A novel non-template solution approach to fabricate ZnO hollow spheres with a coordination polymer as a reactant†

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The methods of coordination chemistry are extended to fabricate hollow spheres of inorganic materials. In particular, in the present work a novel approach is successfully put forward to synthesize ZnO submicrometer hollow spheres, in which the coordination polymer $[Zn(4,4'\text{-bipy})(NCS)_2]_n$ with a 1D chain structure is introduced as a reactant. In this approach, no additional template materials are needed to obtain submicrometer hollow-sphere structures in the reaction process. A possible mechanism is also proposed.

Introduction

In recent years, one of the important goals of material scientists has been to develop ways of tailoring the structure of materials to obtain specific nanomorphologies.[1,2] The shape and size of inorganic nanomaterials are well-known to have an important influence on their electrical and optical properties,[3] which are important in various applications such as catalysis,[4] solar cells,[5] light-emitting diodes[6] and biological labelling.[7] Within specific nanomorphologies, submicrometer hollow spheres are attracting considerable attention because of their specific structure and potential applications as containers for encapsulation, delivery of drugs, development of artificial cells and protection of biologically active agents like proteins, enzymes, or DNA.[8,9]

Several methods have been developed for the fabrication of submicrometer hollow spheres of inorganic materials, such as liquid droplets,[10] latex templates,[11] polymer beads[12] or inorganic nanoparticles.[13] Generally, the above methods require additional template materials to build sphere architectures and the template needs to be removed later. It is obvious that the procedure to obtain hollow-sphere structures of inorganic materials will be greatly simplified if only the essential reactants are used in the reaction process, with no need for supporting templates. Coordination and organometallic chemistry methods have been gradually introduced for the synthesis of 1D inorganic materials in recent years and several successful examples have been reported using zero-dimensional (0D) complexes or three-dimensional (3D) coordination polymers as precursors.[14,15,16] However, these methods still cannot be extended to the fabrication of hollow spheres of inorganic materials. In these methods, the 1D nanostructures of inorganic materials result from either the rigidity of the 0D complexes or the framework of the 3D coordination polymers. Since the rigidity and framework of the coordination precursor have a great influence on the nanoscale morphologies of the final products, this motivated us to explore the morphology of the product that could be obtained if a coordination polymer with a one-dimensional (1D) chain structure was used. It is known that a spherical structure has the least surface tension, therefore, hollow-sphere structures might possibly be obtained from slowly shrunk chain structures when the ligands in the coordination polymer with a 1D chain structure are gradually removed. Thus, suitable coordination polymers may be used as reactants to directly synthesize hollow spheres of inorganic materials without any supporting template.

Being a wide bandgap semiconductor material with a large excitation binding energy, ZnO has long been a focus of both fundamental research and practical studies, due to its promising applications as short-wavelength light-emitting, transparent conductor, piezoelectric material and room temperature ultraviolet (UV) lasing materials.[17,18] Nanoscale ZnO materials such as nanowires[17] and nanotubes[19] have been obtained in previous work, however, to the best of our knowledge ZnO hollow spheres have not yet been reported. We have been employing coordination chemistry methods for the preparation of submicrometer hollow spheres of metal oxides and were looking for the appropriate precursor to achieve this goal. Herein, the coordination polymer $[Zn(4,4'\text{-bipy})(NCS)_2]_n$ with a 1D chain structure is used as a reactant to directly synthesize ZnO submicrometer hollow spheres under simple hydrothermal conditions without any additional supporting template material.

Experimental

Powders of the coordination polymer $[Zn(4,4'\text{-bipy})(NCS)_2]_n$ with a 1D chain structure were prepared *via* a simple process:[20] an aqueous solution (20 ml) of $ZnSO_4 \cdot 7H_2O$ (0.575 g, 2 mmol) and KSCN (0.389 g, 4 mmol) were added into 30 ml ethanol in which 4,4′-bipyridine ($C_{10}H_8N_2 \cdot 2H_2O$; 0.384 g, 2 mmol) was dissolved. The obtained powders were then loaded into a 30 ml Teflon-lined stainless steel autoclave, which was filled with 1.5 ml NH_4OH and 25 ml distilled water. The autoclave was sealed and maintained at 140 °C for 24 h and then allowed to cool to room temperature naturally. The precipitate was filtered off, washed with absolute ethanol and distilled water several times, and then dried in vacuum at 60 °C for 4 h.

