Large Scale Fabrication of NiS Hollow Spheres with Controllable Diameter Sizes

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NiS hollow spheres with controllable diameter sizes have been prepared in large scale by a simple method, where cyclohexylamine, as both solvent and reductant, successfully controlled the rate of releasing S^{2-}. NiS nanoparticles were self-aggregated into hollow spheres around the in situ formed poly(*N*-vinyl-2-pyrrolidone) (PVP, $M_w = 30{,}000$) spherical micelles in the cyclohexylamine media. The as-obtained high-quality NiS hollow spheres with loosely packed nanoparticles would show interesting applications in optical device and lithium-ion battery.

It has been thought that many novel properties and potential applications would emerge from morphology design of inorganic functional materials. The fabrication of hollow spheres of magnetic materials has become a particularly important area of research and is attracting a growing interest, because of their potential applications in ferrofluids, advanced magnetic materials catalysts, colored pigments, high-density magnetic recording media, and medical diagnostics.[1–5] With unique magnetic and optical properties, NiS hollow spheres could be more suitable for clinical diagnosis and the targeted transport of drugs, proteins, viruses, or bacteria. Up to now, method for synthesizing nickel sulfides has been widely investigated, but few progress has been made in preparation of hexagonal NiS hollow structure.[6,7]

In the past decade, many kinds of sulfur sources, such as Na_2S, CS_2, $Na_2S_2O_3$, and thioacetamide, have been introduced to the fabrication of transition-metal sulfide nanomaterials. While there existed much difficulty to control the rate of releasing S^{2-} from the S-containing reagents. For example, Na_2S exists in the form of S^{2-} in water at room temperature, while the thioacetamide usually hydrolyzes at 40–60 °C.[8] Moreover, the S^{2-} could be released from the CS_2–water–ethylenediamine system at 50 °C.[9] Obviously, such reaction systems could not be easily controlled to achieve the high-quality nanostructures at the high temperature owing to the high releasing rate of S^{2-}. An appropriate rate of releasing S^{2-} is probably crucial to the formation and following self-assembly of metal sulfide nanoparticles. Inspired by the fact that the amines (except pyridine) can react with sulfur and produce H_2S at extremely slow rate at room temperature,[10] we chose cyclohexylamine as the reductant for controlling the S^{2-} releasing rate. Another advantage of cyclohexylamine is its good solubility for polymers. Thus, in the present paper, we describe a simple method, in which cyclohexylamine was selected as both solvent and reductant and the polymer of poly(*N*-vinyl-2-pyrrolidone) (PVP, $M_w = 30{,}000$), as soft template. Spherical micelles will form by the self-aggregation due to the different solubility of different groups in cyclohexylamine solvent. The in situ formed micelles can be a good template for the following interface reaction. As an example, NiS hollow spheres with controllable diameter were prepared in large-scale as expected (See S1 in Supporting Information).[14] The as-obtained high-quality NiS hollow spheres comprise loosely packed nanoparticles, which will show the interesting applications in optical device and electrode of lithium-ion battery.

The size and shape of the NiS hollow spheres were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The typical SEM image, as shown in Figure 1A, gives a panoramic picture of the product, showing the NiS hollow spheres with average diameter of 800 nm. Careful observation on a broken hollow sphere (Inset in Figure 1A) can find that the hollow sphere is constructed with a lot of smaller particles and that the wall thickness of hollow spheres is about 120 nm. Figure 1B is a typical TEM image of NiS hollow spheres. Figure 1C shows the XRD patterns of as-obtained hollow spheres, where all the peaks can be indexed as hexagonal NiS (JCPDS file No: 750613).

