Chemical Engineering Journal 153 (2009) 183–186

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Synthesis and characterization of mercury oxide unusual nanostructures by ultrasonic method

Azadeh Askarinejad, Ali Morsali*

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14155-4838, Tehran, Islamic Republic of Iran

ARTICLE INFO

Article history:
Received 28 February 2009
Received in revised form 11 May 2009
Accepted 18 May 2009

Keywords:
Sonochemistry
X-ray diffraction
Mercury oxide
Electron microscopy

ABSTRACT

A facile direct synthesis has been done to prepare HgO nanocrystallites of different shapes. The effect of different parameters such as the presence of alkali salts or stabilizers, power of the ultrasound, time of sonicating, and the starting materials on the size, morphology and crystallinity degree of the products were studied. Scanning electron microscopy observations revealed that using of polyvinyl alcohol (PVA) or alkali salts led to different shapes of product.

1. Introduction

In recent years, the preparation of metal oxide nanostructures has been intensively pursued because of their useful applications in catalysis, energy storage, magnetic data storage, sensors, and ferrofluids [1–4]. Transition metal chalcogenides, as important semiconductor materials, have attracted many attentions because of their special physical and chemical properties, and broad application in many fields [5–10]. Recently, nano-scale chalcogenides are assuming great importance both in theory and in practice owning to their novel properties as a consequence of the large number of surface atoms and the three-dimensional confinement of the electrons [11–14]. These unique properties lead to appearance of many practical properties and new application areas, such as quantum size effect, luminescence properties, non-linear optical properties and their use in solar cells, photo-detectors, light-emitting diodes, and laser communication [15]. Among the semiconductor compounds, HgO was suggested to be the most unusual one in terms of its structural properties at ambient pressure, which are largely determined by the strong tendency for linear coordination of Hg to form the O–Hg–O chain geometry [16]. The structure of HgO is built up of planar O–Hg–O zigzag chains lying in the *ac*-plane. The band gap of the HgO at room temperature was measured to be 2.19 eV from the photoconductivity, and n-type electrical conductivity has been reported [17,18]. In applications, HgO is applied to the cathode in the mercury battery cell, which was widely used in small electronic equipment [19].

Many effective methods have been established for synthesizing of transition metal chalcogenides, such as non-aqueous system [20], microwave irradiation [21], gamma-irradiation [22], sonochemical way [23], pyrolysis [24], vesicles [25], organic-metallic precursor [26], hydrothermal synthesis [27,28], gas reaction, solid reaction and so on, and some new methods are coming out.

Recently, sonochemical synthesis has been used in the preparation of many materials [29–31]. Ultrasound induces chemical changes due to cavitation phenomena involving the formation, growth, and instantaneously implosive collapse of bubbles in liquid, which can generate local hot spots having a temperature of roughly 5000 °C, pressures of about 500 atm, and a lifetime of a few microseconds [32]. These extreme conditions can drive chemical reactions such as oxidation, reduction, dissolution, and decomposition, which have been developed to fabricate a variety of metal, oxide, sulfide, and carbide nanoparticles [33–37].

In the present article, a direct sonochemical method to synthesize mercury oxide nanocrystallites, the influence of different factors on the size, morphology and crystallinity of HgO nanocrystallites is reported.

2. Experimental

HgO nanocrystallites were prepared by the reaction of $Hg(CH_3COO)_2$ with NaOH or tetramethylammonium hydroxide (TMAH) in water as solvent under ultrasound power. The molar ratio

---

[*] Corresponding author. Tel.: +98 2182884416; fax: +98 2188009730.
E-mail address: morsali_a@yahoo.com (A. Morsali).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.05.031

Table 1
Experimental conditions for the preparation of HgO nanocrystallites.

