

Water / Alcohol Mediated Preparation of ZnO Hollow Sphere

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ZINC oxide (ZnO) hollow spheres have been successfully prepared by a template free hydrothermal method with the assistance of polyvinyl pyrrolidone (PVP) at 90°C. PVP was introduced to improve the stabilization of crystalline phase occurred at a rate commensurate with localized Ostwald ripening and self-transformation for producing ZnO hollow spheres. The effect of solvent system (water/ ethanol) composition was studied. The structure, composition and morphology of (ZnO) hollow spheres were characterized by XRD, EDS and SEM. Also, optical properties of the prepared ZnO hollow spheres were studied using UV-vis spectrophotometer. The prepared hollow spheres have hexagonal wurtzite structure with particle size range from 150-600 nm depending on the reaction medium composition and shell thickness from 50 to 70 nm.

Keywords: A.Semiconductors, A. Oxides, B. crystal growth and D. Optical properties.

Recently, more and more attention has been attracted to synthesis of porous materials because their different macroscopic morphologies are found to present different properties, which greatly affect their potential applications. Due to large surface area, high porosity and low density, porous materials are important functional materials which can be applied in the field of catalysis⁽¹⁾, sensor^(2,3), luminescence⁽⁴⁾, gas storage⁽⁵⁾ and host guest chemistry⁽⁶⁾. Porous semiconductor photocatalysis are attractive in applications such as bioengineering and photocatalysis, through minimizing the distance between the site of photon absorption and electron/hole redox reactions to improve efficiency⁽⁷⁾. The conventional method for porous material production involves the introduction of template molecules⁽⁸⁾, directional freezing⁽⁹⁾ and ultrasonic spray pyrolysis⁽¹⁰⁾. Hollow spheres are of great interest among porous materials because of their technical applications in optical, electronic, magnetic, catalytic, acoustic and sensing devices ranging from photonic crystals to drug delivery carriers⁽¹¹⁻¹³⁾. The preparation of hollow spheres with various shapes and varying sizes has got

much more attention, due to their low density, high specific surface area and potential applications⁽¹⁴⁻¹⁷⁾. However, except silica-based porous materials, there are few successful cases about precise control over the morphology of porous materials. Therefore, to explore a simple strategy for morphology controlled synthesis of porous materials is still a significant challenge for modern synthetic science. As an n-type metal oxide semiconductor ZnO is an important wide bandgap (3.37 eV) semiconductor with large excitation binding energy (60 meV)⁽¹⁸⁾. moreover, ZnO has been a focus of current research interest due to its promising applications in various fields, including short-wavelength light-emitting diode and room temperature ultraviolet (UV) lasing diode⁽¹⁹⁾, solar cell⁽²⁰⁾, piezoelectric and optoelectronic device⁽²¹⁾, UV-absorber⁽²²⁾, transparent conductor⁽²³⁾, field-emission display⁽²⁴⁾ and gas sensor⁽²⁵⁾. In addition, it has also been demonstrated that ZnO has potential applications as a photocatalyst for the degradation of organic dyes⁽²⁶⁾. It is well-known that the novel properties of materials are obviously dependent on crystallinity, crystal size, crystallographic orientation and morphology. Therefore, development of a morphologically controllable synthesis of ZnO semiconductor is urgently important to answer the demand for exploring the potential applications of ZnO. Among diverse morphologies of ZnO, ZnO particles with a porous structure have attracted increasing attention in recent years since porous particles may present potential properties superior to corresponding solid structures. As far as we know various porous ZnO structures, including porous pyramids⁽²⁷⁾, porous nanotubes⁽²⁸⁾, mesoporous polyhedral cages⁽²⁹⁾, porous hexagonal disks⁽³⁰⁾, porous nanowires⁽³¹⁾, and porous nanobelts⁽³²⁾, have been successfully prepared by means of various methods, but only a few cases have reported the synthesis of pure porous ZnO spheres⁽³³⁾. This study demonstrates a template-free hydrothermal method to prepare ZnO hollow spheres at 90°C by the aid of PVP and using glucose as reducing agent. Compared with the conventional methods, the present synthetic procedure has the advantages of simplicity (without any special equipments or templates), low growth temperature (90°C) and high efficiency. Effect of water/ethanol mediating system composition was studied.