PVP plays a multiple role in obtaining uniform hollow spheres. Due to the existence of hydrogen bond between the carbonyl group of PVP and the amino group of cyclohexylamine, PVP functions as surfactant in cyclohexylamine as the vinyl group is hydrophobic and carbonyl group is hydrophilic[11,12] (See S2 in Supporting Information).[14] The concentration of PVP influences the size of in situ formed micelles and thus the NiS hollow spheres. Comparative experiments with different concentration of PVP were carried out to understand its growth mechanism. In the absence of PVP, the main product was NiS

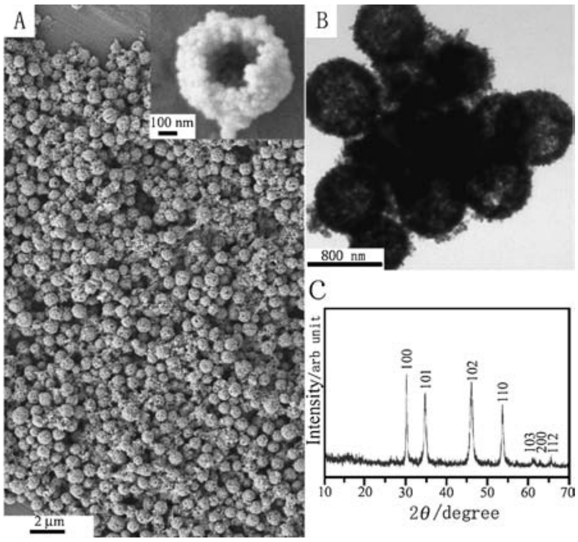


Figure 1. (A) SEM image of NiS hollow spheres insert: a high-magnification FESEM image of a NiS broken hollow sphere. (B) A TEM image of NiS hollow spheres. (c) XRD pattern of NiS hollow spheres.

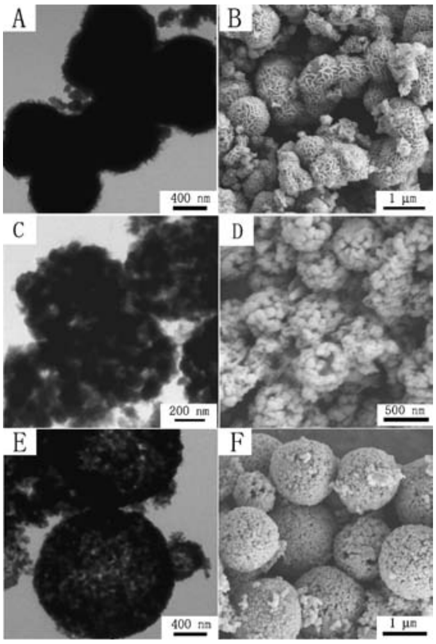
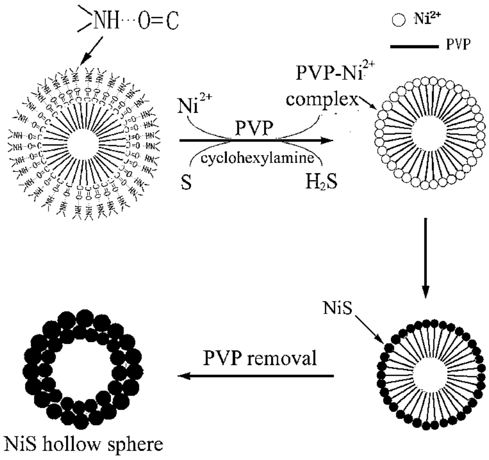


Figure 2. TEM and SEM images of products prepared at different amount of PVP (A) and (B) no PVP; (C) and (D) 0.1 g PVP; (E) and (F) 0.4 g PVP.

spheres consisting of nanoflakes as shown in Figures 2A and 2B. Upon the introduction of PVP, the products were all uniform hollow spheres in a large quantity. The diameter of NiS hollow spheres could be readily controlled by adjusting PVP concentration as shown in Figures 2C–2F. The size of NiS hollow spheres increased at higher concentration of PVP. Keeping other condition unchanged, the diameter of the hollow spheres was about 600 nm in the presence of 0.1 g of PVP (as shown in Figures 2C and 2D). When the amount of PVP increased to 0.4 g, it was found the diameter of NiS hollow spheres was 1.5 μm (as shown in Figures 2E and 2F).