X-Ray powder diffraction (XRD) patterns were obtained with a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromated high-intensity Cu–Ka radiation

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† Electronic supplementary information (ESI) available: X-ray photoelectron spectra and energy-dispersive X-ray analysis of the products. See http://www.rsc.org/suppdata/nj/b3/b304787c/

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($\lambda = 1.54178$ Å). The accelerating voltage was set at 50 kV, with 100 mA flux at a scanning rate of 0.06 ° s^{-1} in the 2θ range of 20° to 70°. The Raman spectrum was acquired at room temperature with a LABRAM-HR Confocal Laser MicroRaman Spectrometer. Field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were collected on a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The room temperature photoluminescence (PL) spectra were recorded on a Jobin Yvon-Labram spectrometer with a He-Cd laser.

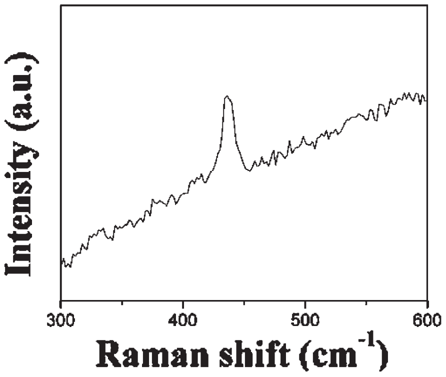

Fig. 2 Raman spectrum of the as-obtained product.

Results and discussion

Synthesis and characterization

The as-obtained product was characterized by XRD. The XRD pattern is shown in Fig. 1 and the Miller indices are indicated for each diffraction peak. All of these peaks can be indexed to wurtzite ZnO (JCPDS card No. 36-1451, $a = 3.249$ Å, $c = 5.206$ Å). The strong and clear peaks reveal the high purity and crystallinity of the as-obtained product. No characteristic peaks were observed for other impurities such as $Zn(OH)_2$.

The Raman spectrum of the as-obtained ZnO hollow spheres is shown in Fig. 2. Wurtzite ZnO has C_{6v} or $6mm$ symmetry and has a typical peak around 441 cm^{-1}, corresponding to the ZnO nonpolar optical phonon E_2 mode.[21] A broadening of the asymmetric Raman peak about 441 cm^{-1} can be clearly seen in our products. The broadening and asymmetry of the Raman peak is one of the characteristics of nanoparticles. Obviously, the Raman spectrum reveals that the as-obtained ZnO hollow spheres are composed of ZnO nanoparticles with a wurtzite structure.

From the FE-SEM image [Fig. 3(A)], one can see that the panoramic morphology of the as-obtained ZnO is spherical with diameters ranging from 300 to 600 nm. Careful observation shows that the surfaces of these spheres are constructed by many nanoparticles with diameters ranging from 20 to 60 nm, as seen in a magnified FE-SEM image [Fig. 3(B)] as well as in two other magnified TEM images [insets of Fig. 3(B)]. From the TEM image [Fig. 3(C) and insets of Fig. 3(B)], it is seen that the insides of these spheres are hollow, which indicates that the as-obtained product is composed of ZnO submicrometer hollow spheres. The hollow nature of the spheres is also confirmed by another typical SEM [inset of Fig. 3(C)], which provided an opporunity to see the ‘opened’ structure. It also can be seen in the TEM image that the diameters of these hollow spheres are mainly in the range of 400–500 nm and the thickness of the wall is about 100–150 nm. The ED pattern [inset of Fig. 3(C)] indicates that all of these particles are polycrystalline. The HRTEM image [Fig. 3(D)] at the edge of the sphere wall is provided, further confirming the good crystallinity of the as-obtained ZnO hollow spheres. From the magnified HRTEM image [inset of Fig. 3(D)], the lattice fringes can be clearly seen; the interplanar distance is about 2.8 Å, corresponding to the (001) plane.

The room temperature PL spectrum of as-obtained ZnO hollow spheres, shown in Fig. 4, was obtained with an excitation wavelength of 385 nm. The green emission of ZnO at about 520 nm comes from the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes.[22]

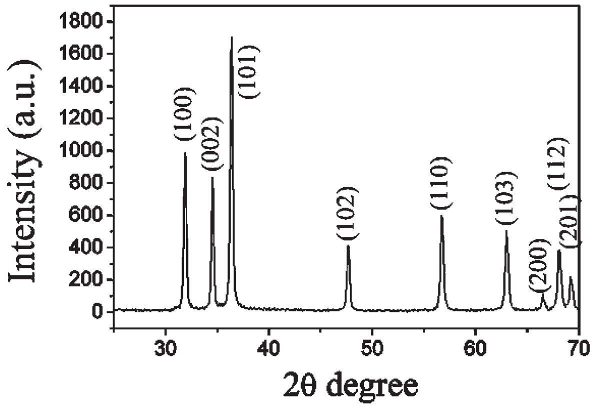

Fig. 1 Powder X-ray patterns of the as-obtained product.