Sample	$Hg(OAc)_2$	Base	Additives	Sonicating time	Ultrasound power
1	50 ml (0.1 M)	50 ml (NaOH 0.2 M)	–	1 h	60–90 W
2	25 ml (0.1 M)	50 ml (NaOH 0.2 M)	–	1 h	60–90 W
3	25 ml (0.1 M)	50 ml (TMAH 0.2 M)	–	1 h	60–90 W
4	25 ml (0.1 M)	50 ml (NaOH 0.2 M)	2 g PVA	1 h	60–90 W
5	25 ml (0.1 M)	50 ml (NaOH 0.2 M)	1 g $NaNO_3$	1 h	60–90 W
6	25 ml (0.1 M)	50 ml (NaOH 0.2 M)	2 g PVA	2 h	60–90 W
7	25 ml (0.1 M)	50 ml (NaOH 0.2 M)	–	1 h	150–180 W
8	25 ml (0.1 M)	50 ml (TMAH 0.2 M)	–	1 h	Without ultrasound

of initial materials, the time of sonicating, the power of the ultrasound and the type of titrated base were optimized. To investigate the role of alkali salts on the size and morphology of nanoparticles, it was used 1 g of $NaNO_3$ in the reaction number 6. Table 1 shows the conditions of reactions in detail. A multiwave ultrasonic generator (Sonicator_3000; Misonix Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert Company with monochromatized Cu Kα radiation. The crystallite sizes of selected samples were estimated using the Scherrer method. TGA and DTA curves were recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating. IR spectra were recorded on a SHIMADZU-IR460 spectrometer in a KBr matrix.

3. Results and discussion

XRD patterns of as-prepared samples are given in Fig. 1. Fig. 1a is corresponding to HgO nanostructures of sample No. 2 and Fig. 1b shows the XRD pattern of sample No. 4. By comparison with the data from JCPDS file No. 37-1469, the diffraction peaks shown in Fig. 1a and also Fig. 1b accord with the orthorhombic crystal system mercury oxide (HgO) with the space group of P_{mnb} and lattice parameters of $a = 5.5254$, $b = 6.6084$, $c = 3.5215$ and $Z = 4$. As it can be seen the XRD pattern obtained for the sample No. 2 (Fig. 1a) with the reaction conditions shown in Table 1, shows very sharp peaks compared with the diffraction peaks obtained for the sample No. 4 with the reaction in which PVA was used as a stabilizer. The sharpening of the peaks is due to the good crystallinity of sample No. 2. No characteristic peaks of impurities are detected in the XRD patterns. The broadening of the peaks indicated that the particles were of nanometer scale. In a diffraction pattern, peak broadening is due to four factors: microstrains (deformations of the lattice), faulting (extended effects), and crystalline domain size and domain size distribution. If we assume that analyzed samples are free of strains and faulting, peak broadening is only due to crystalline domain size D, which can then be calculated by the Scherrer formula [38], so it is always observed that the average size obtained by this formula is less than the one which is obtained from SEM and TEM images. Estimated from the Scherrer formula, $D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively [39], the average size of the particles of sample number 2 was 23 nm, which is to some extent in agreement with that observed from SEM images.

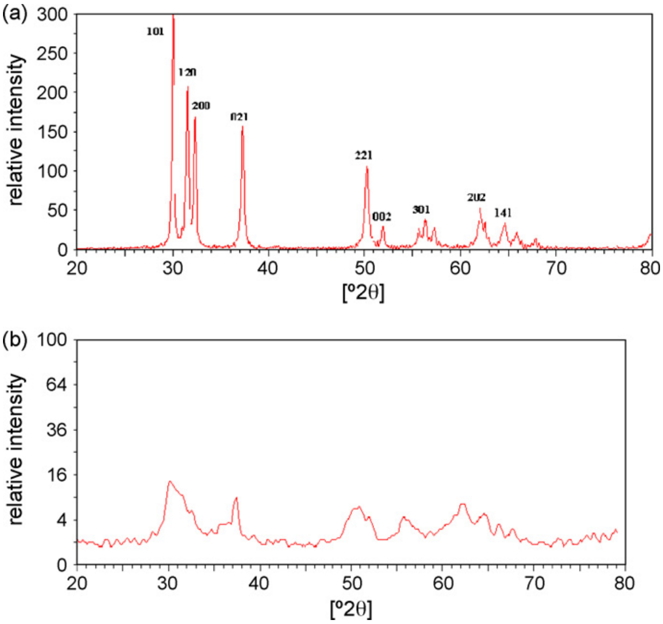

Fig. 1. X-ray powder diffraction pattern of (a) HgO (sample No. 2) and (b) HgO (sample No. 4).

