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Paper

A Facile Approach to Fabrication of Hollow ZnO Nanoparticles

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ABSTRACT: Well-defined, monodispersed hollow ZnO nanoparticles were successfully synthesized by a facile one-pot solution method at room temperature. Hollow ZnO nanoparticles were fabricated using polystyrene nanoparticles as seed particles. The removal of core particles via solvent extraction yields hollow nanoparticles. The structures and morphologies of the obtained products were characterized with Fourier transform infrared (FT-IR), Thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction pattern (XRD) and Scanning electron microscopy (SEM). The formation mechanism of the hollow structure of the ZnO nanoparticles was also investigated. The technique developed here is expected to be useful in the preparation other metal oxides and hollow architectures.

Key Words: ZnO, Hollow morphology, Solvent extraction, Nanostructure

1. INTRODUCTION

In recent years, the fabrication and architecture of hollow nano and microstructures have attracted considerable attention because of their novel structures and unique properties, which include low density and high specific surface area. They have been used extensively for various applications such as gas sensors, lithium ion batteries, drug delivery, luminescent materials and catalysts [1-4]. From a survey of the literature, it is clear that the morphology, crystal structure, and size distribution of the materials plays an important role in the performance of the materials and can significantly influence the function of fabricated devices [5-7]. Consequently, different kinds of inorganic nano- and micromaterials with defined morphology and distribution have been prepared for particular applications, such as nanowires, nanorods, nanosheets, nanocages, nanoflowers, spherical hollow structures and amongst others [8-12]. However, hollow microspheres, self-assembled by a mass of nanostructures, have recently gained great interest due to their unique architecture, which may provide opportunities for exploring novel material characteristics, and may be useful in the manufacturing of advanced devices. Numerous materials with spherical hollow structures comprised of subunits have been prepared to date, such as ZrO, TiO_2, and SiO_2 [13-18].

Among the various functional materials, ZnO has been considered as an exceptionally important and versatile metal oxide. It has been widely investigated for its use in field effect transistors, optical devices, dye-sensitized solar cells and gas sensors [19-21]. The key to its application in these fields lies in its shape and composition. The success of these applications strongly depends on the availability of hollow ZnO nanoparticles with tightly controlled size, uniform distribution and controllable surface properties [22,23]. Thus, it is very important to develop a simple, stable and fast synthetic process to improve the quality and homogeneity of hollow ZnO nanoparticles.

In this study, based on our previous synthesis of well-defined nanoparticles [24], we demonstrate a novel method for synthesizing hollow ZnO nanoparticles with different morphologies by utilizing polystyrene (PS) nanoparticles as templates. The evolution process of hollow ZnO nanoparticles is described, and the corresponding synthetic mechanism is also discussed in detail. The preparation and morphology of hollow ZnO nanoparticles were investigated by XRD, XPS, SEM, and TGA.

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2. MATERIAL AND METHODS

2.1 Materials

All of the chemicals were used as received from Sigma Aldrich without any further purification. Chemical reagent (from Sigma Aldrich) such as Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$). Distilled water was used throughout the experiment.

2.2 Fabrication of hollow ZnO nanoparticlels

Synthesis of hollow ZnO nanoparticles: Hollow ZnO nanoparticles were prepared by a simple, rapid, low temperature solution method using zinc acetate dihydrate as a zinc source. In the first step of the synthesis of PS particles, styrene (5 mL, 43.5 mmol) and 4-styrenesulfonic acid sodium salt hydrate (0.019 g, 0.09 mmol) were dissolved in 25 mL of deionized water with subsequent addition of sodium bicarbonate (0.032 g, 0.38 mmol). The mixture was then stirred at room temperature and then potassium peroxodisulfate (0.09 g, 0.33 mmol) and 25 mL of deionized water were added. The reaction solution was then heated to 72°C for 24 h. In the second step of the synthesis of PS-ZnO core-shell particles, 6 mL of the PS particle solution in 10 mL ethanol was used as a substrate to grow a ZnO shell. Zinc acetate dihydrate (0.878 g, 80 mmol) was dissolved in 20 mL absolute ethanol and was added to the PS solution. Lithium hydroxide (0.5 g, 12 mmol) was dissolved in 20 mL absolute ethanol and stirred at room temperature for 30 min until the solution became transparent [25]. The as-prepared particles were washed using absolute ethanol, and the washing process was repeated 3 times. In the last step, the as-prepared PS-ZnO core-shell particles were dispersed into toluene with stirring for 4 h. The entire process comprised of the PS-ZnO core-shell particles synthesis followed by removal of remaining PS particles by toluene.

