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Sonochemical synthesis, characterization and optical analysis of some metal oxide nanoparticles (MO-NP; M=Ni, Zn and Mn)

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ABSTRACT

Some nanosized metal oxide (MO) such as ZnO, NiO and MnO were successfully synthesized by sonochemistry method in solutions at room temperature. The reactants used are $(M(Ac)_2 \cdot 2H_2O)$ and sodium hydroxide (NaOH), and H₂O/EtOH as a carrier in polyethylene glycol (PEG) template. Some of parameters such as effect concentration of NaOH solution, ultrasound power and sonicating time in growth and morphology of the nanostructures were investigated. The best morphology with smaller particles size and good distribution was obtained by using 0.025 M solution of NaOH and 45 W ultrasound powers in 1 h sonicating time. The particle size of the nanosized metal oxide powders synthesized at room temperature is approximately between 40 and 80 nm. The resulting nanosized powder was characterized by X-ray diffraction (XRD) measurements, Raman, BET, solid state UV-vis and scanning electron microscopy (SEM).

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1. Introduction

Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 kHz-10 MHz). The physical phenomenon responsible for the sonochemical process is acoustic cavitations. Let us first address the question of how 20 kHz radiation can rupture chemical bonds (the question is also related to 1 MHz radiation), and try to explain the role of a few parameters in determining the yield of a sonochemical reaction, and then describe the unique products obtained when ultrasound radiation is used in materials science. A number of theories have been developed in order to explain how 20 kHz sonic radiation can break chemical bonds. They all agree that the main event in sonochemistry is the creation, growth, and collapse of a bubble that is formed in the liquid. The stage leading to the growth of the bubble occurs through the diffusion of solute vapor into the volume of the bubble. The last stage is the collapse of the bubble, which occurs when the bubble size reaches its maximum value. From here we will adopt the hot spot mechanism, one of the theories that explain why, upon the collapse of a bubble, chemical bonds are broken. This theory claims that very high temperatures (5000-25,000 K) [1] are obtained upon the collapse of the bubble. Since this collapse occurs in less than a nanosecond [2,3], very high cooling rates, in excess of 10¹¹ K/s, are also obtained. This high cooling rate hinders the organization and crystallization of the products. For this reason, in all cases dealing with volatile precursors where gas phase reactions are predominant, amorphous nanoparticles are obtained. While the explanation for the creation of amorphous products is well understood, the reason for the nanostructured products is not clear. One explanation is that the fast kinetics does not permit the growth of the nuclei, and in each collapsing bubble a few nucleation centers are formed whose growth is limited by the short collapse. However sonochemistry is one of the earliest techniques used to prepare nanosized compounds. Nanomaterials are at the leading edge of rapidly developing field of nanotechnology [4–7]. A reduction in particle size to nanometer scale results in various special and interesting properties compared to their bulk properties.

In recent years, metal oxide (MO) nanoparticles as a kind of functional material has attracted extensive interests due to its novel optical, electronic, magnetic, thermal and mechanical properties and potential application in catalyst, battery electrodes, gas sensors, electrochemical films, photo-electronic devices and so on. In these applications, it is still needed for synthesizing high-quality and ultra-fine powders with required characteristics in terms of their size, morphology, microstructure, composition purity, crystallizability, etc., which are the most essential factors which eventually determine the microstructure and performance of the final products. Therefore, it is very



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important to control the powder properties during the preparation process. There are many chemical and physical methods to prepare nanometer metal oxide (MO), including the precipitation of metal acetate with NaOH [8-14]. Recently, the interest preparation of nanometer MO has been growing. However, only few practical methods have been reported. The nanomaterials whose synthesis was reported are ZnS [15,16], Sb₂S₃ [17,18], HgSe [19], SnS₂ [20], CdS [21], CdSe [22], PbX (E=S, Se, Te, O) [23], CuS [24], Ag₂Se [25] and CdCO₃ [26]. But the sonochemical method for preparation of nanomaterials is very interesting, simple, cheap and safe. However, in the present work we have developed a simple physical method (sonochemical method) to prepare NiO. MnO and ZnO nanostructures, wherein MO is synthesized by the reaction of (CH₃CO₂)₂M · 2H₂O and NaOH in an ultrasonic device. The MO nanoparticles have been characterized by X-ray powder diffraction (XRD), Raman spectroscopy, solid state UV, BET and also the morphology and size of the nanostructures have been observed by scanning electron microscopy (SEM). We have performed these reactions in several conditions to find out the role of different factors such as the aging time of the reaction in the ultrasonic device and the concentration of the metal acetate on the morphology and size of nanostructures.

