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Doughnut-shaped zinc oxide particles

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Abstract Zinc oxide doughnut-shaped particles were synthesized using a chemical route. A possible growth model has been proposed from a detailed experiment in which samples were picked from the reaction chamber at various time intervals and characterized using scanning electron microscopy (SEM). Particles were also characterized using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Introduction

Recently, synthesis of materials with different sizes, shapes, and architecture has become an interesting as well as important aspect of materials research due to novel applications of such materials ranging from electronics to drug delivery [1–5]. Zinc oxide is an important material for which size- and shape- dependent properties and applications have been demonstrated. It has been grown in a variety of shapes, such as spherical particles, rods, flowers, belts, nanohelices, tubes, tetra pods, wires, needles, combs, dandelions, cages, shells [6–13], etc. with sizes from nanometers to micrometers. Zinc oxide bulk material is a semiconductor with direct wide band gap of 3.3 eV and is useful in many applications such as UV lasers, low-voltage field emitter [14–16] etc. Jezequel et al [17] obtained monodispersed particles of various sizes by changing the rate of reaction. It has been showed by Seeling et al [18] that monodispersed ZnO spheres can be self organized in face centered cubic lattice exhibiting photonic band gap property. Liang et al [19] have synthesized ZnO doughnut-shaped microparticles by hydrothermal route. Thus there is a considerable interest in synthesizing ZnO particles.

In one of our synthesis protocols, we found that we are getting doughnut-shaped ZnO particles. Therefore, we removed the samples at various time intervals during the synthesis and investigated the growth of these doughnut shapes. Here, we discuss the synthesis procedure and present the analysis of these novel particles.

Experimental

Synthesis of zinc oxide particles was carried out as follows: Zinc acetate di-hydrate [$Zn(CH_3COO)_2\ 2H_2O$], and di-ethylene glycol [$(HOCH_2CH_2)_2O$] were used as precursors. In a typical reaction 0.05 M zinc acetate was dissolved in 10 mL double distilled water and 140 mL di-ethylene glycol was added to it. The solution was allowed to stir for 1 h at room temperature and then processed in autoclave [Paar Instrument, USA]. The temperature of the autoclave was increased from room temperature to 160 °C. Heating rate varied from ~4 °C/min to 10 °C/min, in order to investigate the effect of heating rate. The resultant precipitate was washed and dispersed in ethanol. Samples were removed from autoclave at various time intervals from 30 min to 4 h, in an experiment in which heating rate was ~4 °C/min.

Scanning electron microscopy was used to study the morphology of the samples. JEOL JSM-6360 scanning electron microscope was used with accelerating voltage kept at 20 kV and current ~60 µA. Samples were prepared by spin coating the films on glass plates on which thin layers of platinum were sputtered to obtain adequate conductivity.

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X-ray diffraction was done on powder samples using Philips PW 1840 diffractometer with Cu K_α (λ = 0.154 nm) source of X-rays and nickel foil as the filter.

X-ray photoelectron spectroscopy (XPS) was carried out on powder samples using ESCALAB MK II system of the VG Scientific UK. Al K_α ($h\nu$ = 1486.6 eV) was used to excite the photoelectrons and a concentric hemispherical analyzer was used to analyze the photoelectrons. Au $4f_{7/2}$ at binding energy 84.0 ± 0.2 eV was used as an external reference and C 1s at 285.0 eV as an internal reference for the binding energy calibration.

Results and discussion

Monodispersed ZnO spherical colloidal particles have been reported earlier by Jezequel et al [17] and Seeling et al [18]. They have used zinc acetate and diethylene glycol and solution has heated at 160 °C as done in our case. Jezequel et al obtained monodispersed powders of various sizes by changing the rate of reaction. Seeling et al made the synthesis in two steps. The first step is similar to that of Jezequel et al but in the second step they basically remove polydisperse particles by centrifugation and use supernatant solution to grow monodispersed particles. Although we too have used similar chemicals and reaction temperature of 160 °C, our results differ from previous work by Jezequel et al and Seeling et al due to use of autoclave in carrying out the reaction. Using the autoclave we not only controled the heating rate and reaction temperature accurately, but also carried out the reaction at high pressure and not in ambient. As a result, we obtained doughnut-shaped particles in our synthesis.

