

Cite this: *RSC Advances*, 2011, 1, 397–400

www.rsc.org/advances

## COMMUNICATION

## Hierarchical nickel sulfide hollow spheres for high performance supercapacitors†

By Ting Zhu, Zhiyu Wang, Shujiang Ding, Jun Song Chen\* and Xiong Wen (David) Lou\*

Received 28th May 2011, Accepted 29th June 2011

DOI: 10.1039/c1ra00240f

Hierarchical NiS hollow spheres assembled from ultrathin nanosheets are synthesized by an efficient template-engaged conversion method. Silica nanospheres were used as templates, and SiO<sub>2</sub>@nickel silicate core-shell nanostructures were first prepared. In the presence of Na<sub>2</sub>S, the nickel silicate shell completely transformed into NiS nanosheets *via* a hydrothermal treatment, accompanied by the total dissolution of the inner SiO<sub>2</sub> core. This gives rise to uniform hollow nanospheres whose shells are assembled from ultrathin NiS nanosheets. In virtue of the large surface area and enhanced structural stability, the as-prepared NiS hollow spheres exhibit excellent electrochemical performance as electrode materials for supercapacitors.

Hollow micro/nanostructures have attracted tremendous research interest in a myriad of applications, such as lithium-ion batteries,<sup>1–4</sup> catalysis,<sup>5–6</sup> chemical sensors<sup>7–9</sup> and biomedical applications,<sup>10–14</sup> due to their unique structural features including well-defined interior voids, low density, large surface area and surface permeability.<sup>15</sup> Templating against colloidal particles is regarded as the most straightforward and effective route towards hollow structures with narrow size distributions and well-defined shapes.<sup>16–18</sup> In general, templating methods involve the growth of a shell of designed materials on various colloidal templates (*e.g.*, monodisperse latex and silica spheres) and subsequent removal of the template to generate the interiors with desirable complexity. The use of templates in principle allows one to manipulate the size and morphology of resultant hollow particles for better control of the local chemical environment and extraordinary properties. However, difficulties ranging from material incompatibility to the collapse or deformation of hollow structures upon template removal are common in practice. The disadvantage of being time-consuming and the general requirement of a tedious multistep procedure also greatly restrict the extensive application of templating methods.

Nickel sulfides with many different phases such as NiS, NiS<sub>2</sub>, β-Ni<sub>3</sub>S<sub>2</sub>, α-Ni<sub>3+x</sub>S<sub>2</sub>, Ni<sub>4</sub>S<sub>3+x</sub>, Ni<sub>6</sub>S<sub>5</sub>, Ni<sub>7</sub>S<sub>6</sub>, Ni<sub>9</sub>S<sub>8</sub> and Ni<sub>3</sub>S<sub>4</sub> are inexpensive and abundant materials with widespread applications as ceramic tougheners, hydrogenation catalysts and electrode materials,

*etc.*<sup>19–23</sup> Despite the success in the synthesis of various morphologies, including nanochains,<sup>24</sup> hollow spheres<sup>25–26</sup> and layer-rolled structures,<sup>27</sup> the preparation of uniform hierarchical hollow structures of nickel sulfides still remains as a significant challenge. Herein, we report an effective conversion route for controllable synthesis of uniform NiS hollow spheres with a hierarchical structure by template-engaged precipitation of nickel silicates and subsequent *in situ* chemical conversion to NiS phase. Remarkably, these formed hollow spheres are entirely assembled from ultrathin NiS nanosheets with a thickness of a few nanometres, and simultaneously the silica cores are completely removed during the conversion reaction in a basic solution. When evaluated for potential use in supercapacitors, the NiS hierarchical hollow spheres exhibit excellent electrochemical performance due to their unique structure and high surface area.

The scheme in Fig. 1 illustrates our concept for the synthesis of NiS hollow spheres. First, monodisperse silica nanospheres are functionalized with silicate anions in an alkaline solution generated by the hydrolysis of urea. Driven by the interfacial reaction between aqueous solution of nickel nitrate and activated silica nanospheres, uniform deposition of nickel silicate occurs around the scaffold of silica template to form a nickel silicate shell.<sup>28–29</sup> Such SiO<sub>2</sub>@nickel silicate core-shell structures are readily converted into NiS hollow spheres at an elevated temperature by reacting with sodium sulfide (Na<sub>2</sub>S), where the silica cores are etched simultaneously by OH<sup>−</sup> released from the hydrolysis of sulfide ions. Herein Na<sub>2</sub>S not only serves as sulfurizing agent for the phase transformation from nickel silicate to thermodynamically favored nickel sulfide, but also grants the as-formed hollow spheres structural integrity by providing a mild alkaline environment to gradually remove the silica template. As a result of favorable kinetic control over this process, delicate nanosheets are formed as the subunits of the hierarchical hollow spheres.



**Fig. 1** Schematic illustration of the formation of NiS hollow spheres by a template-engaged conversion route: (I) uniform precipitation of a nickel silicate shell on silica nanospheres; (II) chemical conversion to NiS hollow spheres with simultaneous template elimination in the presence of Na<sub>2</sub>S.

School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, 637457, Singapore.