2. Experimental

Typical procedure for preparation of MO nanoparticles: NaOH solution with a concentration of 0.1 M (100 ml) were added to the 0.05 and 0.025 M solutions of $M(CH_3COO)_2 \cdot 2H_2O$ in ethanol/water. To investigate the role of surfactants on the size and morphology of nanoparticles, we used 0.5 g of polyethylene glycol (PEG) in the reaction with optimized conditions. The mixtures were sonicated for 30–60 min, with different ultrasound powers followed by centrifuging with a centrifuge, and separation of the solid and liquid phases. The solid phase was washed for three

Table 1

Experimental conditions for the preparation of MO nanoparticles.

times ethanol and water. Finally, the washed solid phase was calcinated at 500 °C for 30 min. Table 1 shows the conditions of reactions in detail. A multiwave ultrasonic generator (Bandlin Sonopuls Gerate-Typ: UW 3200, Germany) equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 30 kHz with a maximum power output of 780 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 mono chromatized CuK_{γ} radiation. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating. Raman spectra were recorded on a Labram HR 800-Jobin Yvon Horbiba spectrometer. UVeVis spectra were measured with an HP 8453 diode array spectrophotometer. The specific surface area of samples was determined using the Brunauer-Emmet-Teller (BET) method in a volumetric adsorption apparatus (ASAP 2010 M, Micrometritics Instrument Corp).

3. Results and discussion

The reaction between Mn, Ni and Zn acetate and sodium hydroxide to form MO has been shown in Scheme 1.



Scheme 1. Preparation of MO nanoparticles.

Series 1	Mn(OAc) ₂ • 2H ₂ O	NaOH (0.1 M)	Aging time	Ultrasound power	Template
1	50 ml (0.05 M)	100 ml	1 h	30 W	PEG
2	50 ml (0.05 M)	100 ml	1 h	45 W	PEG
3	50 ml (0.025 M)	100 ml	1 h	30 W	PEG
4	50 ml (0.025 M)	100 ml	1 h	45 W	PEG
5	50 ml (0.05 M)	100 ml	30 min	30 W	PEG
6	50 ml (0.05 M)	100 ml	30 min	45 W	PEG
7	50 ml (0.025 M)	100 ml	30 min	30 W	PEG
8	50 ml (0.025 M)	100 ml	30 min	45 W	PEG
Series 2	Ni(OAc) ₂ · 2H ₂ O	NaOH (0.1 M)	Aging time	Ultrasound power	Template
1	50 ml (0.05 M)	100 ml	1 h	30 W	PEG
2	50 ml (0.05 M)	100 ml	1 h	45 W	PEG
3	50 ml (0.025 M)	100 ml	1 h	30 W	PEG
4	50 ml (0.025 M)	100 ml	1 h	45 W	PEG
5	50 ml (0.05 M)	100 ml	30 min	30 W	PEG
6	50 ml (0.05 M)	100 ml	30 min	45 W	PEG
7	50 ml (0.025 M)	100 ml	30 min	30 W	PEG
8	50 ml (0.025 M)	100 ml	30 min	45 W	PEG
Series 3	$Zn(OAc)_2 \cdot 2H_2O$	NaOH (0.1 M)	Aging time	Ultrasound power	Template
1	50 ml (0.05 M)	100 ml	1 h	30 W	PEG
2	50 ml (0.05 M)	100 ml	1 h	45 W	PEG
3	50 ml (0.025 M)	100 ml	1 h	30 W	PEG
4	50 ml (0.025 M)	100 ml	1 h	45 W	PEG
5	50 ml (0.05 M)	100 ml	30 min	30 W	PEG
6	50 ml (0.05 M)	100 ml	30 min	45 W	PEG
7	50 ml (0.025 M)	100 ml	30 min	30 W	PEG
8	50 ml (0.025 M)	100 ml	30 min	45 W	PEG



Fig. 1. X-ray powder diffraction pattern of MO nanoparticles (a) ZnO, (b) NiO and (c) MnO.