The SEM micrographs of the as-prepared HgO nanostructures are shown in Fig. 2. The influence of different factors given in Table 1, on the morphology of HgO nanocrystallites is very obvious. The role of using PVA in the reaction can be seen in Fig. 2d–f which shows an unusual morphology for HgO nanostructures. PVA is one of the surfactants which are used in preparation of nanomaterials in order to control the dispersion of the particles and prevent the particles from agglomeration. As it can be seen from Fig. 2d–f, in this case using PVA has an obvious role in arranging the particles in a one-dimensional order with less agglomeration. The role of using alkali salts can be seen in Fig. 2g. Alkali salts have been used in many procedures of synthesizing nanostructures to change the morphology and to design advanced materials with anisotropic properties. In this case there was not any special change in the morphologies because of using $NaNO_3$.

The rmogravimetric analyses (TGA) were carried out to show that the obtained products of the direct sonochemical route are oxide compounds of Hg. As it can be seen in the TGA curve (Fig. 3) the 98% loss of weight at 430–580 °C is due to the complete decomposing of HgO and the curve seen in the DTA diagram is due to the endothermic reaction of HgO decomposing.

The IR spectrum of HgO nanostructures (Fig. 4) shows the absorption peaks at 470 and 600 cm^{-1} are assigned to the ν(Hg–O) modes, which confirms the formation of HgO nanocrystallites.

