Controlled Fabrication of Polyaniline Spherical and Cubic Shells with Hierarchical Nanostructures

Jinbo Fei,[†] Yue Cui,[†] Xuehai Yan,[‡] Yang Yang,[§] Kewei Wang,[†] and Junbai Li[†,*]

[†]Beijing National Laboratory for Molecular Sciences (BNLMS), International Joint Lab, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China, [‡]Max Planck Institute of Colloids and Interfaces Golm, 14476 Potsdam, Germany, and [§]National Center for Nanoscience and Technology, No. 11, Bei Yi Tiao, Zhong guan cun, Beijing 100190, China

ABSTRACT Polyaniline spherical and cubic shells with hierarchical nanostructures were prepared by using MnO_2 hollow hierarchical nanostructures with different morphologies as reactive templates in a controlled manner. Scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images reveal that the PANI shells as-prepared are narrowly dispersed and possess uniform morphologies. Fourier transform infrared (FT-IR) and UV—vis spectra of the hollow shells indicate that the PANI exists in the emeraldine form. Cyclic voltammogram shows that the PANI exhibits multiple redox behavior during potentiodynamic cycling in acidic media at potentials. This strategy developed can be extended to synthesize other conducting polymers such as PPY shells with the similar controlled 3D hierarchical nanostructures.

KEYWORDS: polyaniline · hierarchical nanostructures · conductive polymers · reactive template

Three-dimensional hierarchical nanostructures have great potential in many applications such as transistors, sensors, and actuators because of their unique properties, compared with zero-, one-, and two-dimensional nanostructures.[1−5] Up to now, it is a new challenge to control self-assembly of micro- and nanostructures with 3D hierarchy for new material synthesis and device fabrication.[6]

As an important conductive conjugated polymer, polyaniline (PANI) has drawn considerable attention because of its chemical and physical properties, which are relative to its oxidation and protonation state.[7,8] Various PANI micro- and nanostructures have been synthesized by different methods.[9−30] Recently, Wan and coworkers have prepared a hollow octahedral structure of PANI using crystal-reductive Cu_2O as a template that was dissolved in the oxidative environment during synthesis.[31] They also reported on conductive and superhydrophobic rambutan-like hollow spheres of PANI prepared by a self-assembly method in the presence of perfluorooctane sulfonic acid (PFOSA).[32] When aiming for controlled PANI three-dimensional nanostructures, the need to use removable "soft templates" poses a challenging problem.[33]

Herein, we report that the spherical and cubic PANI shells with hierarchical nanostructures can be fabricated by using 3D MnO_2 hollow shells as reactive templates. Figure 1 demonstrates the schematic illustration of the controlled synthesis of PANI shells. The templates as-used were oxidative manganese oxide spherical and cubic shells with hierarchical nanostructures,[34] which shaped the PANI microstructures and acted as a chemical oxidative initiator for aniline polymerization at the same time. This strategy causes the templates to be removed spontaneously after the reaction because manganese oxide can be reduced by aniline monomer into soluble Mn^{2+} in acidic environment, which can be removed from the matrices of PANI by deionized water through centrifugation. Therefore, one of advantages by the strategy above is that there is no need to wash the templates before use. The chemical structure of the final product is identical to emeraldine synthesized by using a conventional oxidant in the presence of sulfide acid.

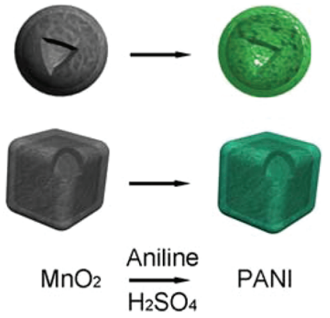

Figure 1. Schematic illustration of the synthesized PANI spherical and cubic shells by using the MnO_2 spherical and cubic shells as oxidants, respectively.

*Address correspondence to jbli@iccas.ac.cn.

Received for review August 3, 2009 and accepted October 26, 2009.