E-mail: chen0575@ntu.edu.sg; xwlou@ntu.edu.sg

† Electronic supplementary information (ESI) available: More XRD, EDX, BET and TEM data for the nanospheres of SiO<sub>2</sub>@nickel silicate and NiS. See DOI: 10.1039/c1ra00240f





**Fig. 4** (A) CV curves of NiS hollow spheres in the range of  $-0.15$  V– $0.55$  V at various scan rates; (B) galvanostatic charge-discharge curves and (C) average specific capacitance of NiS hollow spheres at various current rates; (D) cycling performance of NiS hollow spheres at a current rate of  $4.2$  A g<sup>-1</sup>.

attributed to the unique structural features of these NiS hollow spheres. Specifically, the very high surface area and hierarchical porous structure composed of ultrathin nanosheets offer a large interfacial area between the electrode material and the electrolyte and sufficient physical cavities for fast ionic diffusion, respectively.<sup>33</sup> After extended cycling for another 2000 cycles, around 74.1% of the capacitance at the 1000th cycle can still be maintained, evidently showing its relatively high cycling stability. This improved capacitance retention may be attributed to the enhanced structural integrity of these hierarchical hollow spheres.<sup>34</sup> Nonetheless, it should be pointed out that after prolonged charge-discharge cycling, some of the NiS hollow spheres will be collapsed because of the ultrathin nanosheet shell structure (see ESI, Fig. S6†), leading to the capacitive decay observed from Fig. 4D.

In summary, we have developed an efficient template-engaged conversion route for the preparation of hierarchical NiS hollow spheres assembled from ultrathin nanosheets under hydrothermal conditions. The as-prepared NiS hollow spheres are shown to be very uniform in size, mesoporous in textural property, and structurally robust benefiting from the *in situ* template removal. In virtue of the unique structural features, these NiS hollow spheres exhibit high specific capacitances of  $583$ – $927$  F g<sup>-1</sup> at various current densities of  $4.08$ – $10.2$  A g<sup>-1</sup>. Over 70% of the initial capacitances can be retained even after deep cycling of 1000–3000 cycles. This suggests their promising application as electrode materials for high-performance supercapacitors.

## Experimental

### Synthesis of core-shell structures of SiO<sub>2</sub>@nickel silicate

The SiO<sub>2</sub>@nickel silicate nanospheres were first prepared by a reported method with slight modification.<sup>30</sup> In a typical synthesis, 0.2 g of silica nanospheres were dispersed in 40 ml of de-ionized (DI) water in a capped bottle, followed by addition of 1 g of urea and 0.18 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. The thoroughly mixed solution was stored

in an electric oven at 105 °C for 12 h. After cooling down naturally, the product was harvested by several rinse-centrifugation cycles and was fully dried at 60 °C for further use.

### Synthesis of NiS hierarchical hollow spheres

0.1 g of above synthesized SiO<sub>2</sub>@nickel silicate nanospheres was dispersed in 40 ml of DI water in a Teflon container, followed by addition of 0.1 g of Na<sub>2</sub>S. After thorough mixing, the mixture was heated at 160 °C for 12 h. After cooling down naturally, the black precipitates were collected by several rinse-centrifugation cycles before drying at 60 °C in vacuum for the characterization.

### Material characterization

All samples were characterized by field-emission scanning electron microscopy (FESEM, JEOL, JSM-6340F), transmission electron microscopy (TEM, JEOL, JEM-2010) and X-ray diffraction (XRD, Bruker, D8-Advance X-ray Diffractometer, Cu K $\alpha$ ). Measurements of specific surface area and porosity were carried out at 77 K with a Quantachrome NOVA-3000 system.

### Electrochemical measurements

The electrodes were prepared by mixing NiS hollow spheres with carbon black (super-P-Li) and polyvinylidene difluoride (PVDF) at a weight ratio of 8 : 1 : 1. After thorough mixing, the slurry was pressed onto Ni foam and was dried at 60 °C in vacuum overnight. The electrochemical tests were conducted with a CHI 660C electrochemical workstation in an aqueous KOH electrolyte (2.0 M) with a three-electrode cell where Pt foil serves as the counter electrode and a standard calomel electrode (SCE) as the reference electrode.

### Acknowledgements

The authors are grateful to the Ministry of Education (Singapore) for financial support through the AcRF Tier-1 grant (RG 63/08, M52120096).