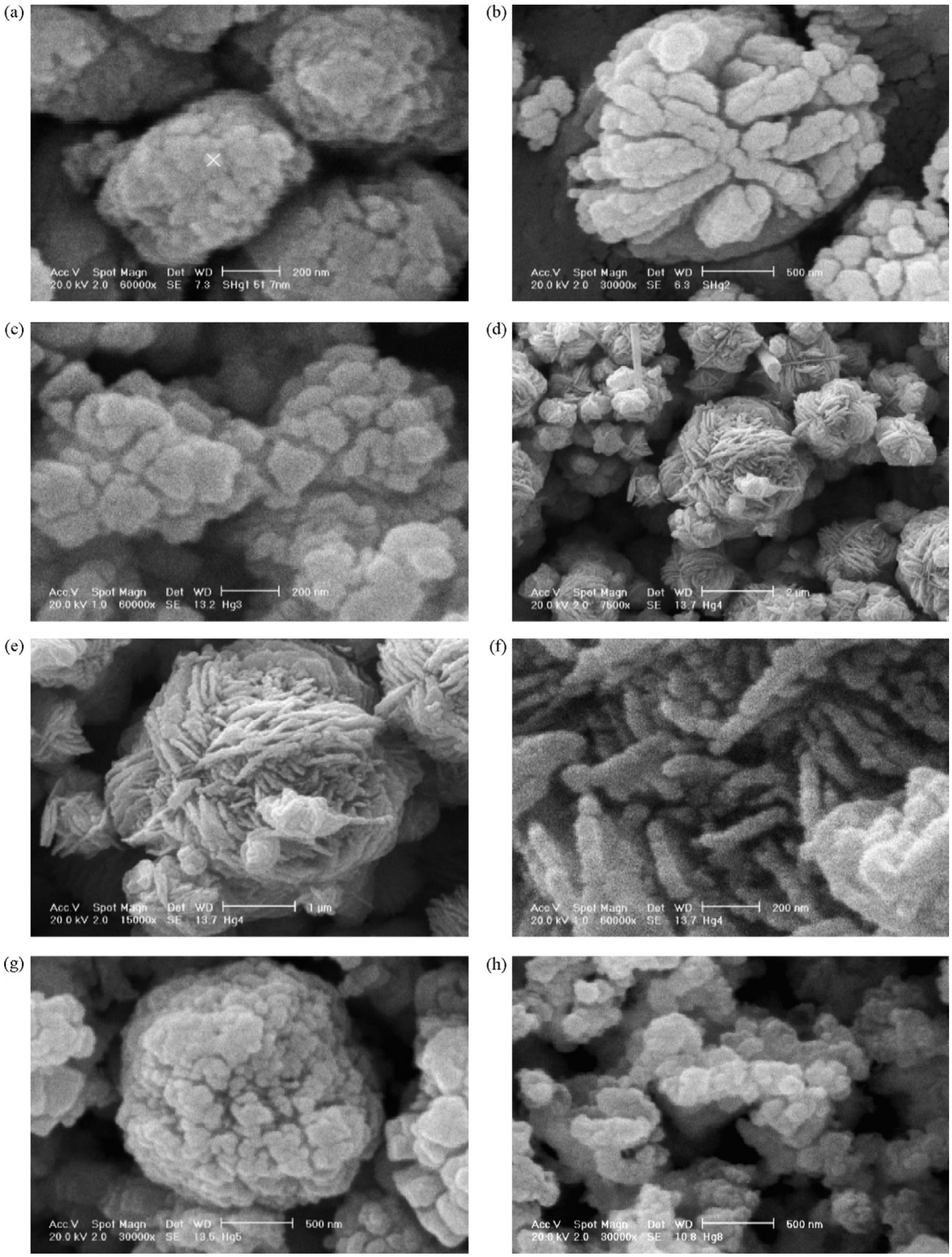

Fig. 2. SEM images corresponding to HgO nanostructures of samples (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4, (e) No. 4, (f) No. 4, (g) No. 5, (h) No. 8 (the scale bar in parts (a), (c) and (f) is 200 nm, parts (b) and (g) is 500 nm, part (e) is 2 μm, part (f) is 1 μm).

To investigate the role of ultrasound irradiation on the composition, size and morphology of the products the reactions of $Hg(CH_3COO)_2$ with TMAH with the same conditions as the reaction No. 3 without any ultrasound irradiation and by mechanical stirring were performed (Table 1, reaction No. 8). The XRD patterns show that the obtained product is HgO with high crystallinity as products of sonicating. SEM images show that the products obtained without ultrasound have totally different morphology from the products of sonicating and the size of the obtained structures is not in nanometer scale (Fig. 2h). So we can approach to this result that ultrasound irradiation have special roles on the morphology of the nanoparticles and their size.

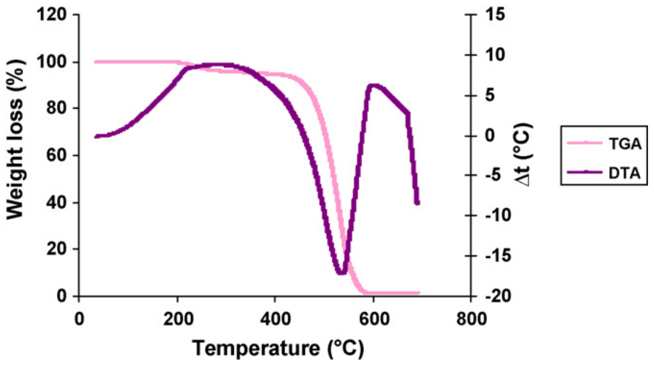

Fig. 3. TG–DTA curves of HgO nanostructures (sample No. 3).

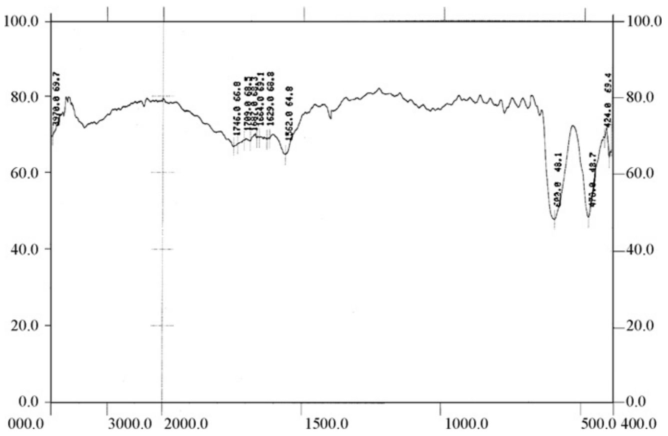

Fig. 4. IR spectrum of HgO nanostructures (sample No. 2).

4. Conclusion

In summary, a simple sonochemical route has been used to synthesize different shapes of HgO nanostructures by modifying different parameters. The SEM images and XRD, TG/DTA and IR analyses confirm the nanostructures of pure HgO. To the best of our knowledge it is probably the first time that HgO nanostructures are synthesized and also the first time that this method is used to prepare HgO nanostructures and it can be used at industrial scale because it does not need special conditions like high temperature, special surfactants, long times or pressure controlling.

Acknowledgement

Supporting of this investigation by Tarbiat Modares University is gratefully acknowledged.