Materials

Zinc acetate monohydrate $Zn(Ac)_2 \cdot H_2O$ 99% was supplied from Sigma&Aldrich Company, Triethanolamine (TEA) 98% Oxford laboratory reagent, sodium hydroxide was supplied from Adwic Company, polyvinylpyrrolidone (PVP) M.wt=10.000 g/mole and Glucose (-D- glucose 96% from El Nasr pharmaceutical chemicals co. Absolute ethanol used in this paper were purchased from Sigma – Aldrich (USA), Distilled water was used through out this study.

Experimental

In typical procedure 0.26 gm of zinc acetate monohydrate and 1.49 g of TEA were dissolved in 60 ml (ethanol: water) in different concentrations as (2:3) (0:1) (1:1) (1:3) (1:0) (3:2) (3:1) (2:1) in volume solutions. The mixture was stirred for 15 min then 0.02 gm of NaOH and 0.8 gm of PVP were added to mixture under

constant stirring. 2 ml of (1M glucose) solution was added with constant stirring. The resulting mixture was transferred into Teflon lined stainless steel autoclave ($v=100$ ml) and put in oven at 90°C for 6 hr and cooled to room temperature. The white precipitate was centrifuged and washed by distilled water and ethanol and finally, dried in vacuum oven at 60°C for 10 hr.

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku D/max-2500X-ray diffractometer with Cu K α radiation ($\lambda=1.5418\text{\AA}$). Scanning electron microscope (SEM) images were performed on a JEOL JEM-6700F microscope operating at 5kV. – Voltage of 200kV. UV–vis absorption spectra were recorded using a spectrophotometer (3100UV–vis–NIR).

Results and Discussion

The crystal structure of the products was confirmed by X-ray diffraction (XRD) as shown in Fig. 1 The positions of the XRD peaks show good agreement with those of the JCPDS (36–1451) data of the zinc oxide with hexagonal phase. The peaks at 2θ values of 31.9° , 34.5° , 36.4° , 47.6° , 56.7° , 62.9° , 68.0° and 69.2° correspond to the crystal planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1), respectively, of the crystalline zinc oxide. The average size of the as synthesized crystalline ZnO, calculated from the half-width of the (1 0 0) diffraction peak using the Scherrer formula⁽³⁴⁾. In particular, it was observed that the increase of organic solvent percentage in the medium of the reaction up to 50% accompanied with decrease in the peak intensities. This behavior indicates the decrease in the crystallite size (table1). Meanwhile with further increase of the ethanol percentage up to 75% it was found that the crystallite size increases again (Table1). But in case of using 100% ethanol there is no distinguished XRD pattern indicating that there was a reaction occurred.

TABLE. 1. Explaining the crystal size for the ZnO hollow spheres.

Ethanol-Water Ratio	Percentage of Water %	Crystal Size
(0 : 1)	100 %	35.24 nm
(1 : 3)	75 %	27.61 nm
(2 : 3)	60 %	14.81 nm
(1 : 1)	50 %	14.49 nm
(3 : 2)	40 %	20.85 nm
(3 : 1)	25 %	24.188 nm
(1 : 0)	0 %	-----

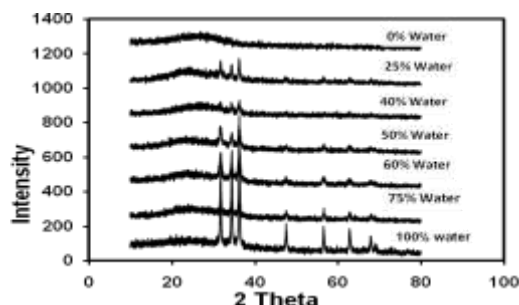


Fig. 1. A typical XRD pattern of the as-prepared ZnO hollow spheres.

Figure 2 shows the SEM images of ZnO prepared by different water/ethanol composition as mediating solvent. The SEM images show that the produced ZnO particles are of spherical structure with diameter range from 150 nm to 600 nm according to medium used in preparation. There was some open mouth or broken spheres indicating that the spheres are hollow structured showing the shell diameter to be 50-70 nm in thickness. It was noticed that the surface of the spheres is coarse suggesting that the shell consists of primary ZnO nanoparticles also the inner surface of produced ZnO spheres is rough. The particle size was found to decrease at first with increasing ethanol content up to 50% and then increase with further increasing up to 75%.

Metal atomic composition (Zn: O atomic ratio) determined by EDS analysis is Zn: O is much closed to 1:1 atomic ratio. During the EDS analysis, no peaks for C or Na were observed, which insure that the reaction takes place and produces pure ZnO samples. In all produced ZnO mediated with different ethanol/water composition except that in case of using ethanol as a solvent peaks belong to carbon appeared which insure that the reaction did not proceed.

