Robust Macroporous Materials of Chiral Polyaniline Composites

Linglu Yang and Weixiao Cao*

College of Chemistry and Molecular Engineering, Peking University, Beijing, China

Received June 29, 2005. Revised Manuscript Received September 14, 2005

3D macroporous materials comprising chiral polyaniline composites were prepared using polystyrene sphere as sacrificial template. By means of diazoresin (DR) as a thermosetting agent or TiO_2 as a reinforcing agent, the pore structure can be maintained perfectly after removal of the template. The porous materials reinforced with TiO_2 are more robust than those thermoset with DR only. The weight percent of TiO_2 in the robust macroporous materials has been determined to be ∼16%.

Introduction

The macroporous materials prepared with 3D-ordered organic or inorganic colloidal crystal as template have been extensively studied and developed rapidly in the past decade because of their potential applications in the fields of band-gap materials, electro- and nonlinear optics, storage, catalysis, separations, and sensors.[1−4] Many approaches have been developed to fill various materials in the interspaces of the colloidal crystal, such as sol−gel,[5] electro-chemical deposition,[6] chemical vapor deposition,[7] co-deposition,[8] centrifugation-filtration,[9] and liquid-phase reactions.[10] After removal of the colloids by chemical etching or calcination, the 3D-ordered macroporous materials were obtained. In most cases, the filling materials are inorganic ones or monomers, which can pack closely, crystallize, or polymerize to ensure the framework of the pores. The organic particles are scarcely selected because they are difficult to pack closely or crystallize.

In the past decade there has been interest in synthesizing chiral conducting polymers (CCPs) due to their potential applications in chiral separations, chiral recognition, surface-modified electrodes, and chemical and biological sensors.[11−14] Among the CCPs, chiral polyaniline (CPA) has been studied extensively because it is inexpensive, easily synthesized, and environmentally stable. Kaner et al. demonstrated that chiral de-doped polyaniline possessed a remarkable chiral recognization capability when exposed to selected amino acids and can be used to separate racemic mixtures of DL-phenylalanine.[14] However, it is difficult for linear polyaniline to be employed in large-scale separation because it cannot be directly filled in a chromatogram column. Therefore, finding composite materials containing chiral polyaniline is necessary. Recently, McCarthy et al. and Li et al. reported a template-guided synthesis to prepare aqueous dispersion of chiral polyaniline nanocomposites (CPACs) with submicrometer size.[15,16] In view of the appropriate size and shape of CPACs, we think it could be filled in the interspaces of colloidal crystals and finally form chiral polyaniline macroporous materials. This kind of macroporous material may be used in the filling of the column and opens up the possibility for large-scale chiral separation.

In this paper, we report two effective approaches to obtain stable macroporous materials of CPACs. In one method, we first modified CPACs with thermo-sensitive diazoresin (DR), and filled them in the interspaces of the colloidal crystal which was built up from ∼5.7 μm polystyrene (PS) beads, followed by heat treatment. After the PS beads were dissolved by tetrahydrofuran (THF), the macroporous materials of CPACs were achieved. In another method the TiO_2 formed from the sol−gel method was introduced into the porous framework of CPACs. In this case TiO_2 plays a reinforcing role for the porous materials.

---

* To whom correspondence should be addressed. Tel: 86-10-62750279. Fax: 86-10-62751708. E-mail: wxcao@pku.edu.cn.

