Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 5324–5328

polymer

www.elsevier.com/locate/polymer

Hollow nanometer-sized polypyrrole capsules with controllable shell thickness synthesized in the presence of chitosan

Xiaoming Yang, Yun Lu*

State Key Laboratory of Coordination Chemistry, Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Received 12 October 2004; received in revised form 13 April 2005; accepted 14 April 2005
Available online 29 April 2005

Abstract

A simple strategy for the one-step synthesis of AgCl/polypyrrole core/shell nanostructures with controllable shell thickness in the presence of chitosan and thus hollow polypyrrole nanoparticles was reported. AgCl, as a template, was formed during the initial polymerization by the interaction between metal cations and oxidizing anions and adsorbed with chitosan whereupon to induce the coating of polypyrrole layers. TEM, FTIR, XRD demonstrated the formation of the core/shell structure. Possible mechanism was proposed for the formation of core/shell structure and thus hollow particles.

Keywords: AgCl; Chitosan; Hollow

1. Introduction

Different morphologies of polypyrrole (Ppy) have been obtained by changing the synthesis methods such as self-assembled method and template method [1]. For instance, Ppy particles with spherical shapes could be obtained by dispersion or emulsion polymerization in the presence of polymeric stabilizers or low molecular weight surfactants [2–4]. Nanotube of polypyrrole has been synthesized by using an alumina membrane template or by self-assembled method in the presence of beta-naphthalene sulfonic acid or *p*-toluenesulfonate acid [5]. However, control over the morphology of conducting polymers using a simple and effective method remains scientifically challenging.

In recent years, hollow nano-spheres or nano-cavities have attracted much attention because of its broad range of applications [6]. For example, it can be used as delivery vehicle for the removal of contaminated waste and for the controlled release of substances such as drugs, cosmetics, dyes, and inks or as a carrier of catalyst [7]. Such nano-cavities were commonly obtained from a stepwise process like gaining the cores firstly, then covering the shell, and finally removing the core materials by using a variety of chemical and physical methods, such as calcinations or solvent etching [8]. Hollow polypyrrole capsules were usually obtained by above mentioned template method. Stella et al. prepared nanometer-sized gold particles that were used as templates to grow polypyrrole shells, and then dissolved to obtain hollow particles [9]. Lingyun Hao et al. utilized silica as core to produce hollow polypyrrole [10]. Herein, we developed a simple and convenient one-step process for the synthesis of silver chloride/polypyrrole core/shell composite microspheres in the presence of chitosan to obtain the uniform hollow nanometer-sized polypyrrole capsules by dissolution of silver chloride.

2. Experiment

Pyrrole (Aldrich) was distilled twice under reduced pressure, stored under nitrogen and refrigerated in the dark. The degree of deacetylation of chitosan (Nantong Shuanglin Biological Product Inc.) was about 90%. Silver(I) nitrate, chitosan and ferric trichloride were of AR grade and used without purification.

---

* Corresponding author. Tel.: +86 25 6204225; fax: +86 25 83317761.
E-mail address: yunlu@nju.edu.cn (Y. Lu).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.04.023

2.1. Synthesis of hollow polymer nanocapsules

In a typical procedure, an aqueous solution of chitosan (0.2%) was prepared by dissolving of chitosan in acetic acid aqueous (2%), and then adding $AgNO_3$ (0.1 M) and pyrrole (0.05 or 0.1 M) to form a homogeneous solution. An aqueous solution of $FeCl_3$ (0.05 M) as an initiator was dropped into above solutions with vigorous stirring. The polymerization was allowed to proceed for 24 h at room temperature. After that the solution was centrifuged for 30 min at 15,000r and the precipitation was then redispersed in deionized water and centrifuged again. The cycle was repeated three times. The final composite was dried under vacuum for 12 h.

The polypyrrole/AgCl nanoparticles were converted to hollow polymer capsules by dissolution of the AgCl in sodium hyposulfite or ammonium chloride aqueous solutions, and the solution was centrifuged as mentioned above.