2.3 Characterization

The sizes and morphologies of the as-prepared samples were characterized by a scanning electron microscope (SEM, JEOL, JSM-7000F). The composition and phase of the hollow ZnO nanoparticles were identified using an X-ray diffractometer (XRD, Bruker D8) with Cu *Kα* radiation and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher). The component analysis of samples was performed by Fourier transform infrared spectroscopy (FT-IR, VERTEX-70, Bruker) in the wavelength range of 400-4000 cm^{-1}. The surface area of the hollow ZnO nanoparticles was evaluated by thermal degradation analyses (TGA, Perkin-Elmer Pyris6-TGA) from 50°C to 800°C at a heating rate of 10°C/min in air.

3. RESULTS AND DISCUSSION

The formation mechanism of the hollow ZnO nanoparticles is depicted in Fig. 1(a). It consisted of three steps. First, PS nanoparticles were prepared as a template via atom transfer radical polymerization (ATRP) process, which was followed by a growth step to form ZnO shells and finally a washing step to remove excess PS particles. During the formation of the ZnO shell, the PS core particles were dissolved to obtain hollow ZnO nanoparticles. The morphology of the as-prepared hollow ZnO nanoparticles was characterized by scanning electron microscopy (SEM). The average diameter of the PS core particles was 430 nm as estimated from the SEM image shown in Fig. 1(b). The SEM images of the PS-ZnO core-shell particles and hollow ZnO nanoparticles are shown in Fig. 1(c) and Fig. 1(d) and were determined to have a diameter of 480 nm and 470 nm, respectively. The as-prepared hollow ZnO nanoparticles are smaller than that of PS-ZnO core-shell particles. The decrease in size was due to shrinkage in the shell after PS core was removed.

A typical XRD pattern of the as-prepared hollow nanoparticles is shown in Fig. 2(a), where all the diffraction peaks are in good agreement with those of the hexagonal structure of ZnO. The calculated lattice constants were α = 3.25 Å and c = 5.21 Å, which were in good agreement with the file of ZnO (JCPDS No. 36-1451). No other diffraction peaks could be observed in the pattern, implying that the PS core particles

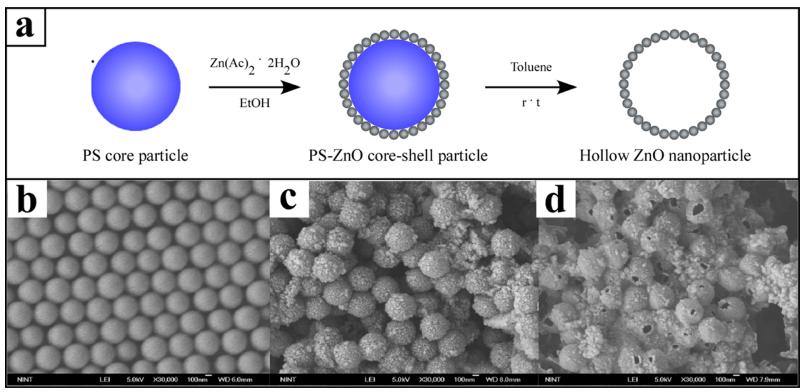

Fig. 1. (a) Schematic representation of the formation of ZnO hollow nanoparticles. SEM image of ZnO (b) PS core particles (CP) (c) PS-ZnO core-shell particles (CSP) (d) ZnO hollow nanoparticles (HP)