Zinc oxide doughnut-shaped particles were synthesized using a chemical route. Reaction time was varied to understand the growth steps involved in the formation of the spheres. It was observed that addition of water plays an important role in the formation of ZnO spheres. No sphere formation was observed without water and the final product was a transparent solution without any precipitate. The chemical reaction responsible for the formation of ZnO can, therefore, be written as

$$\mathrm{Zn(CH_3COO)_2 + 2H_2O \rightarrow Zn(OH)_2 + \ 2(CH_3COOH)}$$

$$\mathrm{Zn(OH)_2 \rightarrow ZnO + H_2O}$$

Initially, the sample processed in autoclave by heating at 160 °C with heating rate of 10 °C/min for 4 h was investigated. Scanning electron micrographs of the doughnut-shaped particles are illustrated in Fig. 1. It can be seen from Fig. 1(a) that most of the particles have a doughnut shape. Magnified image of such doughnut particle has been shown in Fig. 1(b). Inner diameter of the doughnut is ~750 nm and outer diameter is ~5 μm. Similar morphology was observed for the lower heating rate (~4 °C/min), shown in Fig. 2(c). In this case, size of doughnuts is less than that observed for higher heating rate, (~10 °C/min) discussed above. Thus it is clear that heating rate affects size of the doughnuts as it changes the rate at which particle agglomeration is taking place in the initial steps of doughnut formation.

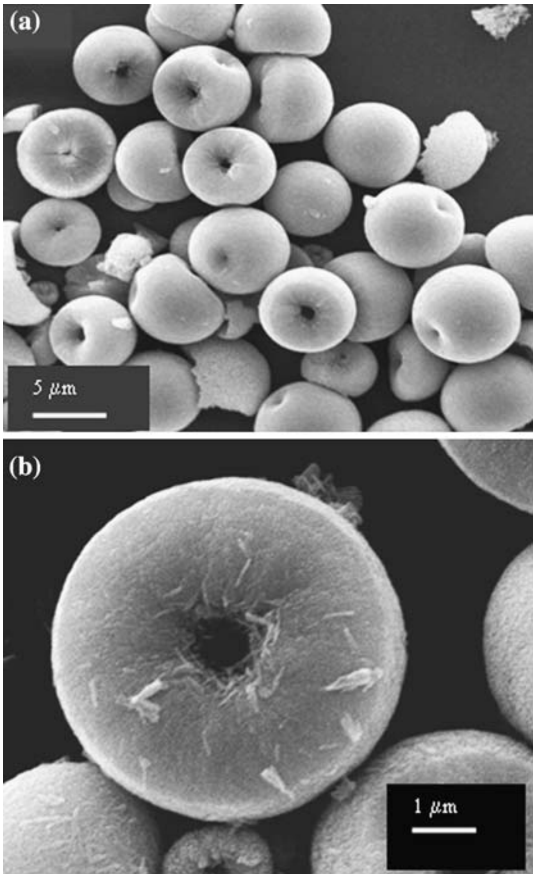

Fig. 1 Scanning Electron Micrographs (SEM) showing ZnO particles. (**a**) Low magnification of uniform doughnut-shaped ZnO particles. (**b**) High magnification of doughnut-shaped ZnO particles. Samples were synthesized with higher heating rate (~ 10 °C /min)

In order to understand the growth of the doughnut-shaped particles, we have carried out scanning electron microscopy analysis for samples with lower heating rate, removed at various time intervals from the autoclave. The doughnut-shaped particles of ZnO grow progressively. Few steps can be understood from the SEM images grabbed as in Fig. 2. Figure 2 (a), which is an SEM image of the sample removed after 180 min, shows agglomerating ZnO spheres. Few of them have been indicated by arrows. The average size of individual agglomerating sphere in this case was observed to be ~900 nm. Size of the bigger particle formed due to such agglomerating particles was calculated to be in the range of 1.5–1.7 μm. After 210 min of reaction

