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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 H_2O/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).

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 10^{11} 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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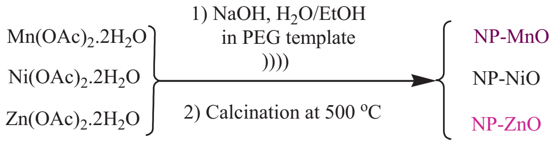
important to control the powder properties during the preparation process. There are many chemical and physical methods to prepare nanometer metal oxide (MO), including the precipitation of metal acetate with NaOH [8–14]. Recently, the interest preparation of nanometer MO has been growing. However, only few practical methods have been reported. The nanomaterials whose synthesis was reported are ZnS [15,16], Sb_2S_3 [17,18], HgSe [19], SnS_2 [20], CdS [21], CdSe [22], PbX (E=S, Se, Te, O) [23], CuS [24], Ag_2Se [25] and $CdCO_3$ [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 $(CH_3CO_2)_2M\cdot 2H_2O$ 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 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$_\alpha$ 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.

Table 1
Experimental conditions for the preparation of MO nanoparticles.

Series 1	$Mn(OAc)_2\cdot 2H_2O$	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
Series 2	**$Ni(OAc)_2\cdot 2H_2O$**	**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
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