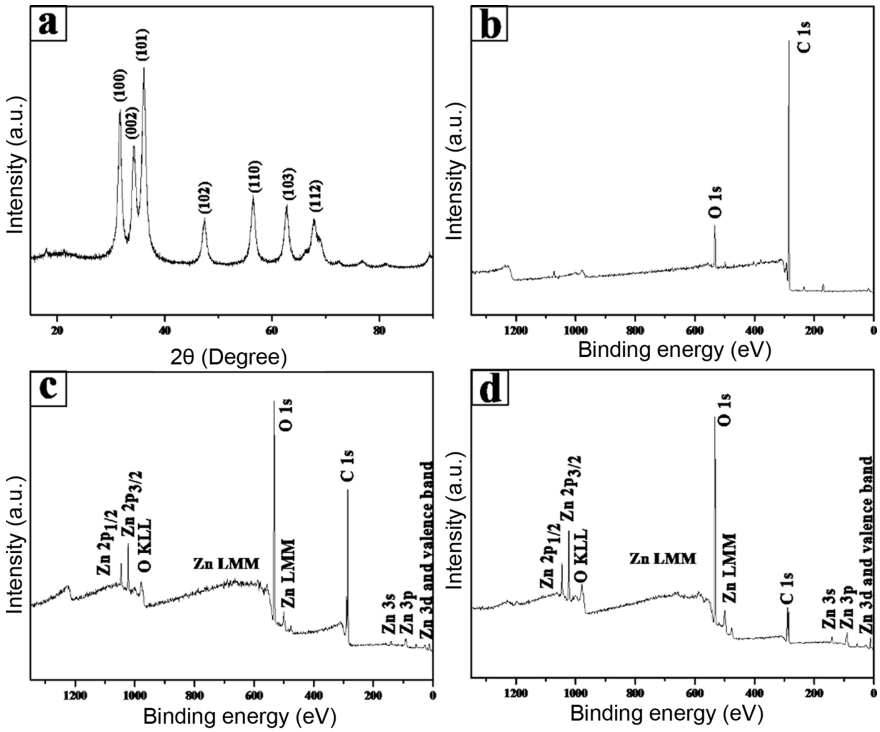

Fig. 2. (a) XRD pattern of the as-obtained ZnO hollow nanoparticles. XPS spectra of ZnO (b) PS core particles (CP) (c) PS-ZnO core-shell particles (CSP) (d) ZnO hollow nanoparticles (HP)

were completely removed. The elemental compositions of the as-prepared samples were analyzed using X-ray photoelectron spectroscopy (XPS) techniques. Fig. 2(b), (c) and (d) show the XPS survey spectra from PS particles, PS-ZnO core-shell particles and ZnO hollow nanoparticles, in which all of the peaks can be only ascribed to Zn, O and C as labeled in Fig. 2(d). The binding energies of both Zn $2p_{1/2}$ (1045.1 eV) and Zn $2p_{3/2}$ (1022.2 eV), as indicated in Fig. 2(c) and (d). In Fig. 2(c) and (d), it is clear that the O_{1s} (531 eV and 532 eV) is asymmetric, indicating that two oxygen species are present in the near field region. After the PS core particles were removed, the carbon C 1s peak (285.0 eV) disappeared.

The FT-IR absorption spectra of the ZnO hollow nanoparticles are shown in Fig. 3(a). In all the samples, the main peaks corresponding to the PS core particles are at 697, 757, 1452 and 1493 cm^{-1}. For the FT-IR spectrum of ZnO hollow nanoparticles, the characteristic peaks of PS are weaker because of the PS core particle removal, but the stretching peaks of ZnO were prominent at 490 cm^{-1}. Fig. 3(b) shows the thermal decomposition behavior of the PS core particles and PS-ZnO core-shell particles as determined by TGA. The decomposition temperature of the PS-ZnO core-shell particles is significantly higher than that of the PS core particles. According to TGA, the weight percentage of ZnO and PS in the PS-ZnO core-shell particles is 71 and 29%, respectively. The final residue mass was 29% of the original, in accordance with the experimental result. This can be related to the overall yield of the total synthesis of ZnO hollow nanoparticles.