(1) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143.
(2) Velev, O. D.; Lenhoff, A. M. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 56.
(3) Temelkuran, B.; Ozbay, E. *Appl. Phys. Lett.* **1999**, *74*, 486.
(4) Painter, O.; Lee, R. K.; Scherer, A.; Yariv, A.; O'Brien, J. D.; Dapkus, P. D.; Kim, I. *Science* **1999**, *284*, 1819.
(5) (a) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538. (b) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802. (c) Holland, B. T.; Abrams, L.; Stein, A. *J. Am. Chem. Soc.* **1999**, *121*, 4308. (d) Wang, D. Y.; Rogach, A. L.; Caruso, F. *Chem. Mater.* **2003**, *15*, 2724.
(6) (a) Attard, G. S.; Bartlett, P. N.; Coleman, N. R. B.; Elliott, J. M.; Owen, J. R.; Wang, J. H. *Science* **1997**, *278*, 838. (b) Braun, P. V.; Wiltzius, P. *Nature* **1999**, *402*, 603. (c) Vlasov, Y. A.; Yao, N.; Norris, D. J. *Adv. Mater.* **1999**, *11*, 165. (d) Yu, A. M.; Meiser, F.; Caruso, F. *Nano Lett.* **2004**, *4*, 177.
(7) (a) Blanco, A.; Chomski, E,; Grabtchak, S.; Ibisate, M.; John, S.; Leonard, S. W.; Lopez, C.; Meseguer, F.; Miguez, H.; Mondia, J. P.; Ozin, G. A.; Toader, O.; Van Driel, H. M. *Nature* **2000**, *405*, 437. (b) Vlasov, Y. A.; Bo, X.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, *414*, 289.
(8) (a) Cong, H. L.; Cao, W. X. *J. Colloids Interface Sci.* **2004**, *278*, 423. (b) Yang, L. L.; Yang, Z. H.; Cao, W. X.; Chen, L.; Xu, J.; Zhang, H. Z. *J. Phys. Chem. B* **2005**, *109*, 11501.
(9) Wang, D. Y.; Caruso, F. *Adv. Mater.* **2001**, *13*, 350.
(10) (a)Yan, H. W.; Blanford, C. F.; Smyrl, W. H.; Stein. A. *Chem. Commun.* **2000**, 1477. (b) Cassagneau, t.; Caruso, F. *Adv. Mater.* **2002**, *14*, 34.
(11) Guo, H. L.; Knobler, C. M.; Kaner, R. B. *Synth. Met.* **1999**, *101*, 44.
(12) Moutet, J. C.; Saintaman, E.; Tranvan, F.; Angibeaud, P. *Adv. Mater.* **1992**, *4*, 7.
(13) Bross, P. A.; Schoberl, U.; Daub, J. *Adv. Mater.* **1991**, *3*, 198.
(14) Huang, J. X.; Egan, V. M.; Guo, H. L.; Yoon, J. Y.; Briseno, A. L.; Rauda, I. E.; Garrell, R. L; Knobler, C. M.; Zhou, F. M.; Kaner, R. B. *Adv. Mater.* **2003**, *15*, 1158.
(15) McCarthy, P. A.; Huang, J. Y.; Yang, S. C.; Wang, H. L. *Langmuir* **2002**, *18*, 259.

10.1021/cm051410v CCC: $33.50

Experimental Section

Materials. (1R)-(−)-10-camphor sulfonic acid ((−)-CSA) and poly(acrylic acid) (PAA) (Mw ca. 90000) are purchased from Acros and used as-received. Diazoresin (DR) was synthesized according to the literature.[17] Polystyrene spheres (donated by Rohm & Haas Company) are almost monodispersed with ∼5.7 μm in diameter. Aniline, ammonium persulfate, tetrabutyl titanate, and ethanol are analytic agents.

Preparation of Macroporous Materials of CPACs with DR as a Thermosetting Agent. CPACs were prepared according to the literature[12] and modified with DR as follows: 0.2 mL of CPACs (20 mg/mL) aqueous dispersion was added into 0.6 mL of DR (Mn ∼ 2000 g/mol) aqueous solution (5 mg/mL) and stirred for 20 min to obtain DR-modified CPACs (DR-CPACs). The preparation of composite colloidal crystal, which consists of PS beads and DR-CPACs, is depicted as follows: 0.3 mL of aqueous dispersion (20 mg/mL) of PS beads was added into 0.8 mL of DR-CPACs dispersion (5 mg/mL) and stirred for 10 min. The mixture was centrifuged for 10 min at 10000 rpm to form composite colloidal crystal, in which the interspaces of PS beads have been fully filled by DR-CPACs. It then was treated thermally at 55 °C overnight and further immersed in 0.3 mL of DR aqueous solution (100 mg/mL) for 2 h to allow infiltration of more DR molecules into the interspaces of the colloids, followed by thermal treatment at 55 °C overnight. The DR infiltration and thermal treatment were repeated once again. Finally, the obtained solid was immersed in tetrahydrofuran (THF) at 25 °C for 6 h three times to dissolve the PS beads. The dark-green cross-linked macroporous materials comprising CPACs was obtained.