It is known that PVP can combine with the Ni^{2+} to form polymer–metal complex, the coordinated atoms are oxygen on carbonyl group and the heteroatom (N atom) adjoining on the pyrrolidone ring.[13] The possible formation process of the hollow spheres is proposed as illustrated in Scheme 1: (1) PVP dissolves in cyclohexylamine to form spherical micelles with carbonyl groups on the outside. (2) PVP combines with Ni^{2+} to form polymer–metal complex. Ni^{2+} only aggregates on the surface of spherical micelles on account of the outside carbonyl group of PVP. (3) While the temperature increases, NiS nanoparticles were formed on the surface of spherical micelles via the interface reaction of Ni^{2+}–PVP complex and the in situ formed H_2S. (4) Finally the product was washed with deionized water and ethanol to remove PVP, and NiS hollow spheres were obtained.

The UV–vis absorption and photoluminescence (PL) measurements were performed to investigate the optical property of as-obtained NiS hollow spheres. The NiS hollow spheres show the remarkable blue-shift which is probably caused by their small dimension of the NiS nanoparticles of the hollow sphere wall(See S3 in Supporting Information).[14]



Scheme 1. Schematic illustration of the possible growth mechanism for NiS hollow spheres.

Also the NiS hollow spheres show good electrochemical properties. The NiS hollow spheres with loosely packed small particles are favorable in facilitating the intercalation and deintercalation of Li ions. Thus, a higher capacity can be achieved. The high capacity (about 570 mA h g^{-1}) and high-rate discharge capability make it attractive as a candidate cathode for rechargeable lithium-ion cells (See S4 in Supporting Information).[14]

In summary, NiS hollow spheres with controllable diameter sizes have been prepared in large scale by a one-step process via the Ni^{2+}–PVP complex spherical micelles. The low releasing rate S^{2-} is benefit to the self-aggregation of NiS nanoparticle on the spherical micelles. A possible growth mechanism has also been proposed on the basis of experimental results. The method could be extended to prepare other transition-metal sulfide hollow spheres.

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References and Notes

1 F. Caruso, M. Spasova, A. Susha, M. Giersig, R. A. Caruso, *Chem. Mater.* **2001**, *13*, 109.
2 Y. Xiong, Y. Xie, S. Chen, Z. Li, *Chem.—Eur. J.* **2003**, *9*, 4991.
3 T. Hyeon, *Chem. Commun.* **2003**, 927.
4 K. Woo, H. J. Lee, J.-P. Ahn, Y. S. Park, *Adv. Mater.* **2003**, *15*, 1761.
5 F. Luo, W. Song, C.-H. Yan, *Chem. Phys. Lett.* **2006**, *431*, 337.
6 X. Jiang, Y. Xie, J. Lu, L. Zhu, W. He, Y. Qian, *Adv. Mater.* **2001**, *13*, 1278.
7 Y. Hu, J. Chen, W. Chen, X. Lin, X. Li, *Adv. Mater.* **2003**, *15*, 726; G. D. Chen, H. B. Chu, X. M. Li, Z. Jin, Y. Li, *Acta. Chim. Sinica* **2006**, *64*, 85.
8 F. Y. Yao, D. W. Guo, M. D. Gui, *Inorganic Chemistry Serious*, **1990**, Vol. 5.
9 J. Huang, Y. Xie, B. Li, Y. Liu, Y. Qian, S. Zhang, *Adv. Mater.* **2000**, *12*, 808.
10 R. E. Davis, H. F. Nakshhendi, *J. Am. Chem. Soc.* **1962**, *84*, 2085.
11 G. Xi, Y. Peng, L. Xu, M. Zhang, W. Yu, Y. T. Qian, *Inorg. Chem. Commun.* **2004**, *7*, 607.
12 A.-M. Cao, J.-S. Hu, H.-P. Liang, L.-J. Wam, *Angew. Chem., Int. Ed.* **2005**, *44*, 4391.
13 F. Xu, Y. Xie, X. Zhang, C. Wu, W. Xi, J. Hong, X. Tian, *New J. Chem.* **2003**, *27*, 1331.
14 Supportting Information is available electronically on the CSJ-journal website; http://www.csj.jp/journals/chem-lett/.

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