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Preparation of nanocrystalline metal oxide powders with the surfactant-mediated method

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Abstract

Nanocrystalline metal oxides (ZnO, NiO, and SnO_2) powders with an average particle diameter of 18–55 nm have been successfully prepared with the surfactant-mediated method. The cationic surfactant (cetyltrimethylammonium bromide, CTAB) and the hydrous metal chlorides ($ZnCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, and $SnCl_4 \cdot 5H_2O$) appear to be the good candidates for obtaining a high yield of nanoparticles. The resultant products have been characterized by thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), and transmission electron microscopy (TEM). The resulting powders are highly crystalline and largely monodisperse oxide particles. The surfactant-mediated method turned out to be suited for the preparation of the nanocrystalline oxide powders. Through this method, it is possible to obtain nanocrystalline metal oxide powders.

Keywords: Nanocrystalline powder; Surfactant-mediated method; Metal oxides; Monodisperse

1. Introduction

Powders with particles of uniform shape and narrow size distribution lying in the nanometer range have been shown to possess interesting properties. Nanoscale oxide particles are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, or ceramic materials [1]. Metal oxide nanoparticles are also widely used in industrial applications as catalysts, ceramic, pigments and so on. In addition, they play an important role in the selective surface modification of various substrates in the form of coatings [2,3]. With regard to all of the applications, in addition to the particle size a low degree of agglomeration and a monogeneous size distribution are desirable to enable a homogeneous arrangement of particles [1]. Thus, an important filed of research is the development of new synthetic processes to produce ultrafine particle with nanocrystalline structure. Many methods for the fabrication of nanoparticles have been developed, ranging from lithographic technologies to chemical methods [4,5]. Because of its advantages, the role of chemistry in materials science has been rapidly growing. Various chemical methods adopted for the preparation of metal oxide nanoparticles include the gas-phase methods, sol–gel methods, evaporative decomposition of solution, and wet chemical synthesis. However, they are difficult to obtain the monodisperse or low degree of agglomeration, or required a very stringent control in various processing parameters, together with a low production yield [6–10]. This communication describes a new surfactant-mediated method to prepare nanocrystalline metal oxide powders. This method is based on the chelation of cations (metal) by surfactant in an aqueous solution. The surfactant not only provides favorable site for the growth of the particulate assemblies, it also influences the formation process, including nucleation, growth, coagulation and flocculation. The surfactant-mediated method applied herein provides a promising preparative approach to nanoparticles such as zinc oxide, nickel oxide, and tin oxide. In this paper the preparation of nanoparticles of ZnO, NiO, and SnO_2 10–60 nm in size is described based on surfactant-mediated method. The properties of the materials were charac-

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terized by X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM).

2. Experimental

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. The purity of CTAB is 98% and of the inorganic precursors are not less than 98%, respectively.

The synthesized method was based on the use of the cationic surfactant (CTAB) and the simple chemical materials (hydrous metal chlorides and NH_4OH) as inorganic precursors. Reaction was performed at room temperature. To prepare ZnO, NiO, and SnO_2 oxide particles, the CTAB were mixed with distilled deionized water with stirring until a homogenous solution (0.08 M) was obtained. The solution of diluted NH_4OH (25 wt% solution, 10 ml) was then added into the CTAB solution with stirring. When the mixing solution became homogenous, a solution of $ZnCl_2$ (0.40 M), $NiCl_2$ (0.25 M), or $SnCl_4$ (0.34 M) was added, respectively, under vigorous stirring. After stirring 4 h, the products were aged at ambient temperature for 96 h. The resulting products were filtered, washed with distilled water to remove surfactant, and then dried at ambient temperature. Complete evolution of the surfactant from the as-synthesized products to yield the oxide nanoparticles was achieved through thermal treatment: 2 h at 500 °C under flowing air atmosphere.

XRD data were carried out with a Rigaku D/max-RB diffractometer with CuK_α radiation ($\lambda = 1.5418$ Å). The sample was scanned from 20° to 80° (2θ) in steps of 0.02°. The crystallite domain sizes (D) have been examined from XRD peaks based on Scherrer's equation: $D = \lambda/(\Delta W \cos\theta)$, where λ is the wavelength of X-ray, θ is the Bragg's diffraction angle, and ΔW is the true half-peak width of the XRD lines. The TEM were made with on the Hitachi-800 transmission electron microscope operated at 200 kV. TGA curves were obtained in flowing nitrogen on TGA2050 with a temperature-increasing rate of 10 °C/min. Powder surface areas were recorded on a Micromeritics ASAP 2010 automated sorption analyzer using nitrogen as adsorbate at 77 K.