Recently, PVP has been used as a surfactant playing a very important role in synthesis of nanomaterials⁽³⁵⁻³⁷⁾. Surfactant in such reactions plays a role of structure directing agents which influence growth direction of zinc oxide nanoparticles^(3,38). PVP with pyrrolidone ring and aliphatic chain provide a large – sized hydrophilic segment and also long slim lipophilic segment. This structure with high carbonyl group density represents different sites of adsorption of primary ZnO clusters initially nucleated from the solution⁽³⁹⁾. As the adsorption of ZnO primary particles on the hydrophilic segment started, new formed ZnO particles adsorbed. Simultaneously, this aggregation of ZnO was produced with certain curvature with the aid of NaOH which may play a role in surface modification to serve as structure - directing agent⁽⁴⁰⁾. Formation mechanism of ZnO hollow spheres could be explained in sight of that in the beginning Zn^{2+} react with NaOH to give $Zn(OH)_2$ which is in second step react with excess $(OH)^-$ group to give a relatively stable complex (Eq. 1, 2)



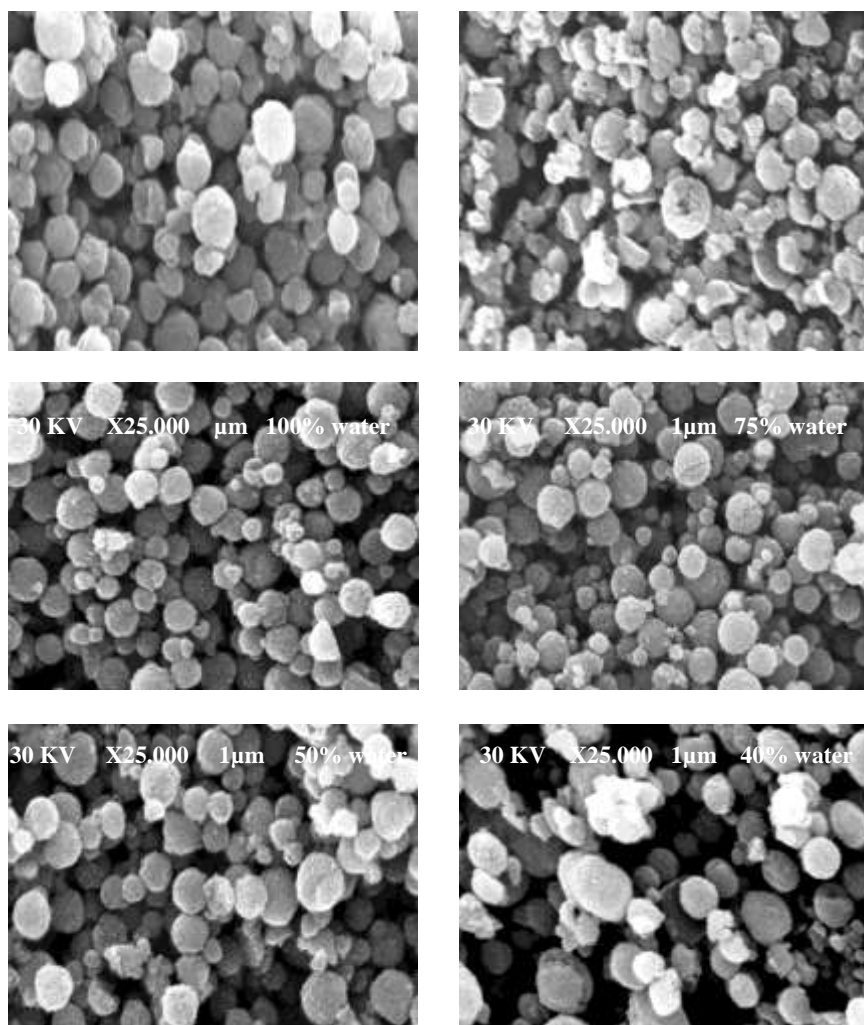


Fig. 2. SEM images of ZnO hollow spheres (a:100%, b:75%, c:60%, d:50%, e:40% and 25%) water.