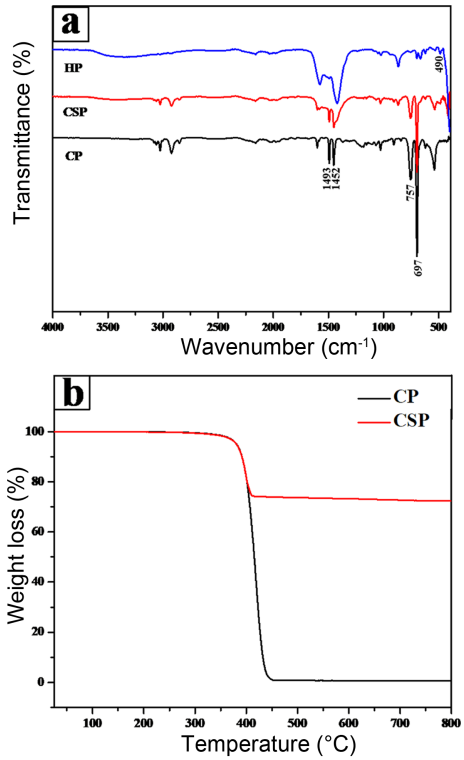

Fig. 3. (a) FT-IR spectra of PS core particles (CP), PS-ZnO core-shell particles (CSP) and ZnO hollow nanoparticles (HP). (b) Thermal degradation behavior of PS core particles (CP), PS-ZnO core-shell particles (CSP), and ZnO hollow nanoparticles (HP)

4. CONCLUSIONS

We have demonstrated that after the removal of PS from the core-shell particles, ZnO hollow nanoparticles with shell thicknesses from 30 to 50 nm were obtained. During the synthesis of the ZnO hollow nanoparticles it was found that the formation process of the PS-ZnO core-shell particles had an important effect on the morphology of the hollow nanoparticles. The methods used in this study are simple and cost-effective, which are suitable for larger scale production of ZnO hollow nanoparticles. The synthetic technique should pave the way for preparation of similar materials with potential application as catalysts, sensors, and photoelectric devices.