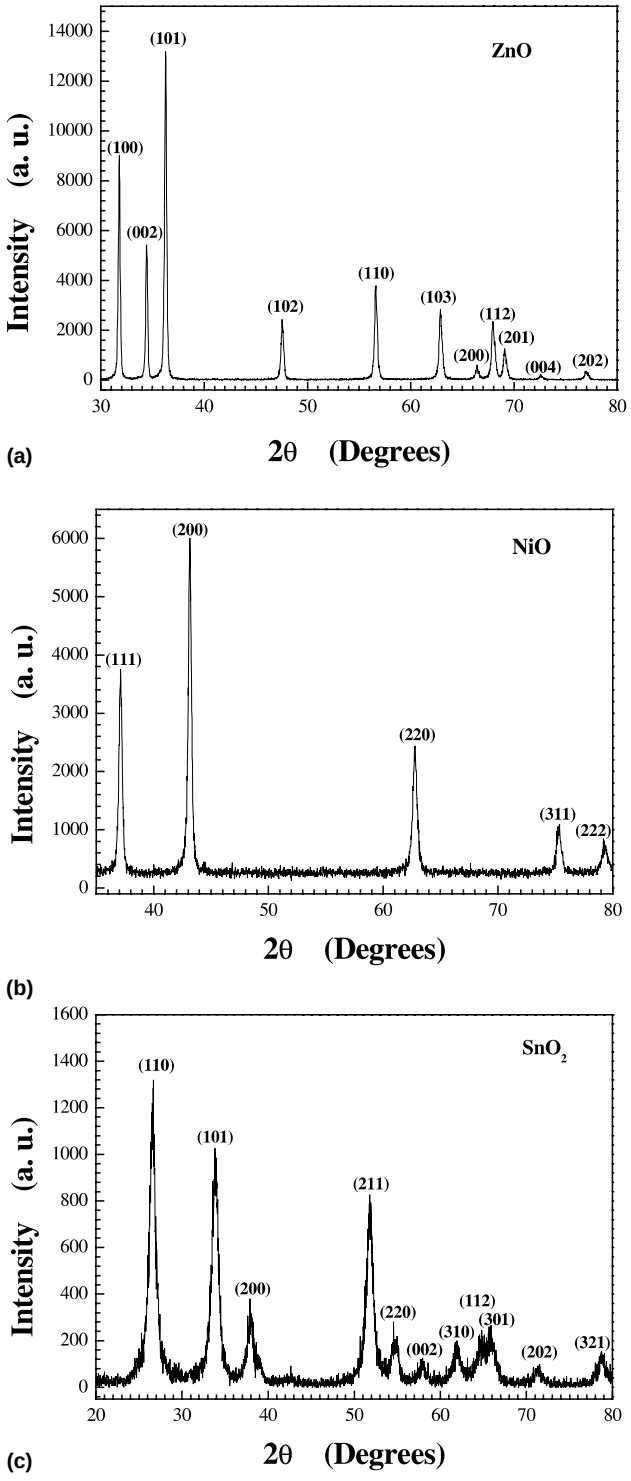

Fig. 1. Powder XRD patterns of (a) ZnO (ICDD-Ref. 36-1451/zincite), (b) NiO (ICDD-Ref. 47-1049/Busenite), and (c) SnO_2 (ICDD-Ref. 41-1445/cassiterite).

3. Results and discussion

TGA of the as-synthesized samples under N_2 showed the loss of the water below 110 °C and surfactant loss started at 178 °C and was completely removed at about 250 °C [11]. The analysis of the as-synthesized sample revealed ~38% total weight loss on heating to 500 °C. The first effect is attributed to the release of adsorbed water, the second to desorption and decomposition of the surfactant template, and the third to dehydroxylation of the surface and removal of little residual surfactant [12–14]. Little further weight loss in the TG curve

Table 1
The particle sizes of nanocrystalline metal oxide powders as measured using three different techniques

Sample	Specific surface area (m^2/g)	Average particle size on the basis of BET (nm)	Crystalline size by Scherrer's equation (nm)	Average particle size from TEM (nm)
ZnO	17.6	60.1	40.4	54.3
NiO	31.7	27.8	22.6	25.5
SnO_2	69.2	12.4	11.1	18.2

is observed at temperature above 500 °C, indicating the completion of any reaction involving a weight change. From these results, it is clear that most of the surfactant CTAB in the as-synthesized powder is eliminated at about 500 °C. Therefore, the calcination of the samples in air has been performed at 500 °C.