10.1021/nn900921v CCC: $40.75

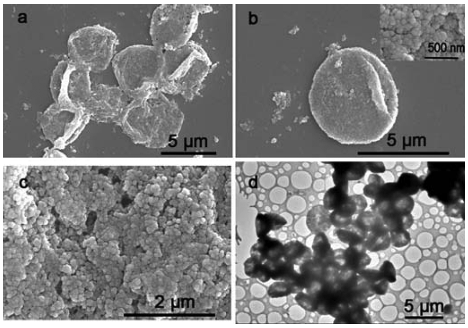

Figure 2. SEM images of (a) PANI spherical shells; (b) a selected single PANI spherical shell, and the inset is higher-magnification of a single PANI shell; (c) PANI nanoparticles as-prepared without removal of the $MnCO_3$ cores; (d) TEM image of PANI shells.

RESULTS AND DISCUSSION

As shown in Figure 2a,b, the diameter of PANI spherical shells as-obtained is about 4−5 μm, which is near that of the MnO_2 precursor (Figure S1a in the Supporting Information). The shells are of hierarchical nanostructures composed of nanoparticles, and the average diameter of nanoparticles is about 100 nm. The shells are full of cockles, perhaps because of the reactive template of MnO_2 without good crystalline.[35] If PANI was prepared directly with $MnCO_3$@MnO_2 composite, PANI nanoparticles obtained were aggregating, shown in Figure 2c. It is supposed that, in the presence of H_2SO_4, the $MnCO_3$ core can be reacted into CO_2 gas quickly, which breaks the formation of the spherical microstructure. Moreover, from the TEM image (Figure 2d), the microstructures of the product are hierarchical hollow shells.

The FTIR spectrum of the sample is shown in Figure 3a. The characteristic peaks at 1566 and 1494 cm^{-1} are due to the stretching vibration of the quinoid ring and the benzenoid ring, respectively.[36−38] The bands at 1295 and 1244 cm^{-1} can be assigned to C−H stretching vibration with aromatic conjugation.[26,39] The absorption peak near 1141 cm^{-1} results from the N−Q−N (Q denotes quinoid ring) stretching mode and is an indication of electron delocalization in PANI.[40] Furthermore, the color of the hollow spheres is green (Figure S2 in the Supporting Information), showing that the PANI as-prepared is the conductive emeraldine salt. It can be further supported by the relevant UV−vis absorption spectrum. As shown in Figure 3b, the UV−vis spectrum has the characteristic absorption peak centered about 452 nm originating from the charge-transfer excitation-like transition from the highest occupied energy level to the lowest unoccupied energy level, which is similar to that reported previously.[40,41] Moreover, the strong peak at about 750 nm from the $\pi-\pi^*$ transition, with a free carrier tail extending into the near-infrared region, is observed, indicating that the hollow hierarchical shells are identical to the doped state of PANI.[42]

Figure 3c shows the XPS results for the PANI hollow microspheres. It exhibits that the PANI spherical shells are mainly composed of C, N, S, and O without the contribution of Mn. C and N are offered by polyaniline. S and O are attributed to sulfate anion which doped PANI. It indicated that the MnO_2 precursor has been reduced into dissolvable Mn^{2+} by aniline monomer during the relevant reaction ($C_6H_7N + MnO_2 + H^+ \rightarrow PANI + Mn^{2+} + H_2O$), and Mn^{2+} can be removed completely from the matrices of PANI by deionized water through centrifugation. In detail, the N1s core-level spectrum in Figure 3d shows that it is almost identical to those of the doped PANI. The doping level calculated by N^+/N ratio is about 0.3.

PANI exhibits multiple redox behavior during potentiodynamic cycling in acidic media at potentials. It is generally accepted that redox processes are accompa-

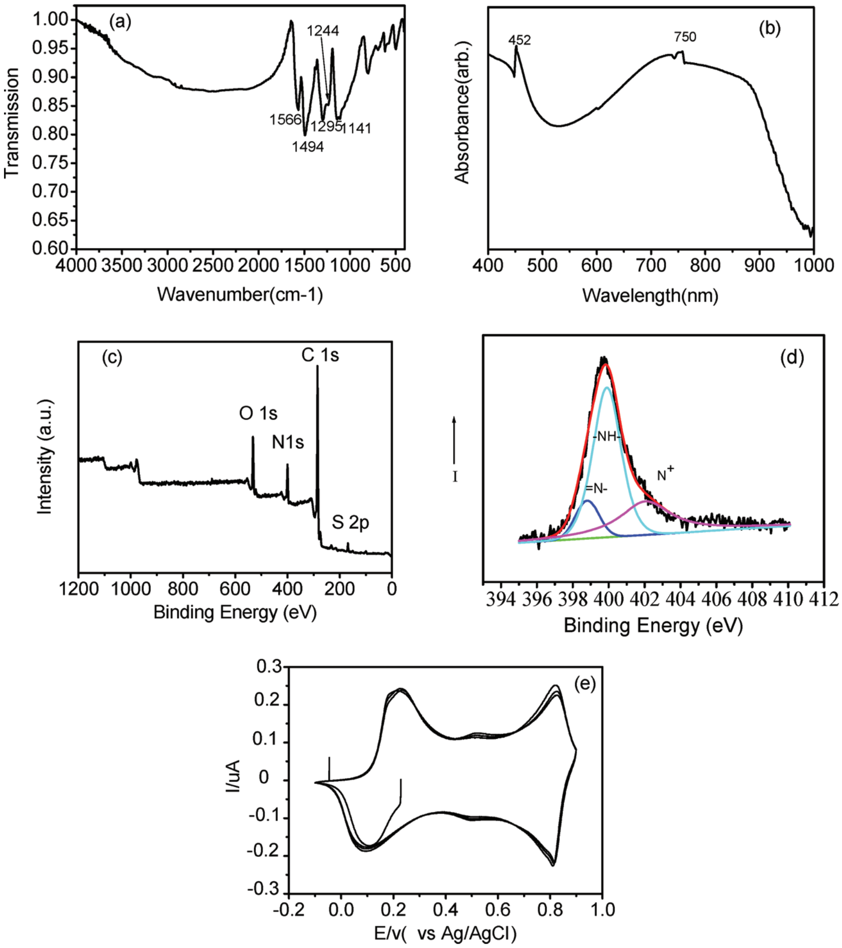

Figure 3. (a) FTIR spectrum of the PANI hollow shells; (b) UV−vis spectrum of the PANI hollow shells dispersed in ethanol; (c) XPS results of PANI hollow shells; (d) XPS core-level N1s spectrum of the PANI hollow shells; (e) cyclic voltammograms of PANI/GCE electrode at the scan rate of 50 mV s^{-1} in 0.5 M of H_2SO_4.

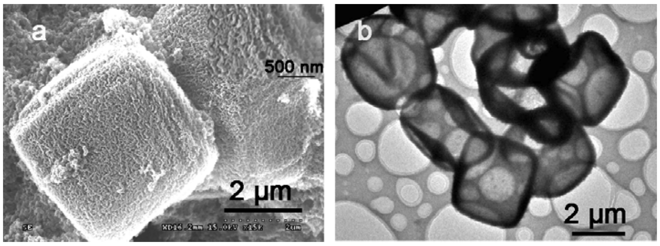

Figure 4. (a) Low-magnification SEM image of PANI cubic shells with 3D nanostructure, and the inset is the higher-magnification SEM image of the surface of the product as-prepared; (b) TEM image of PANI cubic shells.

nied by structural transformations by the doping and undoping of protons and anions.[43] Each transformation is characterized by a current peak on the cyclic voltammogram. The voltammogram for the PANI/GCE electrode in 0.5 M H_2SO_4 recorded at 50 mV s^{-1} is shown in Figure 3e. The oxidation current peak at 0.10 V is due to the transformation of PANI from the leucoemeraldine state (LM) to the emeraldine state (EM). The oxidation peak at 0.75 V is less intense due to the transformation of the EM state to the pernigraniline state (PE). The obtained PANI exhibits high conductivity in the potential region between the transitions of LM/EM and the EM/PE.

When MnO_2 microcubes were used as oxidant to synthesize PANI nanostructures, PANI hierarchical cubic shells could be obtained by the same strategy. As shown in Figure 4a, the diameter of the cubic shells with hierarchical nanostructure is about 5 μm, which are composed of nanoparticles with the diameter of about 50 nm. Compared with the SEM image of the MnO_2 template as-prepared (Figure S1b in the Supporting Information), there still is original morphology after the reactions. The TEM image in Figure 4b shows that the narrowly dispersed microparticles are hollow cubes. The dispersion of PANI cubic shells has a color of light blue (Figure S2 in the Supporting Information).

The synthesized MnO_2 hollow shells can have different thicknesses by changing the reactive ratios of $KMnO_4$ to $MnCO_3$.[34] Similarly, MnO_2 microcubes with different shell thicknesses can be prepared. It is found that, if the reaction occurs with aniline monomer in the presence of H_2SO_4, the thicknesses of MnO_2 hollow shell have an influence on the morphologies of the product as-prepared. Particularly, in the present work, as MnO_2 microcubes with different shell thicknesses change the reactive ratios of $KMnO_4$ to $MnCO_3$, the synthesized PANI cubic shells will have the different folds as well (Figure S3 in the Supporting Information).

The above method can be extended to synthesize other 3D hierarchical nanostructured materials. For instance, polypyrrolidine (PPY) spherical and cubic shells could be prepared as well by mixing MnO_2 hollow microspheres and microcubes with the pyrrolidine with the assistance of H_2SO_4 (Figures S2 and S4 in the Supporting Information). Compared with the morphologies of MnO_2 and PANI as-prepared, PPY has the similar microstructures.

Furthermore, MnO_2 can be used as an oxidant to oxidize the monomer of conductive polymers because of its high redox electropotential in an acid environment ($MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O$ ($E^\circ = 1.2$ V)).[35] On the basis of the above investigation, it is thus suggested that using the different morphological MnO_2 as reactive templates hollow shells with the different 3D morphologies can be prepared, which will show strong potential for shape controlling.

CONCLUSION

In summary, PANI spherical and cubic shells with hierarchical nanostructures were controllably synthesized through a reactive template method. This similar strategy has been extended to prepare PPY with controlled 3D nanostructures. Such hollow shells assembled will have potential applications in electromagnetic interference shielding, electronic devices, and nonlinear optical systems. This approach will find wide acceptance and use in the field of template-directed nanostructure synthesis. It may open a new way to fabricate diverse 3D hollow nanostructures of conducting polymers with control of morphology and properties.

EXPERIMENTS

Preparation of MnO_2 Hollow Microspheres and Microcubes: First of all, $MnCO_3@MnO_2$ microspheres and microcubes were prepared by mixing different quantities of 0.032 M of $KMnO_4$ (Beijing Chemical Reagent Ltd., China) with the solid $MnCO_3$ crystals with different morphologies.[34] In detail, in the preparation of $MnCO_3@MnO_2$ microspheres, the molar ratio of $KMnO_4$/$MnCO_3$ was 1:50. In the fabrication of $MnCO_3@MnO_2$ microcubes with different thicknesses, the molar ratios of $KMnO_4$/$MnCO_3$ are 1:100, 1:50, and 1:25. After the removal of the $MnCO_3$ core by HCl (Beijing Chemical Reagent Ltd., China), MnO_2 hollow microspheres and microcubes were obtained after centrifugation and washed several times by ultrapure water with a resistivity of 18.2 MΩ · cm. As shown in Figure S1 in the Supporting Information, the morphologies of the MnO_2 precursors with hollow hierarchical nanostructures are similar to those reported previously.[34]

Preparation of PANI and PPY Shells with 3D Hierarchical Nanostructures: In a typical synthesis of PANI nanostructures, solution A was prepared by dispersing 0.03 g of the above MnO_2 in 5 mL of H_2O by stirring at room temperature. Solution B was prepared by adding 500 μL of aniline monomer (Beijing Chemical Reagent Ltd., China) into the mixed solution of 3 mL of sulfuric acid and 50 mL of water. After cooled to room temperature, 10 mL of solution B was mixed with solution A quickly. The reaction was carried out for 12 h. The green solid was obtained by centrifugation and washed with water and ethanol thoroughly to remove excess ions and monomers. The final product was dried in vacuum at room temperature for 24 h. Polypyrrolidine shells (PPY) were prepared through a similar route. The only difference was that aniline monomer was replaced by pyrrolidine monomer used as received (Beijing Chemical Reagent Ltd., China).

Characterization: A Hitachi S-4300F scanning electron microscope (SEM) was used to investigate the morphologies of the precursors and final products. For transmission electron microscopy (TEM) observation, the samples were redispersed in ethanol by ultrasonic treatment and dropped on carbon−copper grids. TEM images were collected by using a JEOL JEM 1011 F microscope working at 100 kV. Fourier transform infrared (FTIR) spectrum was measured on a Bruker Tensor 27 spectrophotometer using KBr pressed disks. A Hitachi U-3010 spectrophotometer was used to record the UV−vis spectrum of the product. X-ray photoelectron spectroscopy (XPS, VG ESCA-LAB 220i-XL) was performed to investigate the chemical bonding configurations of the sample. The working electrode of PANI-deposited glass carbon electrode with a geometric area of about 0.72 cm^2 was placed symmetrically between two auxiliary platinum foil electrodes in a glass cell of about 30 cm^3 of capacity. Ag/AgCl (saturated KCl) electrode was used as the reference electrode, and electrode potentials are reported against this electrode. The working electrode was treated in concentrated H_2SO_4, washed thoroughly, and subjected to repeated potential scanning in 0.5 M of H_2SO_4 in the potential range from −0.2 to 1.2 V until the resulting voltammograms were reproducible. The PANI/GCE electrode was washed thoroughly in 0.5 M of H_2SO_4 and was then subjected to cyclic voltammetry at 50 mV s^{-1} in 0.5 M of H_2SO_4. Cyclic voltammetry was performed with a CHI 440 Electrochemical Workstation (from Shanghai Chenhua Corporation). All experiments were carried out at 20 ± 1 °C.

Acknowledgment. The authors acknowledge the financial support of this research by the National Nature Science Foundation of China (No.2009CB930100) as well as the German Max Planck Society collaboration project.

Supporting Information Available: Figures S1−S4. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Whitesides, G. M.; Grzybowski, B. A. Self-Assembly at All Scales. *Science* **2002**, *295*, 2418–2421.
2. Tsssapis, N.; Bennett, D.; Jackson, B.; Weitz, D. A.; Edwards, D. A. Large Porous Carriers of Nanoparticles for Drug Delivery. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12001–12005.
3. Champion, J. A.; Katare, Y. K.; Mitragotri, S. Making Polymeric Micro- and Nanoparticles of Complex Shapes. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 11901–11904.
4. Kang, L. T.; Wang, Z. C.; Cao, Z. W.; Ma, Y.; Xu, H. B.; Yao, J. N. Colloid Chemical Reaction Route to the Preparation of Nearly Monodispersed Perylene Nanoparticles: Size-Tunable Synthesis and Three-Dimensional Self-Organization. *J. Am. Chem. Soc.* **2007**, *129*, 7305–7312.
5. Hu, J. S.; Guo, Y. G.; Liang, H. P.; Wan, L. J.; Jiang, L. Three-Dimensional Self-Organization of Supramolecular Self-Assembled Porphyrin Hollow Hexagonal Nanoprisms. *J. Am. Chem. Soc.* **2005**, *127*, 17090–17095.
6. He, Y.; Ye, T.; Su, M.; Zhang, C.; Ribbe, A. E.; Jiang, W.; Mao, C. D. Hierarchical Self-Assembly of DNA into Symmetric Supramolecular Polyhedra. *Nature* **2008**, *452*, 198–201.
7. Chiang, J. C.; MacDiarmid, A. G. 'Polyaniline' Protonic Acid Doping of the Emeraldine Form to the Metallic Regime. *Synth. Met.* **1986**, *13*, 193–205.
8. Park, S. Y.; Cho, M. S.; Choi, H. J. Synthesis and Electrical Characteristics of Polyaniline Nanoparticles and Their Polymeric Composite. *Curr. Appl. Phys.* **2004**, *4*, 581–583.
9. Qiu, H. J.; Zhai, J.; Li, S. H.; Jiang, L.; Wan, M. X. Oriented Growth of Self-Assembled Polyaniline Nanowire Arrays Using a Novel Method. *Adv. Funct. Mater.* **2003**, *13*, 925–928.
10. Wang, J. X.; Wang, J. S.; Zhang, X. Y.; Wang, Z. Assembly of Polyaniline Nanostructures. *Macromol. Rapid Commun.* **2007**, *28*, 84–87.
11. Li, G. C.; Peng, H. R.; Wang, Y.; Qin, Y.; Cui, Z. L.; Zhang, Z. K. Synthesis of Polyaniline Nanobelts. *Macromol. Rapid Commun.* **2004**, *25*, 1611–1614.
12. Peng, Z. Q.; Guo, L. M.; Zhang, Z. H.; Tesche, B.; Wilke, T.; Ogermann, D.; Hu, S. H.; Kleinermanns, K. Micelle-Assisted One-Pot Synthesis of Water-Soluble Polyaniline−Gold Composite Particles. *Langmuir* **2006**, *22*, 10915–10918.
13. Bhadra, S.; Singha, N. K.; Khastgir, D. Electrochemical Synthesis of Polyaniline and Its Comparison with Chemically Synthesized Polyaniline. *J. Appl. Polym. Sci.* **2007**, *104*, 1900–1904.
14. Wei, Z. X.; Wan, M. X. Hollow Microspheres of Polyaniline Synthesized with an Aniline Emulsion Template. *Adv. Mater.* **2002**, *14*, 1314–1317.
15. Zhang, Z. M.; Wei, Z. X.; Wan, M. X. Nanostructures of Polyaniline Doped with Inorganic Acids. *Macromolecules* **2002**, *35*, 5937–5942.
16. Wei, Z. X.; Zhang, L. J.; Yu, M.; Yang, Y. S.; Wan, M. X. Self-Assembling Sub-micrometer-Sized Tube Junctions and Dendrites of Conducting Polymers. *Adv. Mater.* **2003**, *15*, 1382–1385.
17. Wei, Z. X.; Zhang, Z. M.; Wan, M. X. Formation Mechanism of Self-Assembled Polyaniline Micro/Nanotubes. *Langmuir* **2002**, *18*, 917–921.
18. Zhang, L. J.; Long, Y. Z.; Chen, Z. J.; Wan, M. X. The Effect of Hydrogen Bonding on Self-Assembled Polyaniline Nanostructures. *Adv. Funct. Mater.* **2004**, *14*, 693–698.
19. Wei, Z. X.; Wan, M. X.; Lin, T.; Dai, L. M. Polyaniline Nanotubes Doped with Sulfonated Carbon Nanotubes Made *via* a Self-Assembly Process. *Adv. Mater.* **2003**, *15*, 136–139.
20. Kanungo, M.; Kumar, A.; Contractor, A. Q. Microtubule Sensors and Sensor Array Based on Polyaniline Synthesized in the Presence of Poly(styrene sulfonate). *Anal. Chem.* **2003**, *75*, 5673–5679.
21. Ginic-Markovic, M.; Matisons, J. G.; Cervini, R.; Simon, G. P.; Fredericks, P. M. Synthesis of New Polyaniline/Nanotube Composites Using Ultrasonically Initiated Emulsion Polymerization. *Chem. Mater.* **2006**, *18*, 6258–6265.
22. Martin, C. R. Template Synthesis of Electronically Conductive Polymer Nanostructures. *Acc. Chem. Res.* **1995**, *28*, 61–68.
23. Yang, M.; Ma, J.; Zhang, C. L.; Yang, Z. Z.; Lu, Y. F. General Synthetic Route toward Functional Hollow Spheres with Double-Shelled Structures. *Angew. Chem., Int. Ed.* **2005**, *44*, 6727–6730.
24. Niu, Z. W.; Yang, Z. H.; Hu, Z. B.; Lu, Y. F.; Han, C. C. Polyaniline−Silica Composite Conductive Capsules and Hollow Spheres. *Adv. Funct. Mater.* **2003**, *13*, 949–954.
25. Wang, D. Y.; Caruso, F. Fabrication of Polyaniline Inverse Opals *via* Templating Ordered Colloidal Assemblies. *Adv. Mater.* **2001**, *13*, 350–354.
26. Pan, L. J.; Pu, L.; Shi, Y.; Sun, T.; Zhang, R.; Zheng, Y. D. Hydrothermal Synthesis of Polyaniline Mesostructures. *Adv. Funct. Mater.* **2006**, *16*, 1279–1288.
27. Mallick, K.; Witcomb, M. J.; Dinsmore, A.; Scurrell, M. S. Polymerization of Aniline by Auric Acid: Formation of Gold Decorated Polyaniline Nanoballs. *Macromol. Rapid Commun.* **2005**, *26*, 232–235.
28. Pang, S. P.; Li, G. C.; Zhang, Z. K. Synthesis of Polyaniline−Vanadium Oxide Nanocomposite Nanosheets. *Macromol. Rapid Commun.* **2005**, *26*, 1262–1265.
29. Huang, K. Y.; Zhang, J.; Long, Y. Z.; Yuan, J. H.; Han, D. X.; Wang, Z. J.; Niu, L.; Chen, Z. J. Preparation of Highly Conductive, Self-Assembled Gold/Polyaniline Nanocables and Polyaniline Nanotubes. *Chem.—Eur. J.* **2006**, *12*, 5314–5319.
30. Kinyanjui, J. M.; Hatchett, D. W.; Smith, J. A.; Josowicz, M. Chemical Synthesis of a Polyaniline/Gold Composite Using Tetrachloroaurate. *Chem. Mater.* **2004**, *16*, 3390–3398.
31. Zhang, Z. M.; Sui, J.; Zhang, L. J.; Wan, M. X.; Wei, Y.; Yu, L. M. Synthesis of Polyaniline with a Hollow, Octahedral Morphology by Using a Cuprous Oxide Template. *Adv. Mater.* **2005**, *17*, 2854–2857.
32. Zhu, Y.; Hu, D.; Wan, M. X.; Jiang, L.; Wei, Y. Conducting and Superhydrophobic Rambutan-like Hollow Spheres of Polyaniline. *Adv. Mater.* **2007**, *19*, 2092–2096.

33. Han, J.; Song, G. P.; Guo, R. Nanostructure-Based Leaf-like Polyaniline in the Presence of an Amphiphilic Triblock Copolymer. *Adv. Mater.* **2007**, *19*, 2993–2999.
34. Fei, J. B.; Cui, Y.; Yan, X. H.; Qi, W.; Yang, Y.; Wang, K. W.; He, Q.; Li, J. B. Controlled Preparation of MnO_2 Hierarchical Hollow Nanostructures and Their Application in Water Treatment. *Adv. Mater.* **2008**, *20*, 452–456.
35. Pan, L. J.; Pu, L.; Shi, Y.; Song, S. Y.; Xu, Z.; Zhang, R.; Zheng, Y. D. Synthesis of Polyaniline Nanotubes with a Reactive Template of Manganese Oxide. *Adv. Mater.* **2007**, *19*, 461–464.
36. Shi, X. Y.; Briseno, A. L.; Sanedrin, R. J.; Zhou, F. M. Formation of Uniform Polyaniline Thin Shells and Hollow Capsules Using Polyelectrolyte-Coated Microspheres as Templates. *Macromolecules* **2003**, *36*, 4093–4098.
37. Dong, H.; Prasad, S.; Nyame, V.; Jones, W. E. Sub-micrometer Conducting Polyaniline Tubes Prepared from Polymer Fiber Templates. *Chem. Mater.* **2004**, *16*, 371–373.
38. Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T.; Kawagoe, T. Vibrational Spectra and Structure of Polyaniline. *Macromolecules* **1988**, *21*, 1297–1305.
39. Zeng, X. R.; Ko, T. M. Structures and Properties of Chemically Reduced Polyanilines. *Polymer* **1998**, *39*, 1187–1195.
40. Zhang, Z. M.; Deng, J. Y.; Shen, J. Y.; Wan, M. X.; Chen, Z. J. Chemical One Step Method to Prepare Polyaniline Nanofibers with Electromagnetic Function. *Macromol. Rapid Commun.* **2007**, *28*, 585–590.
41. Masters, J. G.; Ginder, J. M.; MacDiarmid, A. G.; Epstein, A. J. Thermochromism in the Insulating Forms of Polyaniline: Role of Ring-Torsional Conformation. *J. Chem. Phys.* **1992**, *96*, 4768–4778.
42. Huang, J. X.; Virji, S.; Weiller, B. H.; Kaner, R. B. Polyaniline Nanofibers: Facile Synthesis and Chemical Sensors. *J. Am. Chem. Soc.* **2003**, *125*, 314–315.
43. Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsitavis, C. Polyaniline: A Historical Survey. *Synth. Met.* **1990**, *36*, 139–182.