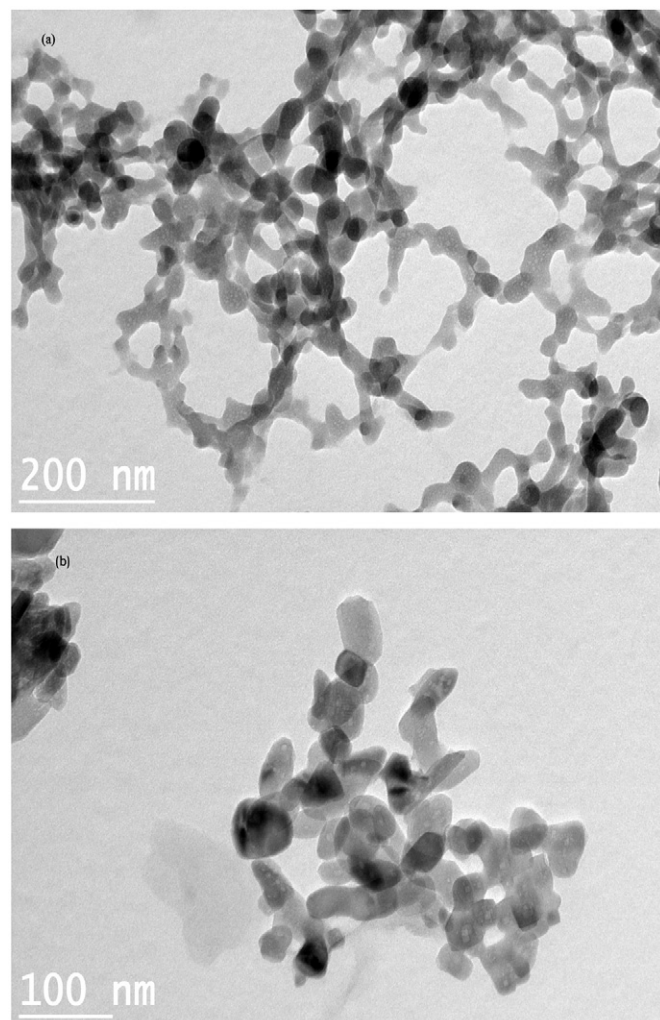
The morphologies and size of the as-prepared samples of α-Mn_2O_3 nanostructures are examined using transmission electron microscope (TEM). Fig. 2 shows the TEM images of α-Mn_2O_3 obtained from oxidation of manganese chloride by using hexamine as a surface active material. From Fig. 2a, it can be observed that α-Mn_2O_3 has uniform cubic structure. The inset in Fig. 2a is the corresponding magnified image of single cube. Similar cubic structure of α-Mn_2O_3 was reported by Music et al. [27] with particle size 20–60 nm, using manganese nitrate as precursor. The TEM image (Fig. 2b) shows that the lattice fringes of the nanocubes, which are structurally uniform, and the interplanar spacing about 0.27 nm, correspond to the distance between (222) plane of α-Mn_2O_3. This observation further confirms the single-crystalline nature of α-Mn_2O_3. Similar result has been reported by
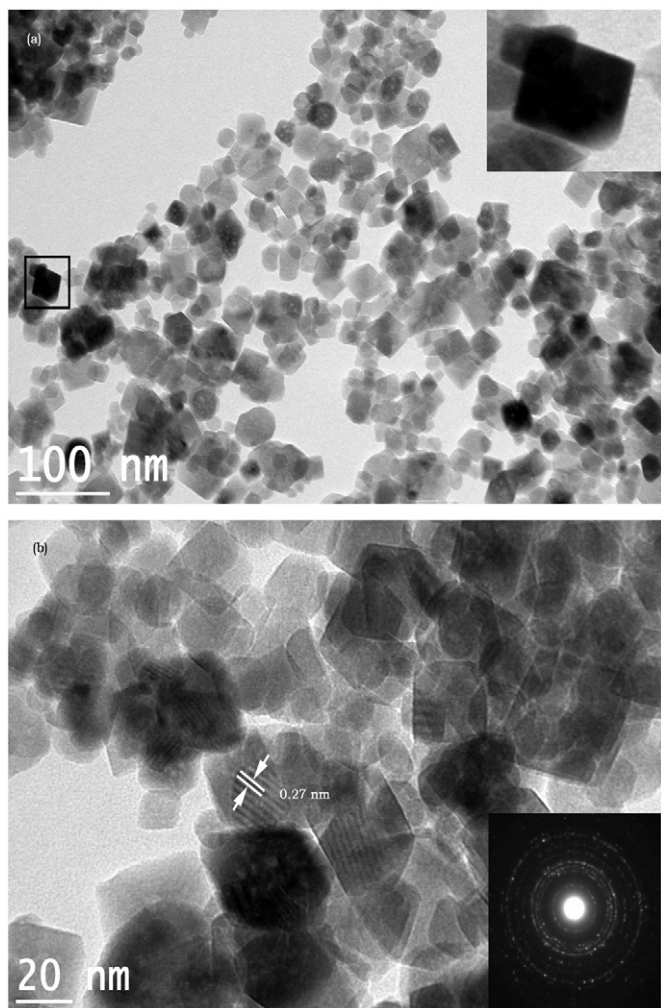
Fig. 2. (a) Typical cubic structure of α-Mn_2O_3. The inset shows the corresponding magnified image of single cube. (b) The lattice fringes of α-Mn_2O_3 nanocubes. The inset shows selected area electron diffraction (SAED) pattern.