References

[1] A.J. Zarur, J.Y. Ying, Nature 403 (2000) 65.
[2] S.A. Majetich, Y. Jin, Science 284 (1999) 470.
[3] C. Nayral, E. Viala, P. Fau, F. Senocq, J.C. Jumas, A. Maisonnat, B. Chaudret, Chem. Eur. J. 6 (2002) 4802.
[4] K. Raj, R. Moskowitz, J. Magn. Mater. 85 (1990) 233.
[5] A.N. Goldstein, C.M. Echer, A.P. Alivisators, Science 256 (1992) 1425.
[6] K. Mitchell, J.A. Ibers, Chem. Rev. 102 (2002) 1929.
[7] N. Heron, J.C. Calabrege, W.E. Garnet, U. Wang, Science 259 (1993) 1426.
[8] D. Yu, Z. Bai, Appl. Phys. Lett. 72 (1998) 3458.
[9] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, C. Dekker, Nature 386 (1997) 474.
[10] S. Frank, P. Poncharal, Z.L. Wang, W.A. de Heer, Science 280 (1998) 1744.
[11] A.P. Alivisatos, Science 271 (1996) 933.
[12] A. Henglein, Chem. Rev. 89 (1989) 1861.
[13] Y. Wang, N. Herron, J. Phys. Chem. 95 (1991) 525.
[14] H. Weller, Adv. Mater. 5 (1993) 88.
[15] X. Changqi, Zh. Zhicheng, Y. Qiang, Mater. Lett. 58 (2004) 1671.
[16] T. Zhou, U. Schwarz, M. Hanfland, Z.X. Liu, K. Syassen, M. Cardona, Phys. Rev. B 57 (1998) 153.
[17] V.V. Shchennikov, Phys. Solid State 35 (1993) 401.
[18] I.M. Tsidil'kowski, V.V. Shchennikov, N.G. Gluzman, Sov. Phys. Semicond. 19 (1985) 901.
[19] M. Choi, H.H. Nahm, C.H. Park, J. Korean Phys. Soc. 47 (2005) 304.
[20] V.N. Konev, V.N. Chebotin, S.A. Fomenkov, Inorg. Mater. 21 (1985) 166.
[21] R. Rossetti, R. Hull, J.M. Gibson, J. Chem. Phys. 82 (1995) 552.
[22] J.J. Watzke, J.H. Fendler, J. Phys. Chem. 91 (1986) 854.
[23] Y.H. Ni, X.W. Ge, H.R. Liu, et al., Chem. J. Chin. Univ. 23 (2002) 176.
[24] R.V. Kumar, O. Palchik, Y. Koltypin, Y. Diamant, A. Gedanken, Ultrason. Sonochem. 9 (2002) 65.
[25] K. Okuyama, I.W. Lenggoro, N. Tagami, S. Tamaki, et al., J. Mater. Sci. 32 (1997) 1229.
[26] S.H. Yu, U.S. Wu, J. Yang, J. Mater. Chem. 9 (1998) 2312.
[27] M. Lade, H. Mays, J. Schmidt, R. Willumeit, R. Schomäcker, Colloids Surf. A: Physicochem. Eng. Aspects 163 (2000) 3.
[28] J. Jiang, L. Li, Mater. Lett. 61 (2007) 4894.
[29] K.S. Suslick, Science 247 (1990) 1439.
[30] D.N. Srivastava, N. Perkas, G.A. Seisenbaeva, Y. Koltypin, V.G. Kessler, A. Gedanken, Ultrason. Sonochem. 10 (2003) 1–9.
[31] X.L. Zhang, Y.H. Kim, Y.S. Kang, Curr. Appl. Phys. 6 (2006) 796–800.
[32] A. Gedanken, Ultrason. Sonochem. 11 (2004) 47–55.
[33] V.G. Pol, A. Gedanken, J. Chem. Mater. 15 (2003) 1111.
[34] T. Gao, Q.H. Li, T.H. Wang, Chem. Mater. 17 (2005) 887.
[35] N.A. Dhas, A. Zaban, A. Gedanken, Chem. Mater. 11 (1999) 806.
[36] T. Gao, T.H. Wang, Chem. Commun. 22 (2004) 2558.
[37] N.A. Dhas, Appl. Phys. Lett. 72 (1998) 2514.
[38] A. Weibel, R. Bouchet, F. Boulc'h, P. Knauth, Chem. Mater. 17 (2005) 2378.
[39] J. Yang, C. Lin, Zh. Wang, J. Lin, Inorg. Chem. 45 (2006) 8973.