This zincate complex may be responsible decreasing the Zn^{2+} concentration in the solution which is lowering the rate of ZnO formation infavor the nucleation and growth of ZnO particles in spherical form. By the reducing action of glucose, the produced $Zn(OH)_2$ reduced to give ZnO (Eq .3)



In water/ethanol mediating system, water provides the strong polar interaction but very weak dispersive interaction. Meanwhile ethanol, as well, provides polar interaction less polar than water and strong dispersive interaction. In general increasing ethanol content in water /ethanol systems increases the dispersive characters of the solvent medium that was leading to decrease of the crystallite size. That was noticed as ethanol content increased up to 50% the crystallite size decreased from 35.24 to 14.49nm. But with further increase in ethanol content from 50 to 75% the crystallite size increased from 14.49 to 24.19nm. This behavior could be attributed to the competition between dispersive action and polarity action where it was cited that as the polarity of the solvent decreases the crystallite size increases⁽⁴¹⁾. In case of using 100% ethanol as solvent it was found that there was no reaction occurred; this could be due to the polarity of ethanol stabilizes the zincate complex form and makes it difficult to transformed into zinc hydroxide which is dissociated to give ZnO.

Figure 3 represents the UV – vis absorption spectra of different aqueous / ethanol mediated ZnO samples. The absorption edge cut off was observed at 390 nm for 100% aqueous mediated ZnO sample, meanwhile absorption edge cut off of 75% water / 25% ethanol mediated ZnO sample was observed at 388 nm and decreased to 368 nm for 50% water / 50% ethanol. Blue shift was observed implying lower particle size of ZnO particles with increasing ethanol percentage in medium composition. This blue shift in the absorption may be due to the decrease of optical scattering caused by grain growth and the reduction of grain boundary density^(42,43). As for ZnO mediated with 40% water / 60% ethanol the edge cut off was observed at 376 nm and increased to 380 nm for 25% water / 75% ethanol implying further increase in particle size with increase of ethanol percentage over 50% of the medium.

Band gap energy calculated to be ranged from 3.185 eV for aqueous mediated ZnO sample with the largest crystallite size to 3.375 eV for 50% aqueous 50% ethanol mediated ZnO sample with the smallest crystallite size. This range of band gap energy is reasonably matching with the reported value (3.37 eV)⁽⁴⁴⁾.

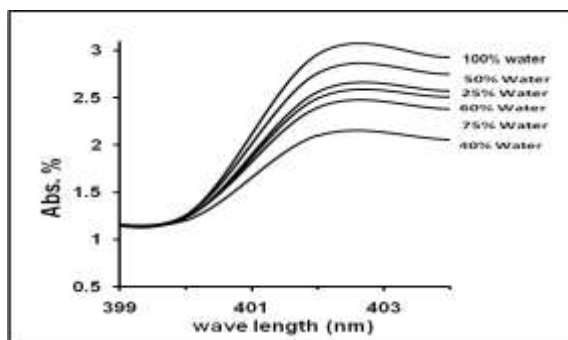


Fig. 3. UV–vis absorption spectra of ZnO hollow spheres.

Conclusion

ZnO hollow spheres were successfully synthesized at lower temperature 90° C with the help of PVP through an effective and simple method. The as-prepared ZnO shows a perfectly hollow spheres structure with diameters of 150 nm-600 nm due to type of solvent as absolute ethanol or distilled water. The formation of hollow spheres might be a PVP-assisted Ostwald ripening process. The ZnO hollow spheres with low density and high surface area prepared using this method could have widespread uses as sensors, catalysts and material encapsulators or carriers. This method is very simple, mild, environmentally safe and economically favored, and it may be a general procedure for the preparation of metal oxide nano/microspheres with a hollow interior.

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تحضير كرات مجوفة من اكسيد الزنك في وسط من الماء والكحول

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و** قسم المتوالفات والمواد متناهية الصغر -مدينة الأبحاث العلمية والتطبيقات
التكنولوجية – الأسكندرية – مصر.

تم تحضير كريات اكسيد الزنك الجوفاء باستخدام وسط للتفاعل مكون من الكحول و الماء بنسب مختلفة و ذلك في وجود البولي فينيل بيروليديون كقالب للتحكم في الشكل. تمت دراسة تأثير النسب المختلفة لوسط التفاعل كذلك تم توصيف اكسيد الزنك الناتج باستخدام حيود الاشعة السينية XRD و الميكروسكوب الضوئي الماسح SEM وكذلك تمت دراسة الخواص البصرية باستخدام جهاز قياس انعكاس و امتصاص الاشعة المرئية و الفوق بنفسجية UV-Vis spectrophotometer. وقد تبين ان الكريات الجوفاء لأكسيد الزنك المتكونة لها شكل بلورى سداسى مع حجم جسيمات يتراوح بين 150-600 nm اعتمادا على تركيب وسط التفاعل و يتراوح سمك القشرة الخارجية للكريات من 50-70 nm.