Preparation of Macroporous Materials of CPACs with TiO_2 as a Reinforcing Agent. To prepare more robust macroporous materials of CPACs, 10 mg of composite colloidal crystal was immersed in 1 mL of tetrabutyl titanate (TBT)−ethanol mixture (1:1/v:v) for 8 h to allow TBT infiltration into the interspaces of the colloids. The solid obtained then was immersed in 1 mL of water/ethanol (1:1/v:v) mixture for 2 h. In the sol−gel process the TiO_2 formed in the interspaces will reinforce the composite colloidal crystal. It then was dried in vacuum overnight at ∼25 °C. The procedures mentioned above were repeated once again. The obtained solid was treated with THF for 6 h at 25 °C three times to dissolve the PS beads. The macroporous materials of CPACs reinforced by TiO_2 were obtained.

Characterization. The circular dichroism (CD) spectra were measured with a Jobin Yvon CD6 instrument. TEM and SEM images were taken with JEM-100cx and STRATA DB 235 microscopes, respectively. XPS analysis was performed with an Axis Ultra spectrometer (Kratos, U.K.) using Mono Al Kα (1486.71 eV) radiation at a power of 225 W (15 mA, 15 kV). To compensate the surface charge effect, binding energies were calibrated using a C 1s hydrocarbon peak at 284.8 eV. Thermogravimetric analysis (TGA) measurement was carried out on a SDT2960 instrument (Thermal Analysis Co. U.S.A.) from room temperature to 800 °C with a temperature increasing rate at 10 °C/min. X-ray diffraction (XRD) was taken on the Dmax/2400 (Rigaku Co. Japan) instrument with a scan range (2θ) from 10° to 60°.

Results and Discussion

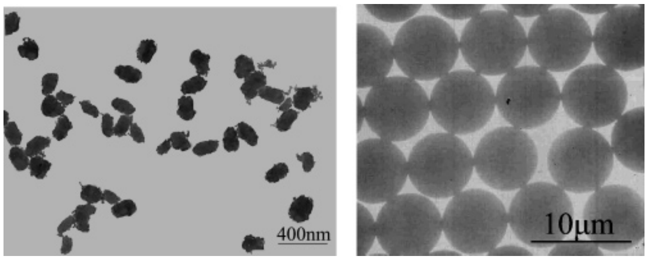


Figure 1. TEM micrographs of CPACs (left) and PS beads (right).

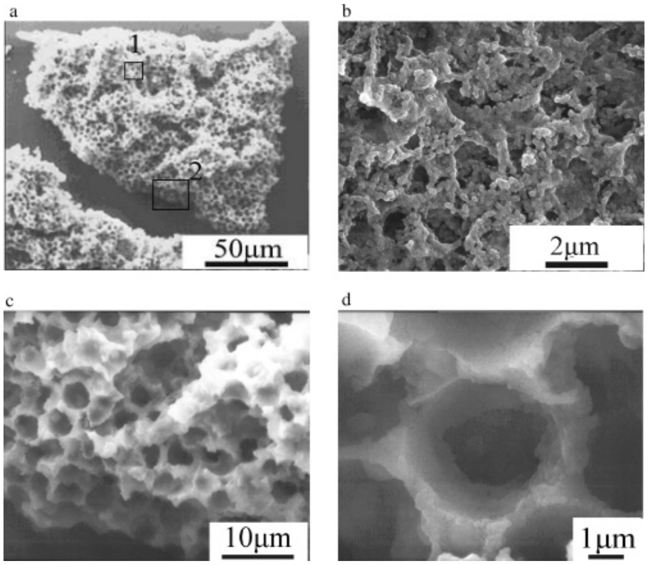


Figure 2. SEM images of macroporous materials of CPACs. (a) Prepared with DR as a thermosetting agent; (b) prepared without DR; (c) a section image of region 2 of 2a; (d) a magnified pore image of region 1 of 2a.

Figure 1 shows the morphology of CPACs and PS beads determined by TEM. The CPACs possess elliptic shape (left) with the length of 150−300 nm and the width of 100−200 nm. The PS beads used as sacrificial template are almost monodispersed with ∼5.7 μm in diameter (right).

Figure 2 shows the SEM images of the porous material of CPACs prepared in the presence and absence of DR as a thermosetting agent. Figure 2a shows a bulky porous material of CPACs. Figure 2c is a section image of Figure 2a (region 2). The porous structure can be observed clearly both in Figures 2a and 2c. The pore size is ∼4.3 μm in diameter on average and is smaller than the original PS beads (∼5.7 μm) due to the shrinkage of the pores in the removal of PS beads. Figure 2d is an image of the magnified pore (region 1 of Figure 2a). We can see that the pore wall is composed of thermoset CPACs. If there is no DR as a thermosetting agent, we can only obtain a collapsed structure of CPACs (Figure 2b). It is obvious that DR plays an important role in keeping the porous structure.