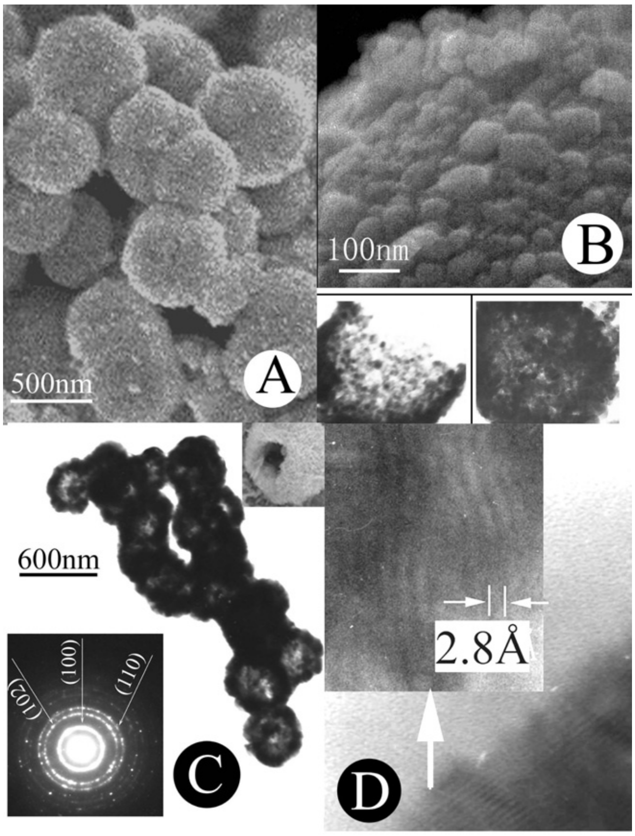

Fig. 3 Morphology of the as-obtained product. (A) SEM image of the sample. (B) Typical magnified SEM image of the sphere wall. The insets are magnified TEM images of two different single spheres. (C) TEM image of the sample. The upper inset is the FE-SEM image of the ‘opened’ structure of a hollow sphere. The lower inset is the ED pattern. (D) HRTEM image of the hollow sphere wall.

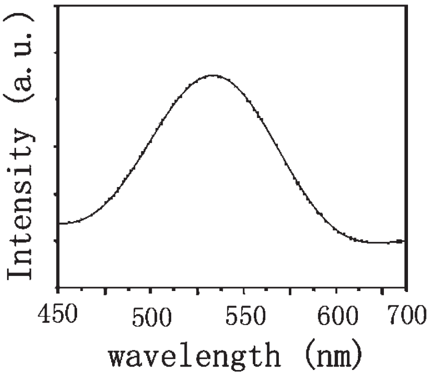

Fig. 4 PL spectrum of the as-obtained products.

Comparing with bulk ZnO, the PL spectrum of the as-obtained product shows a broadened peak due to the small dimension of the nanoparticles in their spherical walls.

Possible formation mechanism

The coordination polymer $[Zn(4,4'\text{-bipy})(NCS)_2]_n$ has a 1D infinite rigid zigzag chain structure (Fig. 5) due to the rigidity of 4,4′-bipyridine, and these chains hardly entwine each other in solvent. To our best knowledge, this is the first time that hollow spheres have been fabricated from a coordination polymer with a 1D chain structure. In previous research, 1D nanostructures rather than hollow spheres were usually obtained from coordination polymers with 1D chain structures.[15,23] Thus, a question arose in our minds: Is the hollow-sphere morphology of the product related to the 1D chain structure? To illuminate this puzzle, several supplementary experiments were carried out under similar experimental conditions except for the nature of the reagents: (1) Zn^{2+} and NH_4OH; (2) Zn^{2+}, KSCN and NH_4OH; (3) Zn^{2+}, KSCN, 4,4′-bipyridine and NH_4OH; (4) Zn^{2+}, 4,4′-bipyridine and NH_4OH. It was found that all experiments led to the production of irregular ZnO particles rather than hollow spheres. These results indicate that the 1D chain structure of the coordination polymer is indispensable to obtain the product with a hollow-sphere morphology. If bulk needle-like single crystals of the coordination polymer, synthesized according to the literature,[20] are used as the reactant instead of the powdered form, ZnO hollow spheres are still obtained, which further confirms the importance of the 1D chain structure of the coordination polymer.