Fig. 3. (a) Chain-like structure of α-Mn_2O_3 and (b) chain-like structure composed of primary nanosized particle.

Chen et al. [13]. The inset shows a selected area electron diffraction (SAED) pattern. It is observed that the SAED pattern consists of many spots. All spots are identified as the diffractions from cubic α-Mn_2O_3, which reveals the single-crystalline nature of α-Mn_2O_3 nanostructure. From the TEM analysis, it can be observed that the prepared material have uniform cubic structure of α-Mn_2O_3 with size of 11–68 nm. Fig. 3 shows the TEM image of α-Mn_2O_3 nanostructure synthesized by using mercaptosuccinic acid as a wetting agent. It can be noticed from Fig. 3a that the sample α-Mn_2O_3 is in the form of chain-like structure. Fig. 3b shows that the chain-like structures are composed of nanosized primary particles with size of 20–60 nm, and the linking nature of mercaptosuccinic acid. Salavati-Niasari et al. [28] have obtained chain-like structure of manganese sesquioxide via thermal decomposition of manganese phthalate polymer as precursor, oleic acid, and triphenylphosphine as stabilizer and capping agent.

The size and functional group of the thiol compounds play an important role in determining the stability and other physicochemical property of the material [29]. Among the thiol group compounds mercaptosuccinic acid combines both the features of mercaptopropionic acid and thioglycolic acid. Mallick et al. [30] have used mercaptosuccinic acid to link enzymes or other biomolecule. Herein, mercaptosuccinic acid is used for the first time in the synthesis of manganese oxide. Carboxyl groups in the mercaptosuccinic acid are capable of linking metal surfaces, it is

observed by chain-like structure of manganese oxide. Thus mercaptosuccinic acid is not only capable of linking enzyme and other bio-molecule, but also capable of linking metal oxide and accelerating growth of the material.

The chemical reaction involved in the synthesis of α-Mn_2O_3 nanostructures at room temperature can be formulated as follows:

$$2MnCl_2 + 4NaOH \rightarrow 2Mn(OH)_2 + 4NaCl$$

$$2Mn(OH)_2 + (1/2)O_2 \rightarrow 2MnOOH + H_2O$$
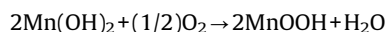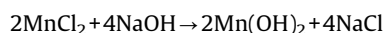
Here, manganese (II) chloride first reacts with sodium hydroxide, forms manganese hydroxide which rapidly oxidizes on exposure to air, and becomes manganese oxyhydroxide (MnOOH), which is unstable and decays into α-Mn_2O_3 and water as follows:

$$2MnOOH \rightarrow Mn_2O_3 + H_2O$$
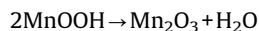
Hexamine is non-polar chelating agent, it will preferentially attach to non-polar facets of the manganese crystal structure, and leaving only the polar facets for growth. While hydrolysis in the reaction bath hexamine decomposes into formaldehyde and ammonia. Thus, it provides OH^- ion, which supports the formation of manganese sesquioxide by forming manganese hydroxide. The release of OH^- ion slowly increases the pH of the solution by the way it controls growth rate of the nanostructure.

4. Conclusion

In an efficient room temperature and green synthesis protocol has been reported to the synthesis of manganese sesquioxide via sol process with its original bixbyite cubic structure and chain-like structure, with assisting hexamine and mercaptosuccinic acid as wetting agent, respectively. The features of nanomaterials have been confirmed by both diffraction studies and microscopic studies. This result confirms that the surfactants have control over the morphology of the prepared material.