The surface of CPACs, which was prepared in the presence of poly(acrylic acid), is carboxyl-rich and easily combines with DR molecules through the Columbic interaction. After heating or exposure to UV light, the ionic bonds between carboxylic groups and $-N_2^+$ groups will be converted to covalent bonds to form a covalently cross-linking structure.[18,19] The reaction between DR and carboxylic CPACs

---

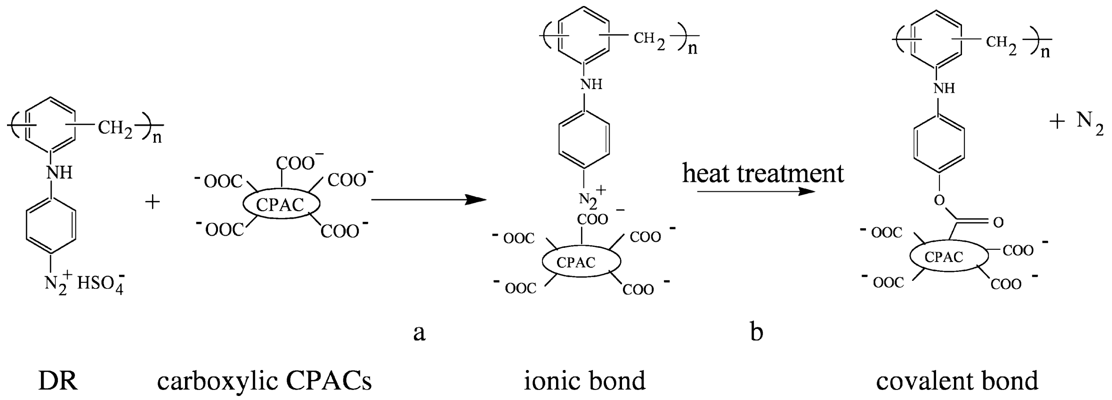
(16) Li, W. G.; McCarthy, P. A.; Huang, J.; Yang, S. C.; Wang, H. L. *Macromolecules* **2002**, *35*, 9975.

(17) Cao, S. G.; Zhao, Ch.; Cao,W. X. *Polym. Int.* **1998**, *44*, 142.

(18) Chen, J. Y.; Huang, L.; Ying, L. M.; Luo, G. B.; Zhao, X. S.; Cao, W. X. *Langmuir* **1999**, *15*, 7208.

(19) Sun, J. Q.; Wu, T.; Sun, Y. P.; Wang, Z. Q.; Zhang, X.; Shen, J. C.; Cao, W. X. *Chem. Commun.* **1998**, *17*, 1853.

Scheme 1. Schematic Representation of (a) the Reaction between DR and Carboxylic CPACs and (b) the Thermosetting Process



and the thermosetting process of CPACs with DR molecules can be schematically represented in Scheme 1.

To determine the chiral stability of CPACs, a five-layer CPACs/DR film was prepared on a quartz wafer. Figure 3 shows the CD spectra of the film before (curve 1) and after heating (curve 2) at 55 °C for 48 h. There is almost no change in the CD spectra. It means that the CPACs possess sufficient thermal stability.

Figure 4 shows the SEM images of the porous materials of CPACs with TiO_2 as a reinforcing agent. Figure 4a is the image of a bulky material and Figure 4b is an image of the magnified pore. We can see that the material has fine pore structure and the pores (~4.7 μm in diameter) are interconnected.

Figure 5 is an XPS diagram of a powder of CPACs macroporous materials with TiO_2 as a reinforcing agent. The appearance of typical Ti $2p_{1/2}$ (465.4 eV), Ti $2p_{3/2}$ (459 eV), Ti 3s (62.4 eV), and Ti 3p (37.4 eV) peaks show that TiO_2 has been successfully incorporated into the porous framework. The presence of the signal of C 1s indicates the existence of modified CPACs. In addition, we also carried out XRD measurement of this sample. Experimental results show that the TiO_2 in macroporous materials is amorphous.