Various conditions for preparation of MO nanostructures were summarized in Table 1. The best morphology with smaller particles and good distribution was obtained for the sample number 4 in series 1, 2 and 3. Fig. 1(a-c) shows the XRD patterns of the direct sonochemicalv synthesized of the ZnO. NiO and MnO nanoparticles. respectively. Sharp diffraction peaks shown in Fig. 1 indicate good crystallinity of MO nanoparticles. No characteristic peak related to any impurity was observed. The broadening of the peaks indicated that the particles were of nanometer scale. The morphology, structure and size of the samples are investigated by scanning electron microscopy (SEM). Fig. 2 indicates that the original morphology of the ZnO, NiO and MnO particles are approximately spherical with the diameter varying between 40 to 80 nm. The role of PEG on the morphology of this sample is obvious. It has been reported that the presence of a capping molecule such as polyethylene glycol (PEG) can alter the surface energy of crystallographic surfaces, in order to promote the anisotropic growth of the nanoparticles. In this work PEG adsorbs on the crystal nuclei and it helps the particles to grow separately. To investigate the size distribution of the nanoparticles, a particle size histogram was prepared for MO nanoparticles, (Fig. 3). Most of the particles possess sizes in the range from 40 to 80 nm. For further demonstration, the EDAX was performed for the MO nanoparticles. The EDAX spectrum given in Fig. 4 shows the presence of Zn, Ni and Mn as the only elementary component in the ZnO, NiO and MnO nanoparticles, respectively. Raman spectra recorded for ZnO, NiO and MnO nanoparticles at room temperature have been depicted in Fig. 5. Several strong and weak bands are observed in these spectra. ZnO shows 3 active Raman modes at 330, 442 and 578 cm⁻¹, NiO show 5 active Raman modes at 270, 398, 526, 577 and 655 cm⁻¹ and MnO show 4 Raman active modes at 382, 384, 690 and 783 cm^{-1} . In order to investigate the role of sonication on the composition, size and morphology of the products, we have done the reaction without sonication with the same conditions of the optimized sample. The XRD pattern of the obtained product is corresponding to CuO but the SEM images show that the particles of the sample without using sonication have larger sizes comparing with the samples obtained via the sonochemical route. Fig. 6 demonstrates the UV-vis spectrum of the MO nanoparticles by ultrasonically dispersing in absolute ethanol. Strong absorption peak in the UV region can be observed. The absorption band gap E_g is usually achieved with the aid of the following equation:

$$(\alpha h v)^n = B(h v - E_g) \tag{1}$$

Concretely, hv is the photo energy; α is the absorption coefficient; *B* is the constant related to the material; and



Fig. 2. Typical SEM micrographs of MO nanoparticles after calcinations: (a) ZnO, (b) NiO and (c) MnO.

n indicates either 2 or 1/2 for direct transition and indirect transition, respectively. The inset of Fig. 5 gives us the typical $(\alpha h v)^2 \sim h v$ curve for the MO samples calcinated at 500 °C. By the extrapolation of E_g (1), we can get the present band gaps as 4.1,







Fig. 4. EDAX analysis of samples No. 4 of MnO, NiO and ZnO nanoparticles.



Fig. 5. Raman spectroscopy of MnO, NiO and ZnO nanoparticles.

3.7 and 3.9 Ev (layout for NiO, ZnO and MnO) indicating the small blue shifts upon size reductions for MO nanoparticles. The surface area analysis was carried out on MO nanoparticles by BET method. Assuming the particles possess solid, spherical shape with smooth surface and same size, the surface area can be



Fig. 6. Solid state UV absorption of MnO, NiO and ZnO nanoparticles.



Fig. 7. BET plots of MnO, NiO and ZnO nanoparticles.

related to the average equivalent particle size by the equation

$$D_{\text{BET}} = 6000 / (\rho Sw)(\text{in nm})$$
 (2)

where D_{BET} is the average diameter of a spherical particle; *Sw* represents the measured surface area of the powder in m²/g; and ρ is the theoretical density in g/cm³. Fig. 7 shows BET plots of MO nanoparticles, the specific surface area of MO nanoparticles calculated using the multi-point BET-equation are 33, 40 and 53 m²/g (layout for NiO, ZnO and MnO), and the calculated average equivalent particle size is 36, 42 and 51 nm (layout for NiO, ZnO and MnO). We noticed that the particles size obtained from the BET and the SEM methods, agree very well with the result given by X-ray line broadening. The results of SEM observations and BET methods further confirmed and verified the relevant results obtained by XRD as mentioned above. Metal oxides are important catalyst in organic chemistry, gas sensors (such as CO₂, NO, SO₂, H₂O and CO) and battery cathode in the course of our research. The results of this investigation will be reported soon.

4. Conclusion

Nanosized of MnO, NiO and ZnO (MO) have been prepared by reaction between corresponding metal acetate and NaOH under ultrasound irradiation in solution at room temperature. Some of parameters such as effect concentration of NaOH solution, ultrasound power and sonicating time in growth and morphology of the nanostructures were investigated. The best morphology with smaller particles size and good distribution was obtained by using 0.025 M solution of metal acetate and 45 W ultrasound powers in 1 h sonicating time. Average particle sizes of the synthesized nanosized MO powders were between 40 and 80 nm. Simple procedure, short reaction times, yields smaller particles and mild reaction conditions at room temperature are noteworthy advantages of this method. The specific surface area of MO nanoparticles calculated using the multi-point BET-equation are 33, 40 and 53 m^2/g (layout for NiO, ZnO and MnO), and the calculated average equivalent particle size is 36, 42 and 51 nm (layout for NiO, ZnO and MnO). We noticed that the particles size obtained from the BET and the SEM methods, agree very well with the result given by X-ray line broadening. The results of SEM observations and BET methods further confirmed and verified the relevant results obtained by XRD as mentioned above.

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