2.2. Characteristics

TEM images were acquired with JEM-200CX transmission electron microscope. Samples were prepared for TEM analysis by placing several drops of suspension on a carbon-coated copper grid and quickly wicking away the solution with filter paper leaving behind a thin colloidal film. Conductivity measurements were made on compressed pellets of the powder using conventional four-point probe technique at ambient temperatures. Fourier-transform infrared spectra (FTIR) of the samples were recorded on a Bruker VECTOR22 spectrometer. X-ray diffraction (XRD) patterns were taken on a shimadzu XD-3A instrument with a Cu K_α X-ray source. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument at a heating rate of 10 °C min^{-1} in air.

3. Results and discussion

Choosing an effective stabilizer is very important for synthesis of polymer nano-particles. Usually, polymeric surfactants such as poly(vinylpyrrolidone) offer the advantage of steric stabilization of dispersions, whereas most low molecular weight surfactants operate only through electrostatic stabilization. Chitosan, a naturally occurring polymer of β-(1-4)-2-amino-2-deoxy-D-glucopyranose, is a biodegradable, non-toxic, and renewable resource commodity. As the biopolymer is insoluble in water at PH = 7 but becomes soluble and positively charged in acidic media, it can be used as a biosurfactant. In fact, it has been successfully used to stabilize polymer nanoparticles such as poly(methyl methacrylate) and poly(butyl cyanoacrylate) due to its electrostatic effect and steric stabilization [11,12]. But it was rarely chosen as a cationic polymeric surfactant to synthesize polypyrrole nanoparticles [13]. In the process for the formation of the silver chloride/polypyrrole core/shell structure, $FeCl_3$ was selected to be an initiator to oxidize pyrrole monomer in the presence of chitosan as a stabilizer. It was found that when $FeCl_3$ aqueous solution was added to chitosan solution containing $AgNO_3$ and pyrrole, a white precipitate AgCl appeared immediately, which gradually turned black in colour in 2 min. Herein, chitosan, not only being a stabilizer but also a polymer ligand, was adsorbed onto the AgCl particles by cooperation bonds between the metal ions and amino and or hydroxyl groups of chitosan. At almost the same time, pyrroles were oxidized by Fe^{3+} to form polycationic Ppy chains, which was just a little slower than the former one. The polymer appears to have nucleated on the adsorbed chitosan, obtaining core/shell nano-sized particles finally. Dissolution of the templates yielded structurally intact hollow polymer capsules with the shell thickness governed by the pyrrole added. The morphology of the composites was analyzed by TEM. The TEM images in Fig. 1(A) and (B) shows the AgCl/Ppy core/shell structure resulting from the above procedures. Silver chloride nanoparticles surrounded by a spherical polymer matrix are evident in the image. The obtained particles with the shell thickness of 20 nm and core diameter of 10–50 nm are uniform in size and about 60–80 nm in diameter as shown in Fig. 1(A). The shell thickness could be controlled by only change the concentration of pyrrole monomer. When the concentration of pyrrole monomer was doubled, the shell thickness increased from 20 to 40 nm as shown in Fig. 1(B). On the other hand, adjusting the ratio of reactants could regulate the number of AgCl particles but could not control the size of the particles because of the fast formation of AgCl particles. Treating the core/shell composite materials with AgCl etching solution (sodium hyposulfite or ammonium chloride aqueous solutions) resulted in structurally intact hollow capsules, as shown in Fig. 1(C) and (D). The sharp contrast between the dark edge and the pale center in the TEM image proved the hollow morphology. The inner diameter of the capsules matched the diameter of the template particle, only a little reorganization, collapse, or shrinkage occurs when the capsules are dried for TEM.

The molecular structure of the Ppy spheres was characterized by Fourier-transform Infrared (FTIR) spectroscopy (Fig. 2). No obvious difference was found in the FTIR spectra of the Ppy core/shell samples from those of Ppy obtained by common methods. The characteristic bands of the Ppy samples were the pyrrole ring fundamental vibration at 1534 cm^{-1}, C–N stretching vibration in the ring at 1455 cm^{-1}, and the =C–H in plane vibration at 1171 cm^{-1} [14]. Only the shift of the band at 1534–1545 cm^{-1} is observed, which is most likely related to the different ions doped and their degree of doping. In the case of common method, polypyrrole oxidized by $FeCl_3$ is doped by Cl^-, while the core/shell polypyrrole particles are doped by NO_3^- because of nucleation of Cl^- with silver ions in the polymerization. It is notable that intensity of the peak at