### References

- X. W. Lou, L. A. Archer and Z. C. Yang, *Adv. Mater.*, 2008, **20**, 3987–4019.
- X. W. Lou, C. M. Li and L. A. Archer, *Adv. Mater.*, 2009, **21**, 2536–2539.
- H. Ma, F. Y. Cheng, J. Chen, J. Z. Zhao, C. S. Li, Z. L. Tao and J. Liang, *Adv. Mater.*, 2007, **19**, 4067–4070.
- N. Du, H. Zhang, J. Chen, J. Y. Sun, B. D. Chen and D. R. Yang, *J. Phys. Chem. B*, 2008, **112**, 14836–14842.
- H. P. Liang, H. M. Zhang, J. S. Hu, Y. G. Guo, L. J. Wan and C. L. Bai, *Angew. Chem., Int. Ed.*, 2004, **43**, 1540–1543.
- S. W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, **124**, 7642–7643.
- B. X. Li, Y. Xie, M. Jing, G. X. Rong, Y. C. Tang and G. Z. Zhang, *Langmuir*, 2006, **22**, 9380–9385.
- J. H. Lee, *Sens. Actuators, B*, 2009, **140**, 319–336.
- H. R. Kim, K. I. Choi, K. M. Kim, I. D. Kim, G. Z. Cao and J. H. Lee, *Chem. Commun.*, 2010, **46**, 5061–5063.
- J. F. Chen, H. M. Ding, J. X. Wang and L. Shao, *Biomaterials*, 2004, **25**, 723–727.
- Y. F. Zhu, J. L. Shi, W. H. Shen, X. P. Dong, J. W. Feng, M. L. Ruan and Y. S. Li, *Angew. Chem., Int. Ed.*, 2005, **44**, 5083–5087.
- K. An and T. Hyeon, *Nano Today*, 2009, **4**, 359–373.
- J. Liu, S. Z. Qiao, S. B. Hartono and G. Q. Lu, *Angew. Chem., Int. Ed.*, 2010, **49**, 4981–4985.

- 14 J. Liu, S. B. Hartono, Y. G. Jin, Z. Li, G. Q. Lu and S. Z. Qiao, *J. Mater. Chem.*, 2010, **20**, 4595–4601.
- 15 L. Zhang, S. Z. Qiao, Y. G. Jin, Z. G. Chen, H. C. Gu and G. Q. Lu, *Adv. Mater.*, 2008, **20**, 805–809.
- 16 Z. Z. Yang, Z. W. Niu, Y. F. Lu, Z. B. Hu and C. C. Han, *Angew. Chem., Int. Ed.*, 2003, **42**, 1943–1945.
- 17 F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 1998, **282**, 1111–1114.
- 18 X. M. Sun and Y. D. Li, *Angew. Chem., Int. Ed.*, 2004, **43**, 597–601.
- 19 C. H. Lai, K. W. Huang, J. H. Cheng, C. Y. Lee, W. F. Lee, C. T. Huang, B. J. Hwang and L. J. Chen, *J. Mater. Chem.*, 2009, **19**, 7277–7283.
- 20 X. J. Zhu, Z. Y. Wen, Z. H. Gu and S. H. Huang, *J. Electrochem. Soc.*, 2006, **153**, A504–A507.
- 21 T. Takeuchi, H. Sakaebe, H. Kageyama, T. Sakai and K. Tatsumi, *J. Electrochem. Soc.*, 2008, **155**, A679–A684.
- 22 J. Wang, S. Y. Chew, D. Wexler, G. X. Wang, S. H. Ng, S. Zhong and H. K. Liu, *Electrochem. Commun.*, 2007, **9**, 1877–1880.
- 23 K. Aso, H. Kitaura, A. Hayashi and M. Tatsumisago, *J. Mater. Chem.*, 2011, **21**, 2987–2990.
- 24 W. Zhou, W. M. Chen, J. W. Nai, P. G. Yin, C. P. Chen and L. Guo, *Adv. Funct. Mater.*, 2010, **20**, 3678–3683.
- 25 P. T. Zhao, Q. M. Zeng and K. X. Huang, *Mater. Lett.*, 2009, **63**, 313.
- 26 Y. Hu, J. F. Chen, W. M. Chen, X. H. Lin and X. L. Li, *Adv. Mater.*, 2003, **15**, 726–729.
- 27 X. C. Jiang, Y. Xie, J. Lu, L. Y. Zhu, W. He and Y. T. Qian, *Adv. Mater.*, 2001, **13**, 1278–1281.
- 28 Y. Q. Wang, C. J. Tang, Q. A. Deng, C. H. Liang, D. H. L. Ng, F. L. Kwong, H. Q. Wang, W. P. Cai, L. D. Zhang and G. Z. Wang, *Langmuir*, 2010, **26**, 14830–14834.
- 29 J. Zheng, B. H. Wu, Z. Y. Jiang, Q. Kuang, X. L. Fang, Z. X. Xie, R. B. Huang and L. S. Zheng, *Chem.–Asian J.*, 2010, **5**, 1439–1444.
- 30 P. Jin, Q. W. Chen, L. Q. Hao, R. F. Tian, L. X. Zhang and L. Wang, *J. Phys. Chem. B*, 2004, **108**, 6311–6314.
- 31 H. L. Wang, H. S. Casalongue, Y. Y. Liang and H. J. Dai, *J. Am. Chem. Soc.*, 2010, **132**, 7472–7477.
- 32 H. Pang, Q. Y. Lu, Y. C. Lia and F. Gao, *Chem. Commun.*, 2009, 7542–7544.
- 33 M. Q. Wu, G. A. Snook, G. Z. Chen and D. J. Fray, *Electrochem. Commun.*, 2004, **6**, 499–504.
- 34 T. Zhu, J. S. Chen and X. W. Lou, *J. Mater. Chem.*, 2010, **20**, 7015–7020.