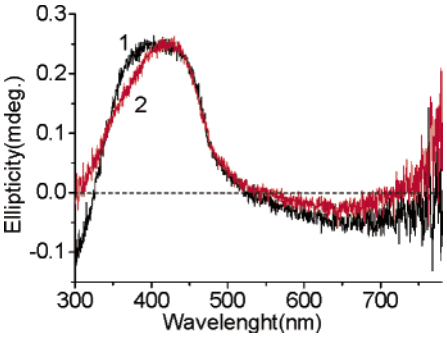


Figure 3. CD spectra of CPACs film before (curve 1) and after (curve 2) heating at 55 °C for 48 h.

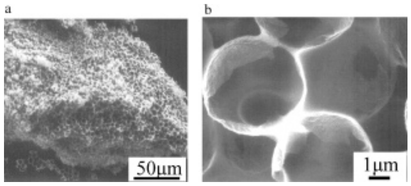


Figure 4. SEM images of the porous materials of CPACs with TiO_2 as a reinforcing agent: (a) image of a bulk sample; (b) image of the magnified pores.

TGA measurement from room temperature to 800 °C shows that the gross gravity loss of the porous material reinforced by TiO_2 is ~84 wt %, which means TiO_2 occupies ~16 wt % in it (Figure 6a). After sintering of the porous material at 450 °C for 150 min, the remaining TiO_2 fragment can be visualized clearly (Figure 6b). Therefore, we consider that TiO_2 is discontinuous in the framework of macroporous materials.

The CPACs porous materials were immersed in DMF at ~25 °C for 24 h to examine their solvent stability. The pore shape and size of the material using TiO_2 as a reinforcing agent (Figure 7a) are maintained perfectly. However, the pore

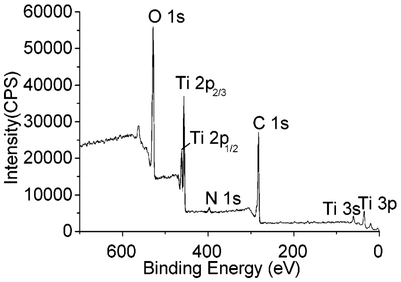


Figure 5. Survey-scan X-ray photoelectron spectrum of the porous materials of CPACs.

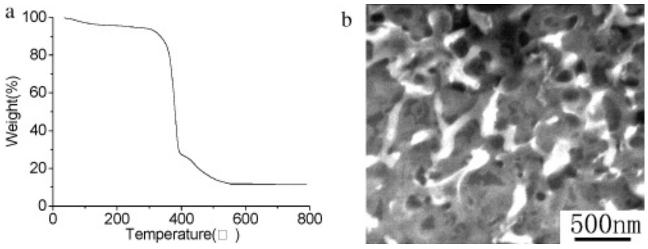


Figure 6. (a) TGA diagram of the CPACs porous material reinforced with TiO_2; (b) SEM image of the macroporous material after sintering.

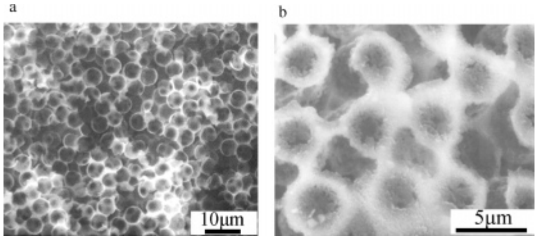


Figure 7. SEM images of CPACs porous materials after immersion in DMF: (a) with TiO_2 as a reinforcing agent; (b) with DR as a thermosetting agent.

structure of the sample using only DR as a thermosetting agent will be deformed after immersion (Figure 7b). It indicates that the stability of the porous materials reinforced with TiO_2 is better than that using DR as a thermosetting agent.

Conclusion

Robust macroporous materials of chiral polyaniline composites (CPACs) using diazoresin (DR) as a thermosetting agent or reinforced by TiO_2 were prepared for the first time with 5.7 μm polymer beads as sacrificial template. The formed porous materials reinforced by TiO_2 are more stable than those using DR as a thermosetting agent toward the etching of solvents. The weight percent of TiO_2 in porous materials is ∼16%. This kind of porous materials may be useful in practice as a chiral-separation agent.

Acknowledgment. The authors are grateful to the NSFC for financial support of this work (Grant No: 20274002 and 90406018). We thank Dr. B. W. Jiang (Rohm & Haas Company) for donating the PS spheres.

CM051410V