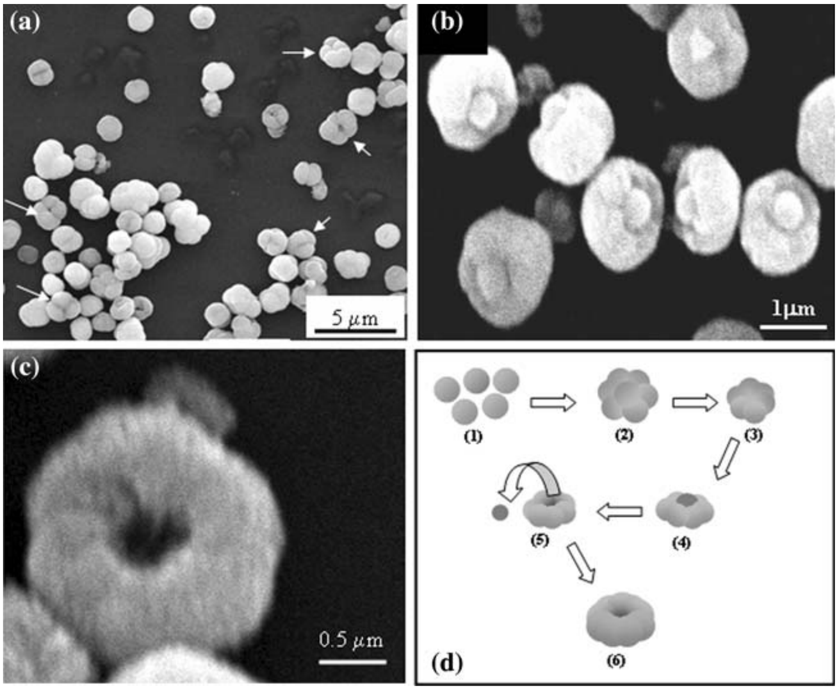

Fig. 2 SEM images of (**a**) Agglomerating particles, (**b**) step where a particle at center was forced out due to shrinking (**c**) Doughnut-shaped particles with central cavity and (**d**) growth model for steps involving in formation of ZnO doughnut-shaped particles based on SEM observations. Samples were synthesized with lower heating rate (~ 4 °C /min)

an interesting thing was observed. Agglomerating particles take form of a coalesced spherical particle with central part as a distinct particle. With more reaction time the spheres continue shrinking in the size and after 240 min spherical particle at the center is forced out to form a cavity which is observed in Fig. 2(c).

This leads us to propose (see Fig. 2d) that ZnO particles in step (1) come together to form nearly hexagonal particles (step 2). With increasing reaction time (step 3 and 4) the particles start contracting and push (step 5) the central particle out, forming a doughnut shape as in step 6.

X-ray diffraction analysis of doughnut-shaped ZnO particles reveals that the particles are highly crystallized and exhibit hexagonal wurtzite structure. The interplanner distances were calculated for the various planes observed in the diffraction pattern (Fig. 3) and compared with standard JCPDS data [JCPDS data card no: 05- 0664].

In order to determine the purity of the particles, X-ray photoelectron spectroscopy was performed. Figure 4 (a–d) gives survey scan and detailed scans for zinc, oxygen, and carbon core levels. From the survey scan it is clear that no other element than zinc and oxygen is present in the sample apart from some carbon. Figure 4 (b) gives the Zn 2p spectrum. Binding energy positions recorded for Zn $2p_{3/2}$ and $2p_{1/2}$ are 1021.9 and 1044.9 eV respectively. Spin orbit splitting is thus 23.0 eV. Comparison with standard data [20] reveals that Zn is in the oxide form.

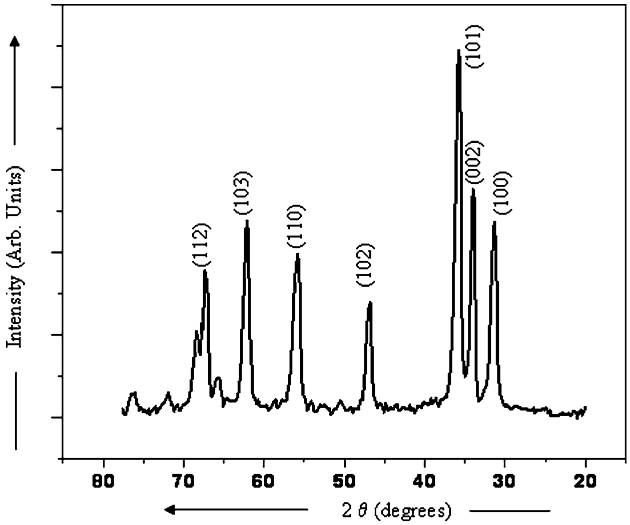

Fig. 3 X-ray diffraction pattern of doughnut-shaped ZnO particles

Figure 4(c) gives O 1s spectrum with peak at binding energy of 531.5 eV. Concentrations of zinc, oxygen and carbon calculated are 33.4%, 47.8% and 18.8% respectively. More oxygen than zinc seen is possible in case of ZnO as it is known that excess oxygen is always present on the surface of the particles in the form of hydroxide [18, 21]. In order to confirm this, oxygen 1s spectrum was deconvoluted. Two components with FWHM of 2.0 eV could be fitted. A component at 531.5 eV is due to the oxygen present in the sample in co-ordination with Zn and another component at 533.2 eV is probably, due to the oxygen in the form of hydroxide present on the surface of the particles. However, hydroxide component is much smaller than that to pure oxides. Thus, we have obtained pure, crystalline ZnO doughnut-shaped particles with small amount of $Zn(OH)_2$ in surface region. Figure 4(d) shows detailed scan

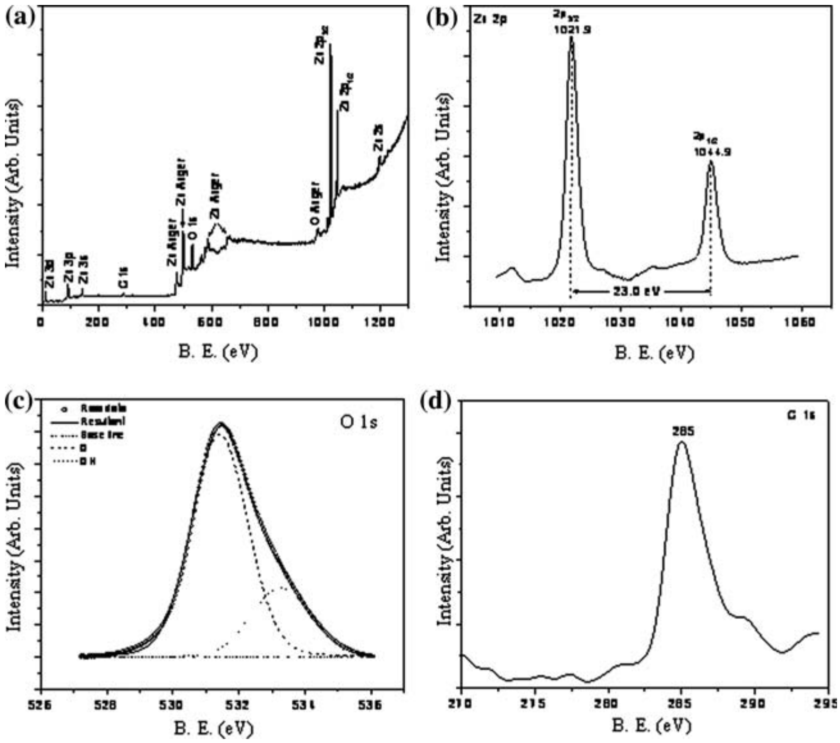

Fig. 4 XPS of doughnut-shaped ZnO particles. (**a**) survey scan, (**b**) detail scan for Zn 2p and (**c**) detailed scan for O 1s deconvoluted into two components (**d**) detailed scan for carbon 1s

for carbon 1s spectrum. Peak appearing at 285.0 eV is due to aliphatic carbon from the zinc acetate and di-ethylene glycol used in the synthesis. The peak may also have some contribution from sample handling, presence of some carbon or carbon gases in analysis chamber. A small component present at $\sim$289.0 eV is due to the carbon bonded to oxygen in the di-ethylene glycol [20].

Removal of samples at various time intervals and their analysis has led to the understanding of processes occurring during the growth of doughnut shape ZnO particles. However, more experiments using transmission electron microscopy (TEM) along with selected area diffraction and theoretical analysis would be necessary for complete understanding of the growth. Such efforts are in progress.

Conclusion

Chemical synthesis of novel doughnut-shaped ZnO spheres has been demonstrated. XRD and XPS study shows that spheres are of wurtzite structure and of high purity. SEM analysis of samples suggests that spherical particles agglomerate to form bigger spherical particles which eventually contract. This results in the removal of central particles which is responsible for the formation of novel doughnut shape particles.

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