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REFERENCES

1. Zhu, C., Lu, B., Su, Q., Xie, E., and Lan, W., "A Simple Method for the Preparation of Hollow ZnO Nanospheres for Use as a High Performance Photocatalyst," *Nanoscale*, Vol. 4, 2012, pp. 3060-3064.
2. Zhang, J., Wang, S., Wang, Y., Xu, M., Xia, H., Zhang, S., Huang, W., Guo, X., and Wu, S., "ZnO Hollow Spheres: Preparation, Characterization, and Gas Sensing Properties," *Sensors and Actuators. B*, Vol. 139, 2009, pp. 411-417.
3. Tang, S., Huang, X., Chen, X., and Zheng, N., "Hollow Mesoporous Zirconia Nanocapsules for Drug Delivery," *Advanced Functional Materials*, Vol. 20, 2010, pp. 2442-2447.
4. Wang, Z., Zhou, L., and Lou, X.W., "Metal Oxide Hollow Nanostructures for Lithium-ion Batteries," *Advanced Materials*, Vol. 24, 2012, pp. 1903-1911.
5. Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., Yin, Y., Kim, F., and Yan, H., "One-dimensional Nanostructures: Synthesis, Characterization, and Applications," *Advanced Materials*, Vol. 15, 2003, pp. 353-389.
6. Lee, S.B., Kim, J.B., Lee, S.K., Park, K.Y., and Yi, J.W., "Preparation of Polymer Composites Containing Hollow Magnetic Particles and Measurement of Their Electromagnetic Properties," *Composites Research,* Vol. 21, 2008, pp. 31-35.
7. Lee, J.W., Kim, S.M., and Lee, I.S., "Functionalization of Hollow Nanoparticles for Nanoreactor Applications," *Nano Today*, Vol. 9, 2014, pp. 631-667.
8. Lou, X.W., Archer, L.A., and Yang, Z., "Hollow Micro-/nanostructures: Synthesis and Applications," *Advanced Materials*, Vol. 20, 2008, pp. 3987-4019.
9. Wang, Y., Su, X., Ding, P., Lu, S., and Yu, H., "Shape-controlled Synthesis of Hollow Silica Colloids," *Langmuir*, Vol. 29, 2013, pp. 11575-11581.
10. Tao, C., Yan, H., Yuan, X., Yao, C., Yin, Q., Zhu, J., Ni, W., Yan, L., and Zhang, L., "Synthesis of Shape-controlled Hollow Silica Nanostructures with a Simple Soft-templating Method and Their Application as Superhydrophobic Antireflective Coatings with Ultralow Refractive Indices," *Colloids and Surface A: Physicochemical and Engineering Aspects*, Vol. 501, 2016, pp. 17-23.
11. Wang, Y., Su, X., and Lu, S., "Shape-controlled Synthesis of TiO_2 Hollow Structures and Their Application in Lithium Batteries," *Journal of Materials Chemistry*, Vol. 22, 2012, pp. 1969-1976.
12. Cheng, K., and Sun, S., "Recent Advances in Syntheses and Therapeutic Applications of Multifunctional Porous Hollow Nanoparticles," *Nano Today,* Vol. 5, 2010, pp. 183-196.
13. Lee, S.B., Kim, J.B., Lee, S.K., Park, K.Y., and Yi, J.W., "Preparation of Polymer Composites Containing Hollow Magnetic Particles and Measurement of Their Electromagnetic Properties," *Composites Research*, Vol. 21, 2008, pp. 31-35.
14. Deng, T.S., and Marlow, F., "Synthesis of Monodisperse Polystyrene@Vinyl-SiO_2 Core–Shell Particles and Hollow SiO_2 Spheres," *Chemistry of Materials,* Vol 24, 2012, pp. 536-542.
15. Zhang, L., Lan, J., Yang, J., Guo, S., Peng, J., Zhang, L., Zhou, C., and Ju, S., "Facile Synthesis of Nanocrystal Tin Oxide Hollow Microspheres by Microwave-Assisted Spray Pyrolysis Method," *Journal of Materials Science & Technology*, Vol. 33, 2017, pp. 874-878.
16. Fuji, M., Shin, T., Watanabe, H., and Takei, T., "Shape-controlled Hollow Silica Nanoparticles Synthesized by an Inorganic Particle Template Method," *Advanced Power Technology*, Vol. 23, 2012, pp. 562-565.
17. Arnal, P.M., Weidenthaler, C., and Schüth, F., "Highly Monodisperse Zirconia-Coated Silica Spheres and Zirconia/Silica Hollow Spheres with Remarkable Textural Properties," *Chemistry of Materials*, Vol. 18, 2006, pp. 2733-2739.
18. Deng, Z., Chen, M., Gu, G., and Wu, L., "A Facile Method to Fabricate ZnO Hollow Spheres and Their Photocatalytic Property," *The Journal of Physical Chemistry B*, Vol. 112, 2008, pp. 16-22.
19. Xu, Z., and Wang, Y., "Hollow ZnO/Zn_2SiO_4/SiO_2 Sub-microspheres with Mesoporous Shells: Synthesis, Characterization, Adsorption and Photoluminescence," *Journal of Alloys and Compounds*, Vol. 555, 2013, pp. 268-273.
20. Dong, Z., Lai, X., Halpert, J.E., Yang, N., Yi, L., Zhai, J., Wang, D., Tang, Z., and Jiang, L., "Accurate Control of Multishelled ZnO Hollow Microspheres for Dye-Sensitized Solar Cells with high Efficiency," *Advanced Materials*, Vol. 24, 2012, pp. 1046-1049.
21. Yin, M., and Liu, S., "Preparation of ZnO Hollow Spheres with Different Surface Roughness and Their Enhanced Gas Sensing Property," *Sensors and Actuators B: Chemical*, Vol. 197, 2014, pp. 58-65.
22. Sinha, A.K., Basu, M., Pradhan, M., Sarker, S., and Pal, T., "Fabrication of Large-Scale Hierarchical ZnO Hollow Spheroids for Hydrophobicity and Photocatalysis" *Chemistry-A European Journal,* Vol. 16, 2010, pp. 7865-7874.
23. Song, P., Wang, Q., and Yang, Z., "Acetone Sensing Character-

istics of ZnO Hollow Spheres Prepared by One-pot Hydrothermal Reaction," *Materials Letters,* Vol. 86, No. 1, 2012, pp. 168-170.

24. Lee, D.H., and Lee, C.H., "Preparation of Silica Hollow Composite Particles," *Bulletin of the Korean Chemical Society,* Vol. 35, No. 11, 2014, pp. 3303-3306.
25. Meulenkamp, E.A., "Synthesis and Growth of ZnO Nanoparticles," *The Journal of Physical Chemistry B*, Vol. 102, 1998, pp. 5566-5572.