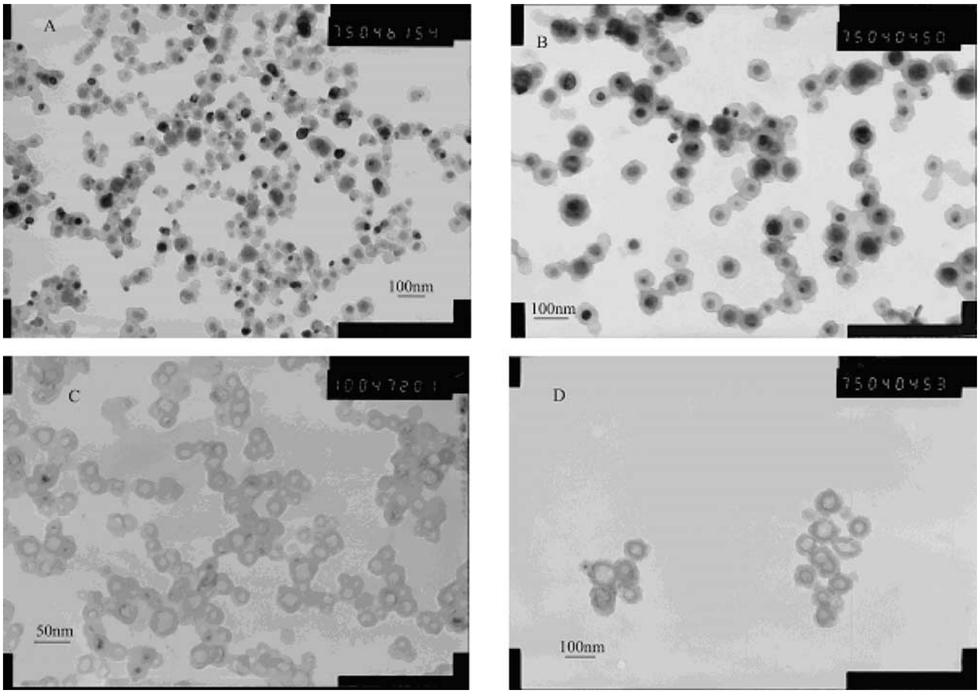

Fig. 1. TEM images of AgCl/polypyrrole core/shell particles obtained at different concentration of pyrrole and their hollow structure. A: 0.05 M of pyrrole; B: 0.1 M of pyrrole; C: after removing the AgCl core of A; D: after removing the AgCl core of B (the reaction condition: $AgNO_3$ 0.1 M; $FeCl_3$ 0.05 M; chitosan 2%).

1091 cm^{-1} typical of conducting Ppy form was reduced after dissolution of AgCl, which can be explained due to the low stability or decreased degree of doping of polypyrrole in air and aqueous solutions. This is in the accordance with the decreased conductivity of hollow composites (3 S cm^{-1}) by comparing with that of core/shell composites (15 S cm^{-1}). Moreover, disappearance of the peak at 1383 cm^{-1} after dissolution of AgCl, suggests that there may be some interaction between AgCl and Ppy.

The presence of AgCl crystallites was confirmed on the spectra by a diffraction line. As can be seen in Fig. 3 The diffraction of (111), (200), (220), (311), (222) plans positioned on $2\theta = 27.83$, 32.24, 46.234, 54.83, and 57.48°, which is consistent with literature data for powder diffraction of isotropic AgCl [15]. Distinct reflection centered at $2\theta = 25$ °C is characteristic of the doped Ppy [16].