References

[1] R.E. Cavicchi, R.H. Silsbe, Phys. Rev. Lett. 52 (1984) 1453–1456.
[2] P. Ball, L. Garwin, Nature 355 (1992) 761–766.
[3] M. Baldi, V.S. Escribano, J.M. Gallardo-Amores, F. Milella, G. Busca, Appl. Catal. B 17 (1998) L175–L182.
[4] M. Baldi, E. Finocchio, F. Milella, G. Busca, Appl. Catal. B 16 (1998) 43–51.
[5] P. Zhang, Y. Zhan, B. Cai, C. Hao, J. Wang, C. Liu, Z. Meng, Z. Yin, Q. Chen, Nano Res. 3 (2010) 235–243.
[6] M.Y. Liao, J.M. Lin, J.H. Wang, C.T. Yang, T.L. Chou, B.H. Mok, N.S. Chong, H.Y. Tang, Electrochem. Commun. 5 (2003) 312–316.
[7] F. Jiao, P.G. Bruce, Adv. Mater. 19 (2007) 657–660.
[8] X. Chen, X. Li, Y. Jiang, C. Shi, X. Li, Solid State Commun. 136 (2005) 94–96.
[9] Y.F. Chang, J.G. McCarty, Catal. Today 30 (1996) 163–170.
[10] Y. Yang, L. Xiao, Y. Zhao, F. Wang, Int. J. Electrochem. Sci. 3 (2008) 67–74.
[11] Chugai Electric Industrial Co. Ltd., Jpn. Kokai Tokkyo Koho JP 02, 35, 915 [90, 35, 915], February 6, 1990.
[12] C.N.R. Rao, S.R.C. Vivekchand, K. Biswas, A. Govindaraj, Dalton Trans. (2007) 3728–3749.
[13] Y. Chen, Y. Zhang, Qi-Zhi Yao, Gen-Tao Zhou, S. Fu, H. Fan, J. Solid State Chem. 180 (2007) 1218–1223.
[14] L.Z. Wang, Y. Ebina, K. Takada, T. Sasaki, Chem. Commun. (2004) 1074–1075.
[15] Z.Y. Yuan, Z.L. Zhang, G.H. Du, T.Z. Ren, B.L. Su, Chem. Phys. Lett. 378 (2003) 349–353.
[16] S.J. Lei, K.B. Tang, Z. Fang, Q.C. Liu, H.G. Zheng, Mater. Lett. 60 (2006) 53–56.
[17] W.N. Li, L.C. Zhang, S. Sithambaram, J.K. Yuan, X.F. Shen, M. Aindow, S.L. Suib, J. Phys. Chem. C 111 (2007) 14694–14697.
[18] S. Thota, B. Prasad, J. Kumar, Mater. Sci. Eng. B 167 (2010) 153–160.
[19] L. Liu, Z. Yang, H. Liang, H. Yang, Y. Yang, Mater. Lett. 64 (2010) 891–893.
[20] J. Cao, Y. Zhu, K. Bao, L. Shi, S. Liu, Y. Qian, J. Phys. Chem. C 113 (2009) 17755–17760.
[21] C. Tsang, J. Kim, A. Manthiram, J. Solid State Chem. 137 (1998) 28–32.
[22] T. Ahmad, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, J. Mater. Chem. 14 (2004) 3406–3410.
[23] Z. Yang, W. Zang, Q. Wang, X. Song, Y. Quian, Chem. Phys. Lett. 418 (2006) 46–49.
[24] C. Wang, Q. Ma, X. Su, J. Nanosci. Nanotechnol. 8 (2008) 4408–4414.
[25] R. Jenkins, R.L. Snyder, in: Robert J. Cernik, Chemical Analysis: Introduction to X-Ray Powder Diffractometry, John Wiley and Sons Inc., New York, 1996, p. 90.
[26] N. Chandra, S. Bhasin, M. Sharma, D. Pal, Mater. Lett. 61 (2007) 3728–3732.
[27] S. Music, M. Ristic, S. Popovic, J. Mol. Struct. 924–926 (2009) 243–247.
[28] M. Salavati-Niasari, F. Mohandes, F. Davar, K. Saberyan, Appl. Surf. Sci. 256 (2009) 1476–1480.
[29] G. Lan, Y. Lin, Y. Hung, H. Chang, J. Mater. Chem. (2007) 2661–2666.
[30] K. Mallick, M.J. Witcomb, M.S. Scurrell, Gold Bull. 39 (2006) 166–174.