XRD analysis of the as-synthesized products showed that the amorphous phases were formed [15], while metal oxide crystallizations occurred after heat treatment at 500 °C for 2 h. The identification of the intermediate amorphous phase suggests the presence of a nucleation growth process in the surfactant-mediated method. XRD patterns are presented for products calcined at 500 °C for 2 h as shown in Fig. 1. The resulting powders are highly cystalline after their calcination. For crystalline materials, the size of primary nanoparticles can be estimated by the amount by which the X-ray line is broadened. Table 1 shows the crystallite sizes of the metal oxides ZnO, NiO, and SnO_2. The analysis of XRD line broadenings clearly reveals the nearly zincite (ZnO), bunsenite (NiO), or cassiterite (SnO_2) character of these crystallites whose sizes are 40.4 nm (ZnO), 22.6 nm (NiO), or 11.1 nm (SnO_2) estimated by using Scherrer's equation.

The size of primary nanoparticles can be determined from imaging by TEM. Use of TEM for determining the particle is preferred over X-ray line broadening [16]. This technology is more direct and less likely to be affected by experimental errors and/or other properties of the particles such as strain or a distribution in the size of the lattice parameter. Fig. 2 depicts the bright field TEM micrographs of ZnO, NiO, and SnO_2, respectively. The figures indicate that most particles are fine and spherical while some are elongated. When calcined at 500 °C for 2 h, the crystalline oxide particles remain well dispersed. As shown, the particles of NiO, SnO_2 are nearly uniform and the diameters are in the range of 10–40 nm and 10–26 nm, respectively. The particles of ZnO are also near uniform but slightly larger than those of NiO and SnO_2. Particle sizes can be measured directly from TEM images. From Fig. 3, it can be seen that the size distributions of particles are narrowly dispersed with a modal size of about 50 nm (ZnO), 25 nm (NiO), and 21 nm (SnO_2), respectively.

Table 1 summarizes the surface area and particle sizes as measured using different techniques for the three samples. The particle size calculated on the basis of BET

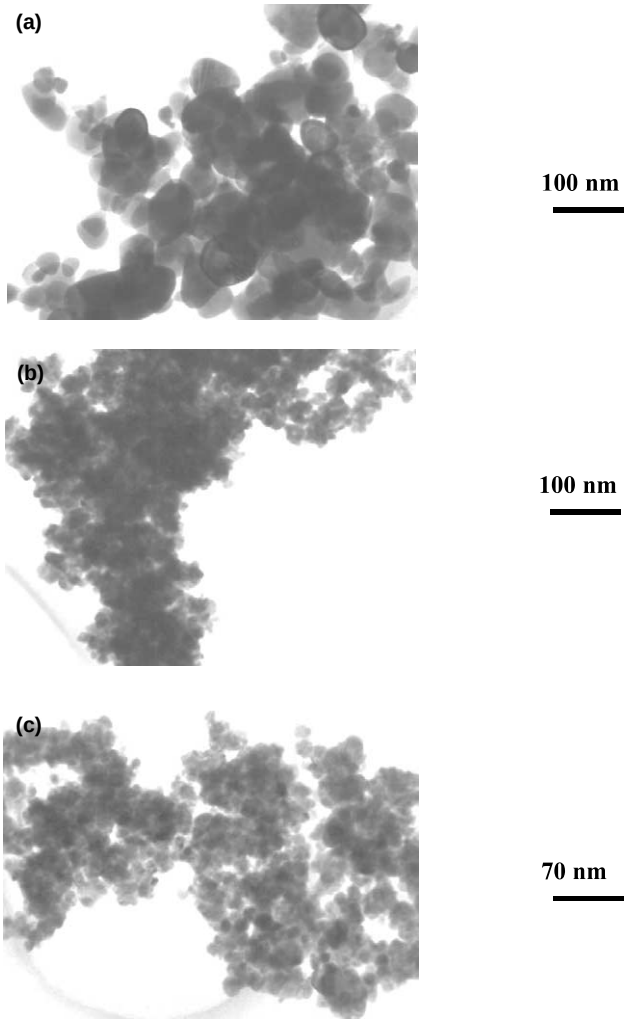

Fig. 2. The TEM micrographs of nanocrystalline metal oxides powders: (a) ZnO, (b) NiO, and (c) SnO_2.

specific surface area can only be regarded as the estimation, as the calculation assumes that the powder consists of monosized spherical particles. The calculation using Scherrer's equation on the basis of peak broadening in XRD trace gives crystallite size, whereas the direct observation using TEM gives information on the discrete particle size, although it is a rather tedious process in order to work out a reliable size distribution by counting enough particles [6]. Therefore, the crystallite and particle sizes summarized in Table 1 are for comparison purposes only.