The core/shell structure was also proved by the thermo-gravimetric studies. Fig. 4 summarizes the results of the thermo-gravimetric studies on the core/shell particles and

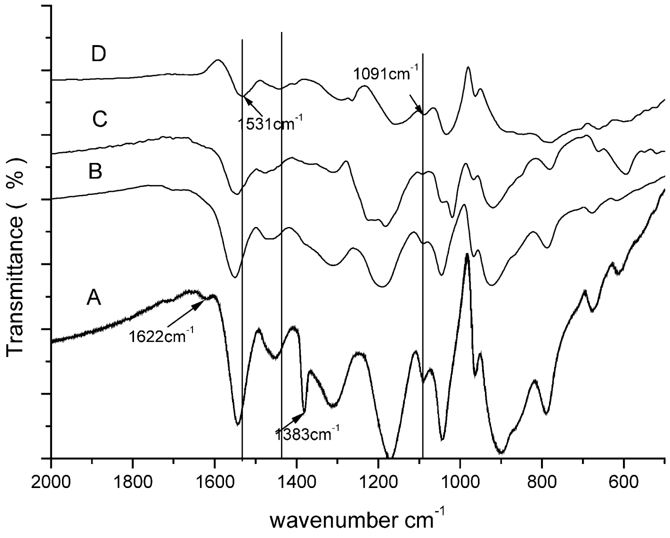

Fig. 2. FTIR spectra of A: AgCl/polypyrrole core/shell composites; B: hollow polypyrrole obtained after dissolving AgCl by sodium hyposulfite aqueous solutions; C: hollow polypyrrole obtained after dissolving AgCl by ammonium chloride aqueous solutions; D: polypyrrole oxidized by $FeCl_3$.

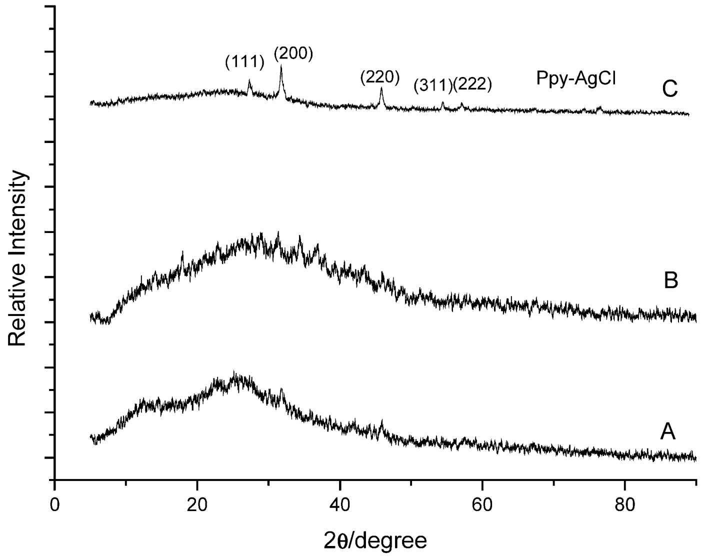

Fig. 3. X-ray diffraction patterns of polypyrrole A: polypyrrole obtained after dissolving AgCl by ammonium chloride aqueous solutions; B: polypyrrole obtained after dissolving AgCl by sodium hyposulfite aqueous solutions; C: polypyrrole/AgCl core/shell composites.

hollow polypyrrole particles. The TGA curves of the core/shell particles show a three-step weight loss. The weight loss in the first step is attributed to the loss of residual moisture. The second step starting around 260 °C, corresponds to polymer degradation [17]. The third step around 720 °C is due to the decomposition of AgCl.

Without the chitosan or with a common stabilizer PVP, the core/shell structure could not form. It is known that specific functional groups can be used to induce coating during the precipitation and surface reactions on the cores. Chitosan is a usefully steric agent to promote a strong interaction between the AgCl particles and the pyrrole monomers. We think the amino and hydroxyl groups of chitosan would be beneficial for the adherence between polymer shell and inorganic core. The adsorbed chitosan might provide active sites on the AgCl so as to induce the growing polycationic PPy chains to complete the coating of Ppy layers. The possible mechanism for the formation of core/shell and hollow particles could be shown in Fig. 5.

4. Conclusion

Summarizing, we have demonstrated the one-step synthesis of AgCl/Ppy core/shell nanocomposites and thus hollow polypyrrole particles with chitosan as stabilizer. The method shows the merits of easier preparation compared with the conventional stepwise process and controlled shell thickness could be obtained by adjusting the quantity of pyrrole added. TEM gave the direct evidence of the

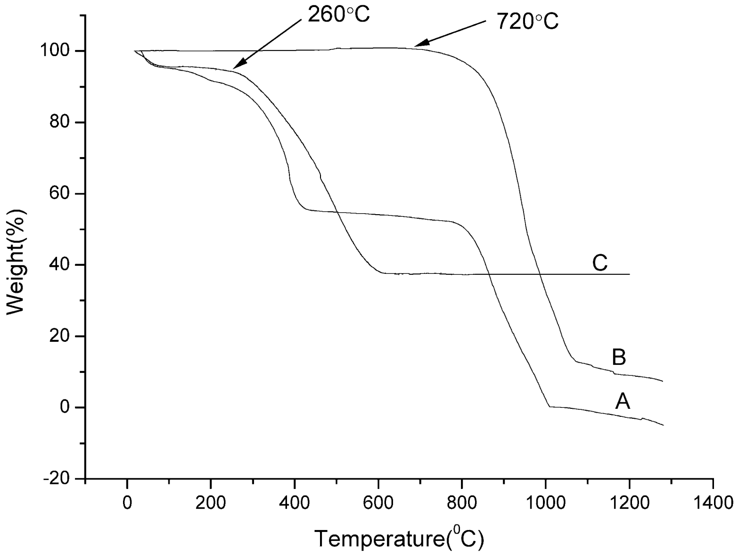

Fig. 4. TGA curves for the A: AgCl/polypyrrole core/shell composites; B: AgCl; C: hollow polypyrrole.

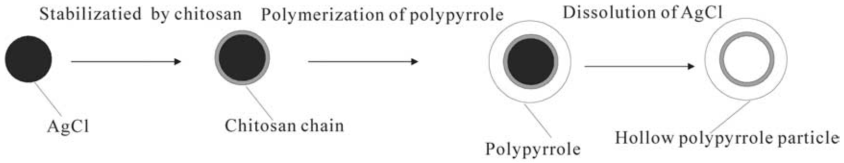

Fig. 5. Schematic illustration of the formation process of AgCl/polypyrrole core/shell and hollow polypyrrole particles.

core/shell structure; FTIR confirmed the formation of polypyrrole and XRD showed the presence of AgCl. Possible formation mechanism of the silver/Ppy core/shell nano-particles was proposed.

Acknowledgements

The authors are grateful for the supports from the National Natural Science Foundation of China (No. 20174016) and Testing Foundation of Nanjing University.

References

[1] Wei ZX, Zhang ZM, Wan MX. Langmuir 2002;18(3):917–21.
[2] Kinlen PJ, Liu J, Ding Y. Macromolecules 1998;31(6):1735–44.
[3] Stejskal J, Omastova M, Fedorova S, Proke J, Trchova M. Polymer 2003;44(5):1353–8.
[4] Pich A, Lu Y, Adler HJP, Schmidt T, Arndt KF. Polymer 2002;43(21): 5723–9.
[5] Zhang ZM, Wei ZX, Wan MX. Macromolecules 2002;35(15): 5937–42.
[6] Caruso F. Adv Mater 2001;13(1):11–22.
[7] Shuchukin DG, Sukhorukov GB. Adv Mater 2004;16(8):671–82.
[8] Yang ZZ, Niu ZW, Lu YF. Angew Chem Int Ed 2003;42(17):1943–5.
[9] Marinakos SM, Novak JP, Brousseau LC. J Am Chem Soc 1999; 121(37):8518–22.
[10] Hao LY, Zhu CL, Chen CN. Synth Met 2003;139(2):391–6.
[11] Chem CS, Lee CK, Ho CC. J Polym Sci, Polym Chem 1999;37(10): 1489–99.
[12] Yang SC, Ge HX, Hu Y, Jiang XQ, Yang CZ. Colloid Polym Sci 2000;278(4):285–92.
[13] Khor E, Whey JLH. Carbohydr Polym 1995;26(3):183–7.
[14] Dhanabalan A, Mello SV, Oliveira ON. Macromolecules 1998;32(6): 1827–32.
[15] Zayat M, Einot D, Reisfeld R. J Sol-Gel Sci Technol 1997;10(1): 67–74.
[16] Lee DK, Lee SH, Char K. Macromol Rapid Commun 2000;21(16): 1136–9.
[17] