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Electromagnetic Functional Urchin-Like Hollow Carbon Spheres Carbonized by Polyaniline Micro/Nanostructures Containing $FeCl_3$ as a Precursor

Ying Zhu,[a,b] Jiuming Li,[b] Meixiang Wan,*[b] and Lei Jiang*[a,b]

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Hollow, urchin-like carbon spheres with electromagnetic function were prepared by a carbonization process at 1200 °C under an argon atmosphere by using template-free-synthesized, urchin-like, hollow spheres of polyaniline containing $FeCl_3$ as the precursors. The resulting hollow, urchin-like carbon spheres not only have a high conductivity at room temperature ($\approx 12.3\ S\,cm^{-1}$), but they also exhibit ferromagnetic properties. The high conductivity at room temperature results from the graphite-like structure, whereas α-Fe or γ-Fe_2O_3 nanoparticles produced by $FeCl_3$ during the carbonization at 1200 °C are attributed to the ferromagnetic properties. Interestingly, the electromagnetic functional hollow urchin-like carbon spheres could be used as a reversible dye adsorbent.

Introduction

Since the discovery of carbon nanotubes in 1991,[1] nanostructured carbon materials have attracted tremendous interest in technology as a result of their unique structural, mechanical, and electronic properties.[2–7] Among these nanostructured carbon materials, 3D hollow carbon spheres are desirable because of their low density, high surface area, and large pore volume,[8] which have led to various applications in active-material encapsulation, drug delivery, and heterogeneous catalysis, and their use as electrodes and lithium-ion secondary batteries.[7,9–11] So far, chemical vapor deposition,[12] the template method,[13–15] and other methods[16] have been employed to prepare 3D hollow carbon spheres. In recent years, much attention has been paid to the modification of the carbon nanostructures to improve their physical and chemical properties and to extend the technical applications of carbon materials.[9,17] In particular, carbon nanostructures with a magnetic function have received a considerable amount of attention from the viewpoint of scientific studies and industrial applications.[18–30] So far, magnetic particles (Fe_3O_4) embedded in bamboo-shaped carbon microtubes by redox reaction between ferrocene and glycerol in a stainless autoclave,[21] iron carbide oxide filled carbon nanotubes by catalytic chemical vapor deposition of coal gas with ferrocene as catalyst,[22] the Fe_2O_3-impregnated magnetic carbon nanotubes by a chemical oxidation polymerization associated with the carbonization process,[23] have been reported. To the best of our knowledge, electromagnetically functionalized 3D microstructures of carbon materials constructed from their 1D nanostructure have not been reported yet.

Here, we exposed a simple route of carbonization associated with template-free-synthesized, urchin-like hollow spheres of polyaniline (PANI) containing $FeCl_3$ as the carbon precursor to prepare electromagnetically functionalized hollow urchin-like carbon spheres (abbreviated by EMFHRCSs) at 1200 °C under an argon atmosphere. The reasons for choosing micro/nanostructured PANI containing $FeCl_3$ as the precursors are as follows: Firstly, PANI as the carbon precursor is cheap and easy to prepare on a large scale in comparison to other conducting polymers.[31] Secondly, the hollow urchin-like spheres of PANI synthesized by a template-free method are 3D microstructures assembled from 1D nanostructures.[32] The hollow urchin-like spheres of PANI as the carbon precursors not only provide a source of carbon through dehydration of PANI during the carbonization process at 1200 °C, but they also maintain the special and complex morphology of the PANI micro/nanostructure. Moreover, the $FeCl_3$ existing in the urchin-like hollow spheres of PANI would lose its halogen atoms to form iron oxide (e.g., γ-Fe_2O_3) or to form α-Fe by reduction of iron oxide during the carbonization process. The formed γ-Fe_2O_3 or α-Fe contributed to the magnetic properties of the EMFHRCSs. On the basis of above ideas, the synthetic procedure of EMFHRCSs consists of three steps: the first step is to synthesize the hollow urchin-like PANI spheres by a template-free method in the presence of

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[a] School of Chemistry and Environment, Beijing University of Aeronautics and Astronautics,
Beijing 100191, P. R. China
Fax: +86-10-82627566
E-mail: jianglei@iccas.ac.cn
[b] Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100190, P. R. China
E-mail: wanmx@iccas.ac.cn

perfluorooctane sulfonic acid (PFOSA) as the dopant, as previously reported.[32] In the second step, the hollow urchin-like PANI spheres containing $FeCl_3$ are then prepared by immersing the hollow spheres into an aqueous solution of $FeCl_3$, followed by washing with deionized water (4×) and drying for 12 h. The third step in the preparation of the EMFHRCSs involves a carbonization process at 1200 °C under an argon atmosphere by using the urchin-like, hollow PANI spheres containing $FeCl_3$ as the carbon precursor. Morphology, structure, and composition of the EMFHRCSs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), and energy-dispersive X-ray spectroscopy (EDX). The electrical and magnetic properties were measured by a four-probe method and superconducting quantum interference device, respectively. The use of EMFHRCSs as a reversible dye adsorbent was also evaluated.

Results and Discussion

Similar to our previous report,[32] the template-free PANI synthesized in this paper is composed of hollow urchin-like spheres, as measured by SEM and TEM. As shown in Figure 1a, the PANI spheres with an average diameter of 870 nm are self-assembled from the nanofibers (an average diameter of ca. 20 nm). TEM images further proved that the PANI spheres are hollow, 870 nm in diameter, and 190 nm in shell thickness (Figure 1b). Figure 1c,d give the typical SEM image of EMFHRCSs with a loading of 2 M $FeCl_3$ and carbonized at 1200 °C for 3 h. It is clear that the EMFHRCSs maintained the hollow, urchin-like sphere morphology of PANI (Figure 1a), indicating that complete micro/nanostructures of carbon materials can be prepared by a carbonization process associated with PANI 3D microstructures self-assembled from 1D nanostructures as the carbon precursors at a high temperature. However, the diameter and the shell thickness of the EMFHRCSs are slightly reduced from 870 and 190 nm to ≈650 and 100 nm, respectively. This might be due to dehydrogenation, denitrogenation, or aromatization during the carbonization process. As Figure 1d shows, some dark particles (≈20 nm in diameter) are encapsulated or dispersed in the EMFHRCSs. These dark particles are regarded as the magnetic particles, as proved by the electron diffraction pattern, in which some diffuse and spotty rings are observed in Figure 1e. In contrast, these dark particles are absent in the urchin-like hollow spheres of PANI.[32]

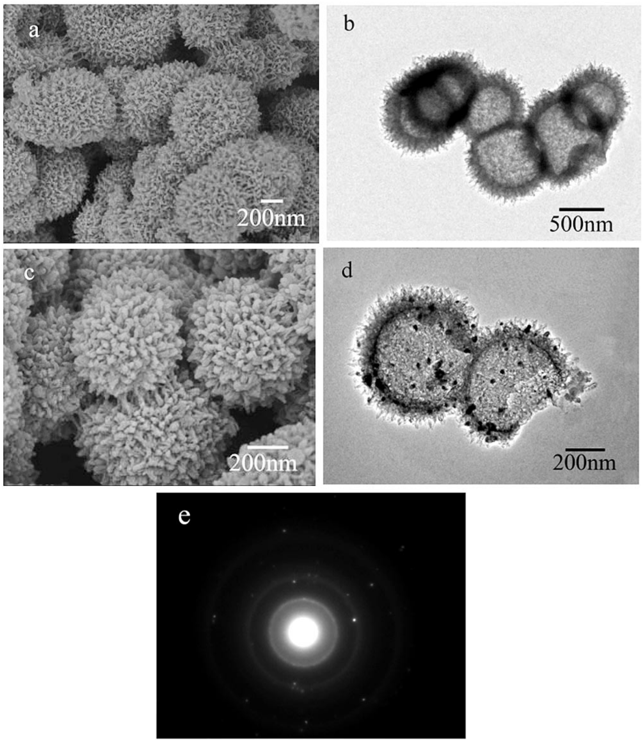

Figure 1. Typical SEM and TEM images: (a) and (b) template-free-synthesized, urchin-like, PANI–PFOSA hollow spheres; (c) and (d) the EMFHRCSs with a 2 M loading of $FeCl_3$ at 1200 °C for 3 h; (e) the electron diffraction pattern of the EMFHRCSs in (c).

The component of the EMFHRCSs with a loading 2 M $FeCl_3$ was measured by EDX and XPS. The EMFHRCSs are composed of 85.55% carbon (C), 8.42% oxygen (O), 5.65% nitrogen (N), and 0.22% iron (Fe) as measured by EDX. These data are slightly different from the 91.03% C, 4.41% O, 1.08% N, and 2.37% Fe measured by XPS as a result of different measuring methods. However, both data proved that the EMFHRCSs contain carbon as the major component, but a small amount of N and Fe is detected. It should be noted that the quantity of Fe in the EMFHRCSs measured by EDX is smaller than that by XPS, indicating that the magnetic iron particles are mainly encapsulated within the hollow spheres rather than on the surface of the spheres. In addition, the N1s signal at a bonding energy of 401 eV, which is characteristic of nitrogen atoms present in grapheme sheets,[27] is also observed (Figure 2b). On the basis of above results, we therefore conclude that the EMFHRCSs are N-doped carbon hollow spheres containing some iron. The graphite-like carbon was further proved by XRD by the strong peaks at $2\theta = 26.4°$ and the weaker peak at $2\theta = 44.7°$ assigned as characteristic (002) and (100), reflection of graphitic carbon was observed[23,30] (see Figure 2c). Besides, the characteristic peaks of magnetic α-Fe and γ-Fe_2O_3 nanoparticles[33] are also observed in the EMFHRCSs, which are marked as "F" and "E", respectively. These results further indicate that the EMFHRCSs are mainly composed of carbon, but a little nitrogen and magnetic nanoparticles (e.g., γ-Fe_2O_3 and α-Fe) also exist. During the carbonization at 1200 °C, the PANI micro/nanostructures are mainly transformed into carbon by dehydration, whereas $FeCl_3$ embedded in the PANI hollow spheres loses its halogen atoms to form iron oxide (e.g., γ-Fe_2O_3) or α-Fe by reduction of iron oxide. These results suggested that the grapheme-like structure might contribute

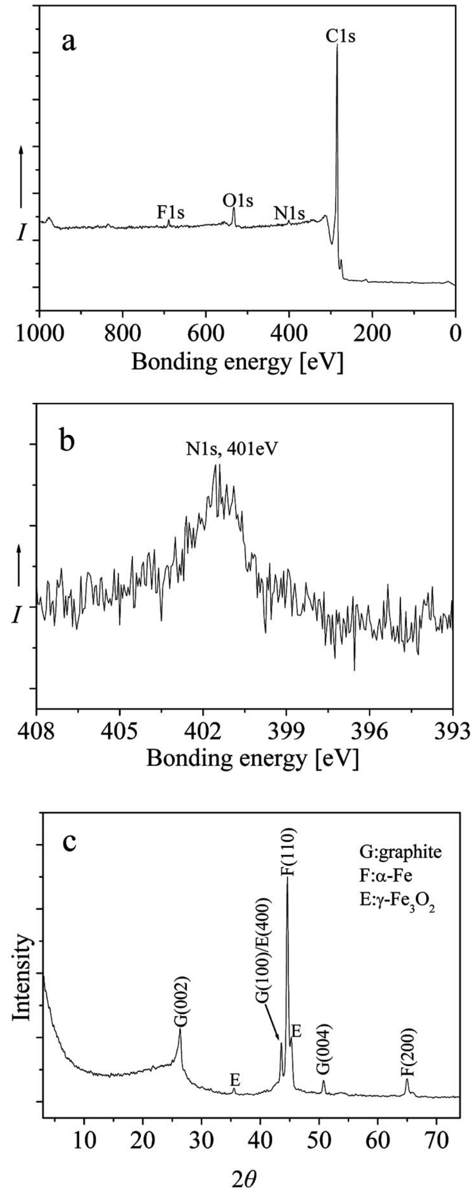

Figure 2. Structural characterization of the EMFHRCSs with a 2 M loading of $FeCl_3$ by (a) XPS (the inset is the N1s spectrum) and (b) XRD.

to the electrical properties of the EMFHRCSs, while the coexistence of γ-Fe_2O_3 and α-Fe results in the magnetic properties of the EMFHRCSs.

To confirming the above proposal, the electrical and magnetic properties of the EMFHRCSs with a 2 M $FeCl_3$ loading were measured. As predicted, the EMFHRCSs have a conductivity as high as 12.3 $S\,cm^{-1}$, as measured by a four-probe method, which is a consequence of the presence of graphitic species. Magnetization with the applied magnetic field further proved the magnetic properties of the EMFHRCSs. Figure 3a,b show a typical hysteresis loop for the EMFHRCSs with a loading of 2 M $FeCl_3$ at 300 K. The saturation magnetization (M_s) of the EMFHRCSs is estimated to be ca. 19.7 $emu\,g^{-1}$, which is considerably smaller than that of bulk iron (M_s = 220 $emu\,g^{-1}$)[33] as a result of a low loading of $FeCl_3$ in the EMFHRCSs. As shown in Figure 3b of the enlarged hysteresis loop, the coercive force (H_c) is calculated to be about 43 Oe. Especially, the magnetic properties of EMFHRCSs can be adjusted by changing the concentration of $FeCl_3$ filled in the PANI hollow spheres and the carbonization temperature. As shown in Figure 4a, the values of M_s decrease from 32.9 to 19.7 and 1.7 $emu\,g^{-1}$ when the loading concentration of $FeCl_3$ is changed from 3 to 2 and 1 M, respectively, as a result of different Fe contents in the EMFHRCSs. However, the values of H_c do not change in an obvious manner with a change in the loading concentration of $FeCl_3$, which is within the experimental error (Figure 4b). In contrast, the values of M_s and H_c of the EMFHRCSs with a loading of 2 M $FeCl_3$ are strongly affected by the carbonization temperature, as shown in Figure 4c,d. It can be seen form Figure 4c that the value of M_s decreased from 19.7 and 4.3 to 2.7 $emu\,g^{-1}$ with a decrease in the carbonization temperature from 1200 to 1000 and 800 °C, respectively. However, the value of H_c increases from 43 to 267 and 335 Oe with a decrease in the carbonization temperature (Figure 4d). These features might originate from a size effect.[34]

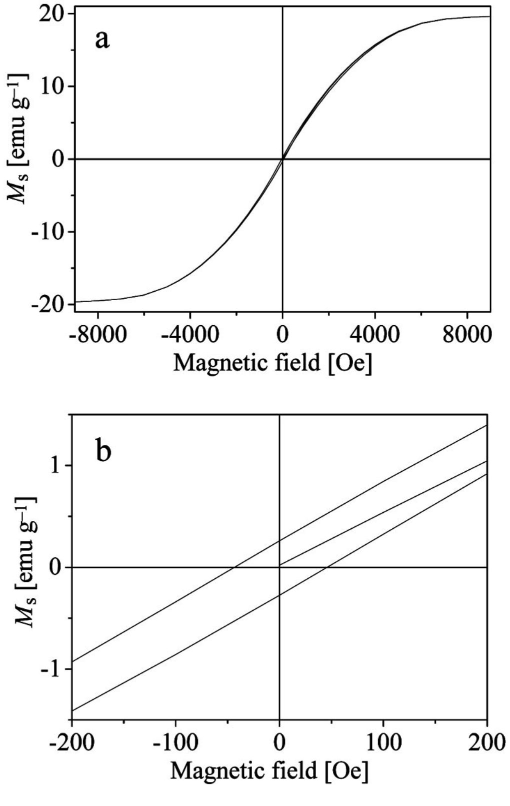

Figure 3. Magnetic properties of the EMFRHCSs with a 2 M loading of $FeCl_3$ measured by: (a) hysteresis loop of the EMFRHCSs with an applied magnetic field (–8000 to +8000 Oe) measured at 300 K; (b) hysteresis loop of the EMFRHCSs with the applied magnetic field (–200 to +200 Oe) measured at 300 K; (c) a photo to show that the EMFRHCSs are attracted by a magnet, proving the magnetic feature of the EMFHRCSs.

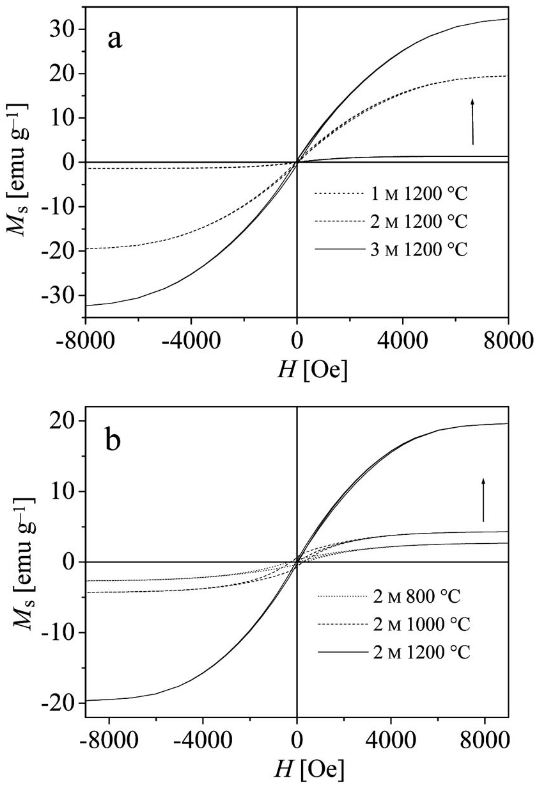

Figure 4. Hysteresis loops of the EMFHRCSs are affected by preparation conditions: (a) with loadings of 3, 2, and 1 M $FeCl_3$ at 1200 °C for 3 h; (b) with loading of 2 M $FeCl_3$ at 800, 1000, and 1200 °C.

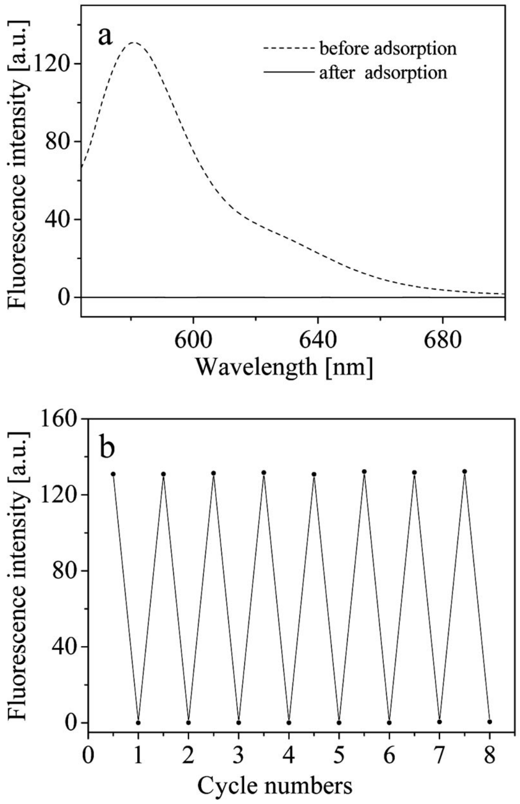

Figure 5. Reversible adsorption/deadsorption of RhB dye by a magnet with the use of the EMFHRCSs as the dye adsorbent: (a) fluorescence spectra of the solution containing 1 mg L^{-1} RhB before and after adsorption treatment of the EMFRHCSs; (b) cycle numbers of the dye adsorption of the EMFRHCSs.

The above-described magnetic properties suggested that the EMFHRCSs might be used as recoverable dye adsorbents. Thereby, RhB dye was used as a fluorescence probe to confirm this idea, which involves the following: firstly, fresh EMFHRCSs are added to a water solution containing RhB to adsorb the dye; secondly, the EMFHRCSs with adsorbed RhB are separated by a magnet, resulting in clean water; thirdly, the EMFHRCSs with adsorbed RhB are transferred into ethanol to release the dye and then separated by a magnet to regenerate clean EMFHRCSs. The RhB solution is red in color, which is consistent with a fluorescence peak of RhB at 580 nm,[35] as shown in Figure 5a. It was observed that the red color dissipated to afford a colorless solution after adding 20 mg of EMFHRCSs in 20 mL of RhB solution (1 mg L^{-1}) over 30 min, indicating that the RhB dye was completely adsorbed by the EMFHRCSs, which is also consistent with disappearance of the peak at 580 nm in the fluorescence spectra of the solution of the RhB dye containing EMFHRCSs (Figure 5a). Since the standard errors of the fluorescence intensities before and after eight adsorption treatments are 0.583 and 0.204, respectively, the level of adsorbing RhB dye by the EMFHRCSs is almost unchanged after eight adsorbing/deadsorbing cycles (Figure 5b), indicating that the EMFHRCSs are easily regenerated and can be developed as a new type of reversible dye adsorbent.

Conclusions

A simple carbonization process associated with template-free-synthesized, urchin-like, hollow spheres of PANI–PFOSA as the precursor at 1200 °C under an argon atmosphere was used to prepare urchin-like hollow carbon spheres with a conductivity as high as 12.3 S cm^{-1} and ferromagnetic properties. The urchin-like hollow carbon spheres are typical 3D microstructures assembled from 1D nanofibers. The high conductivity results from the graphite-like structures, whereas the ferromagnetic properties are attributed to magnetic α-Fe or γ-Fe_2O_3 produced during carbonization of the urchin-like hollow spheres containing $FeCl_3$ as the additive. The magnetic properties are controlled by adjusting the loading of $FeCl_3$ in the samples and the carbonization temperature. It showed that the EMFHRCSs might be used as an adsorbent for removal of dyes in pollutants by a magnet.

Experimental Section

Materials: Aniline monomer (Beijing Chem. Co.) was distilled under reduced pressure before use. Ferric chloride ($FeCl_3$) and perfluorooctane sulfonic acid [PFOSA, $CF_3(CF_2)_7SO_3H$] were purchased from the Beijing Chemical and Heide Chem. Develop. Co., respectively. Both were used as received without further treatment.

Preparation of EMFHRCSs: The hollow, urchin-like, PANI spheres were synthesized by a template-free method in the presence of PFOSA and $FeCl_3$ as the dopant and oxidant, respectively, according to a synthesis procedure reported previously.[32] The typical synthesis of urchin-like, PANI, hollow spheres is as follows: PFOSA (0.2 mL) was dissolved in distilled water (10 mL) and then mixed with aniline (0.4 mL) under supersonic stirring to form a mixture of uniform emulsion. $FeCl_3$ (5.41 g) dissolved in distilled water (5 mL) was then added to the above mixture and allowed to polymerize at room temperature for 24 h. The product was thoroughly washed with water and ethanol to remove the reagent and dried under vacuum oven for 12 h at room temperature to obtain green powders of the hollow, urchin-like, PANI spheres. The hollow, urchin-like, PANI spheres (0.25 g) were then immerged in an aqueous solution of $FeCl_3$ (1 M, 10 mL) for 7 h, followed by washing with water and drying in an oven for 12 h to produce hollow, urchin-like, PANI spheres loaded with $FeCl_3$. The EMFHRCSs ware finally prepared by a carbonization process at 1200 °C under an argon atmosphere by using the hollow, urchin-like, PANI spheres filled with $FeCl_3$ as the precursor. To study the influence of the $FeCl_3$ contents on the magnetic properties of the EMFHRCSs, immergence processes of PANI spheres in different concentrations of $FeCl_3$ aqueous solutions were performed under other conditions unchanged. The effect of the carbonization temperature (e.g., 800 and 100 °C) on the magnetic properties of the EMFHRCSs was also investigated.

Characterization: Morphologies of the precursor and the EMFHRCSs were measured with a JEOL JSM-6700F field-emission scanning electron microscope and a Hitachi-9000 transmission electron microscope. Components and crystals of the EMFHRCSs were measured by EDX, XPS, and XRD. EDX data was collected with a Hitachi-530 scanning electron microscope coupled with an EDX facility. XPS was carried out with a VG ESCALAB 220i-XL instrument with a monochromatic Al-K_α X-ray source. XRD was carried out with a Regaku D/max2500 diffractometer at a voltage of 40 kV and a current of 200 mA with Cu-K_α radiation (λ = 1.5406 Å) and by employing a scanning rate of 0.02°s^{-1} in the 2θ ranging from 5 to 70°. Magnetic measurement was carried out with a magnetic property measurement system (MPMS-XL, Quantum Design), whereas the conductivity of the compressed pellets of the EMFHRCSs at room temperature was measured by a standard four-probe method by using a Keithley 196 system DMM Digital Multimeter and an Advantest R1642 programmable DC voltage/current generator as the current source.

Dye Adsorption and Deadsorption: The EMFHRCSs (20 mg) and RhB (Rhodamine B) stock solution (1 mg L^{-1}, 20 mL) were mixed and stirred at room temperature. The EMFHRCSs with adsorbed RhB were separated by a magnet and then immersed into ethanol (20 mL) at room temperature whilst stirring. The released medium solution was analyzed at set time intervals and then replaced with the same volume of ethanol. Adsorption and deadsorption was evaluated with the use of a Hitachi F-4500 fluorescence spectrophotometer.

Acknowledgments

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[1] S. Iijima, *Nature* **1991**, *354*, 56–58.
[2] H. W. Zhu, C. L. Xu, D. H. Wu, B. Q. Wei, R. Vajtai, P. M. Ajayan, *Science* **2002**, *296*, 884–886.
[3] N. Sano, H. Wang, M. Chhowalla, I. Alexandrous, G. A. J. Amaratunga, *Nature* **2001**, *414*, 506–507.
[4] P. M. Ajayan, J. M. Nugent, R. W. Siegel, B. Wei, Ph. Kohler-Redlich, *Nature* **2000**, *404*, 243.
[5] C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, M. S. Dresselhaus, *Science* **1999**, *286*, 1127–1129.
[6] M. Shim, A. Javey, N. W. S. Kam, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 11512–11513.
[7] S. Han, Y. Yun, K. W. Park, Y. E. Sung, T. Hyeon, *Adv. Mater.* **2003**, *15*, 1922–1925.
[8] F. Su, X. S. Zhao, Y. Wang, L. Wang, J. T. Lee, *J. Mater. Chem.* **2006**, *16*, 4413–4419.
[9] K. T. Lee, Y. S. Jung, S. M. Oh, *J. Am. Chem. Soc.* **2003**, *125*, 5652–5653.
[10] Y. Piao, K. An, J. Kim, T. Yu, T. Hyeon, *J. Mater. Chem.* **2006**, *16*, 2984–2989.
[11] B. Liu, D. Jia, Q. Meng, J. Rao, *Carbon* **2007**, *45*, 668–670.
[12] Y. Xia, R. Mokaya, *Adv. Mater.* **2004**, *16*, 886–891.
[13] A. M. Herring, J. T. McKinnon, B. D. McCloskey, J. Filley, K. W. Gneshin, R. A. Pavelka, H.-J. Kleebe, D. J. Aldrich, *J. Am. Chem. Soc.* **2003**, *125*, 9916–9917.
[14] G. Hu, D. Ma, M. Cheng, L. Liu, X. Bao, *Chem. Commun.* **2002**, *17*, 1948–1949.
[15] S. B. Yoon, K. Sohn, J. Y. Kim, C. H. Shin, J. S. Yu, T. Hyeon, *Adv. Mater.* **2002**, *14*, 19–21.
[16] C. Yin, Q. Huang, B. Liu, X. Wang, Y. Xie, L. He, M. Zhang, X. Yang, *Mater. Lett.* **2007**, *61*, 4015–4018.
[17] Y. Wang, F. Su, J. Y. Lee, X. S. Zhao, *Chem. Mater.* **2006**, *18*, 1347–1353.
[18] Z. Sun, Z. Liu, Y. Wang, B. Han, J. Du, J. Zhang, *J. Mater. Chem.* **2005**, *15*, 4497–4501.
[19] I. Mönch, A. Meye, A. Leonhardt, K. Krämer, R. Kozhuharova, T. Gemming, M. P. Wirth, B. Büchner, *J. Magn. Mater.* **2005**, *290–291*, 276–278.
[20] R. V. Ramanujan, S. Purushotham, M. H. Chia, *Mat. Sci. Eng. C* **2007**, *27*, 659–664.
[21] L. Xu, J. Du, P. Li, Y. Qian, *J. Phys. Chem. B* **2006**, *110*, 3871–3875.
[22] J. Qiu, Q. Li, Z. Wang, Y. Sun, H. Zhang, *Carbon* **2006**, *44*, 2565–2568.
[23] J. Jang, H. Yoon, *Adv. Mater.* **2003**, *15*, 2088–2091.
[24] J. Lee, S. Jin, Y. Hwang, J.-G. Park, H. M. Park, T. Hyeon, *Carbon* **2005**, *43*, 2536–2543.
[25] B. Jia, L. Gao, *J. Phys. Chem. B* **2007**, *111*, 5337–5343.
[26] S. V. Pol, V. G. Pol, A. Frydman, G. N. Churilov, A. Gedanken, *J. Phys. Chem. B* **2005**, *109*, 9495–9498.
[27] S. C. Tsang, V. Caps, I. Paraskevas, D. Chadwick, D. Thompsett, *Angew. Chem. Int. Ed.* **2004**, *43*, 5645–5649.
[28] Z. Sun, L. Wang, P. Liu, S. Wang, B. Sun, D. Jiang, *Adv. Mater.* **2006**, *18*, 1968–1971.
[29] J. Lee, D. Lee, E. Oh, J. Kim, Y.-P. Kim, S. Jin, H.-S. Kim, Y. Hwang, J. H. Kwak, Je-G. Park, C.-H. Shin, J. Kim, T. Hyeon, *Angew. Chem. Int. Ed.* **2005**, *44*, 7427–7432.
[30] J. Jan, J. H. Oh, G. D. Stucky, *Angew. Chem. Int. Ed.* **2002**, *41*, 4016–4019.
[31] A. G. MacDiarmid, *Angew. Chem. Int. Ed.* **2001**, *40*, 2581–2590.
[32] Y. Zhu, D. Hu, M. Wan, L. Jiang, W. Yen, *Adv. Mater.* **2007**, *19*, 2092–2096.
[33] J. Jang, H. Yoon, *Small* **2005**, *1*, 1195–1199.
[34] J. N. Wang, L. Zhang, F. Yu, Z. M. Sheng, *J. Phys. Chem. B* **2007**, *111*, 2119–2124.
[35] R. W. Bigelow, *J. Phys. Chem.* **1977**, *81*, 88–89.

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