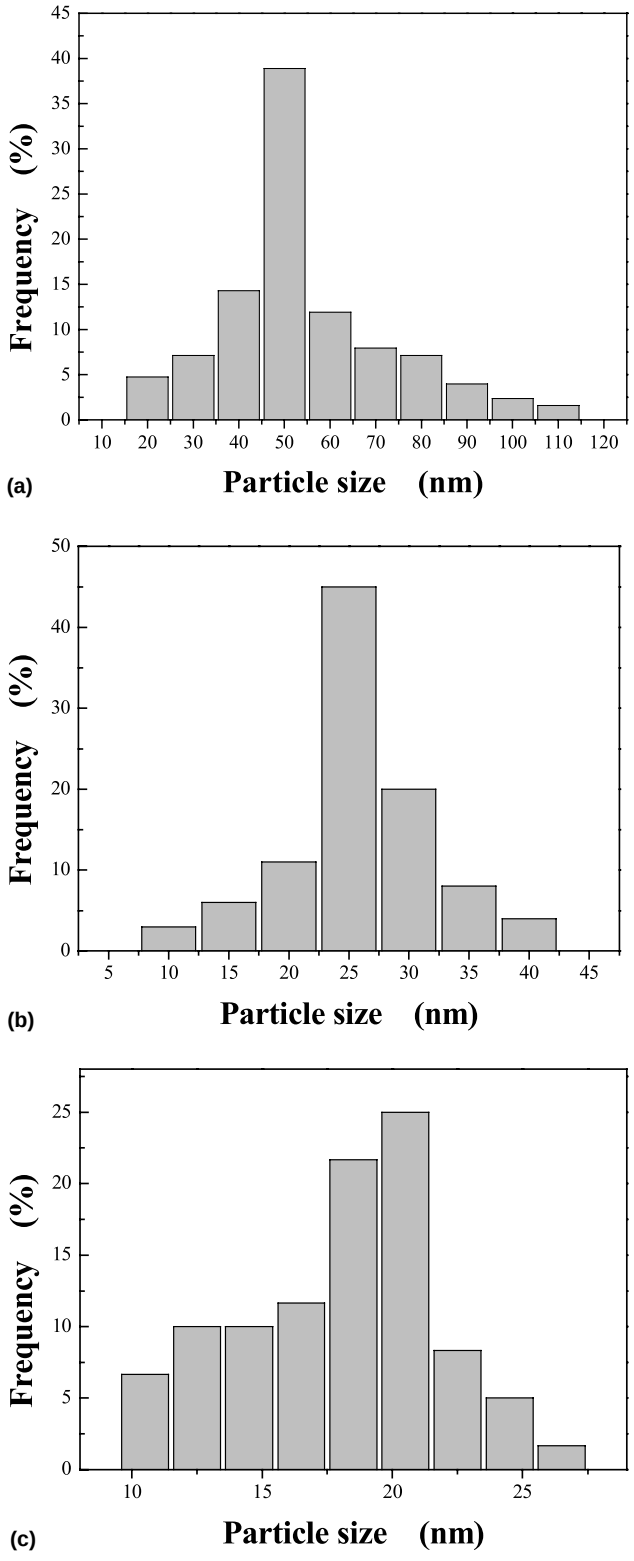

Fig. 3. Mean particle size and particle distribution of nanocrystalline metal oxide powders: (a) ZnO, (b) NiO, and (c) SnO_2. Results were obtained from TEMs.

Particle formation is a very complex process. It involves nucleation, growth, coagulation and flocculation, all of which may be influenced significantly by the surfactant assemblies [17]. The addition of surfactant CTAB can effect the nucleation during the oxides crystallization process. After nucleation, surfactant can influence particle growth, coagulation and flocculation. Therefore, surfactant plays an important role in the preparation of these metal oxides nanoparticles. This work only involves an aspect that can be applied to the synthesis of nanocrystalline materials prepared by the surfactant-mediated method. More detailed studies about the factors of control particle size, as well as the effects of nucleation growth process, are currently in progress.

4. Conclusion

This paper described the feasibility synthesis of nanocrystalline metal oxides (ZnO, NiO, and SnO_2) powders in a surfactant medium. Surfactant appears to play an important role in this synthesis. It is used to produce dispersed particles in the synthesis process or disperse as-synthesized agglomerated fine particles. Present investigations prove that the surfactant-mediated method is a new useful method for the preparation of nanocrystalline metal oxides powders. With the method, nanocrystalline ZnO, NiO, and SnO_2 powders with narrow particle distribution and an average 54.3, 25.5, and 18.2 nm particle sizes were obtained.

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