NH_4OH is thought to provide weakly basic conditions in the airtight autoclave when the whole system is maintained at 140 °C. Although NH_4^+ can coordinate with Zn^{2+}, $Zn(NH_3)_4^{2+}$ probably does not form in this process due to its instabilty in a basic environment, as it would rapidly transform into $Zn(OH)_2$. The overall reaction process can be described as follows:

$$[Zn(4,4'\text{-bipy})(NCS)_2]_n + 2nNH_4OH \rightarrow$$
$$nZnO + n4,4'\text{-bipyridine} + 2nNH_4^+ + 2nNCS^- + nH_2O$$

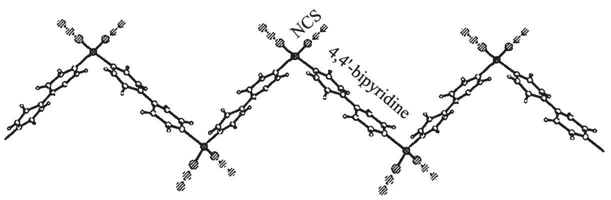

Fig. 5 Illustration of the structure of the 1D infinite rigid chain in the coordination polymer $[Zn(4,4'\text{-bipy})(NCS)_2]_n$.

Although the details of the reactions involved in the transformation of the Zn^{2+} metal ions in the coordination polymer to hollow sphere ZnO are not very clear, the following mechanism can be proposed, based on the existing information. The NCS^- ligand has a stronger coordination to Zn^{2+} than to 4,4′-bipyridine, as can be seen from their bond lengths [Zn–N (NCS) 1.908 Å, Zn–N (4,4′-bipy) 2.033 Å] in the coordination polymer.[20] Thus, 4,4′-bipyridine will be preferentially removed when attacked by OH^- and the infinite chains of the coordination polymer will gradually be broken. The broken chains with two –OH at either end are likely to aggregate through a dehydration process in the heated basic environment. The dehydration process occurring along the 1D chain direction most probably builds bent or circular structures, due to their lower surface tension, rather than 1D straight chains. Meanwhile, when –NCS groups on both sides of the broken 1D chains are gradually removed by the attacking OH^-, the dehydration process occurring between different broken chains will build cross-linked bent structures. As the removal of ligands (including 4,4′-bipyridine and –NCS) and the dehydration of –OH are repeated, the cross-linked bent chains will gradually shrink to form a spherical framework. The newly formed framework still contains some ligands to support the sphere structure. As the ligands are continuously removed, many small empty spaces will emerge in the walls, allowing the newly formed $Zn(OH)_2$ in a certain region to aggregate into ZnO nanoparticles and leading to the final hollow-sphere morphology of ZnO.

It is worth noting that NH_4OH plays a crucial role by ensuring the slow progress of the reactions, which is the key to constructing hollow structures in the above proposed mechanism. It is known that NH_4OH can easily be dissolved in water to give a basic environment, while NH_3 can also be driven out of water by boiling. There thus exists two equilibria when NH_4OH in the airtight autoclave is heated to 140 °C:

$$NH_4OH_{(liquid)} = NH_{3(gas)} + H_2O_{(liquid)}$$
$$NH_4OH = NH_4^+ + OH^-_{\text{(in solution)}}$$

The liquid-gas and NH_4OH ionization equilibria provide stable weakly basic conditions in the system, meaning that the ligands of the 1D rigid chain are slowly removed. Comparison experiments with different amounts of NH_4OH show that ZnO hollow spheres only can be obtain when the amount of NH_4OH is less than 5 ml in our experiments. Even with smaller quantities, the amount of NH_4OH also has an influence on the morphology of the final product. Fig. 6 shows the TEM images of the products obtained using 1, 2 and 6 ml NH_4OH. From Fig. 6(A) and Fig. 6(B), one can see that the walls of the hollow spheres vary from thin to thick with increasing concentration of NH_4OH. Fig. 6(C) shows that ZnO solid spheres can be obtained at a concentration of NH_4OH above 5 ml, since the ligands in the coordination polymer are removed faster during the reaction process when carried under more basic conditions.

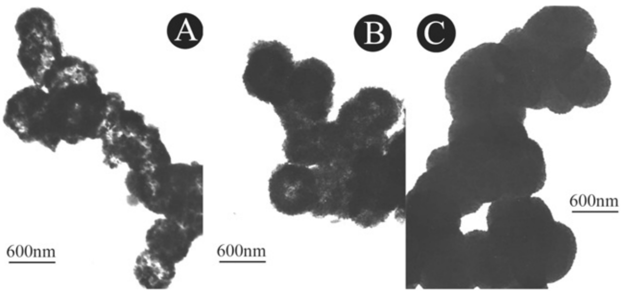

Fig. 6 TEM images of comparison experiments with different amounts of NH_4OH: (A) 1 ml, (B) 2 ml and (C) 6 ml NH_4OH.

Conclusion

In summary, the methods of coordination chemistry were extended to fabricate hollow spheres of inorganic materials. In particular, in the present work a novel approach has been successfully put forward to synthesize ZnO submicrometer hollow spheres, in which the coordination polymer $[Zn(4,4'\text{-}bipy)(NCS)_2]_n$ with a 1D chain structure was introduced as a reactant. In this approach, no additional template materials are needed to obtain submicrometer hollow sphere structures. It is noteworthy that the 1D rigid chain of the coordination polymer and the amount of NH_4OH are crucial to the formation of ZnO hollow spheres. A possible mechanism has also been proposed.

Acknowledgements

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References

1 S. Lijima, *Nature (London)*, 1991, **354**, 56.
2 N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie and A. Zettl, *Science*, 1995, **269**, 966.
3 A. P. Alivisatos, *Science*, 1996, **271**, 933.
4 T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. Elsayed, *Science*, 1996, **272**, 1294.
5 W. Huynh, X. Peng and A. P. Alivisatos, *Adv. Mater.*, 1999, **11**, 923.
6 M. C. Schlamp, X. G. Peng and A. P. Alivisatos, *J. Appl. Phys.*, 1997, **82**, 5837.
7 W. C. W. Chan and S. M. Nie, *Science*, 1998, **281**, 2016.
8 E. Mathlowitz, J. S. Jacob, Y. S. Jong, G. P. Carino, D. E. Chickering, P. Chaturvedl, C. A. Santos, K. Vijayaraghavan, S. Montgomery, M. Bassett and C. Morrell, *Nature (London)*, 1997, **386**, 410.
9 R. D. Thomas and H. Huang, *J. Am. Chem. Soc.*, 1999, **121**, 11 239.
10 D. Walsh and S. Mann, *Nature (London)*, 1995, **377**, 320.
11 F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 1998, **282**, 1111.
12 Z. Y. Zhong, Y. D. Yin, B. Gates and Y. N. Xia, *Adv. Mater.*, 2000, **12**, 206.
13 S. Y. Chang, L. Liu and S. A. Asher, *J. Am. Chem. Soc.*, 1994, **116**, 6745.
14 K. Soulantica, A. Maisonnat, F. Senocq, M. C. Fromen, M. J. Casanove and B. Chaudret, *Angew. Chem., Int. Ed.*, 2001, **40**, 2983.
15 Y. J. Xiong, Y. Xie, Z. Q. Li and C. Z. Wu, *Chem.-Eur. J.*, 2003, **9**, 1645.
16 Y. J. Xiong, Y. Xie, Z. Q. Li, R. Zhang, J. Yang and C. Z. Wu, *New J. Chem*, 2003, **27**, 588.
17 M. H. Huang, S. Mao, H. N. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo and P. D. Yang, *Science*, 2001, **292**, 1897.
18 H. Cao, J. Y. Xu, D. Z. Zhang, S. H. Chang, S. T. Ho, E. W. Seelig, X. Liu and R. P. H. Chang, *Phys. Rev. Lett.*, 2000, **84**, 5584.
19 J. Zhang, L. D. Sun, C. S. Liao and C. H. Yan, *Chem. Commun.*, 2002, 262.
20 L. Pan, N. W. Zheng, Y. G. Wu, X. L. Jin and X. Y. Huang, *J. Coord. Chem.*, 1999, **47**, 269.
21 T. C. Damen, S. P. S. Porto and B. Tell, *Phys. Rev.*, 1966, **142**, 570.
22 K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt and B. E. Gnade, *J. Appl. Phys.*, 1996, **79**, 7983.
23 Y. J. Xiong, Z. Q. Li, R. Zhang, Y. Xie, J. Yang and C. Z. Wu, *J. Phys. Chem. B*, 2003, **107**, 3697.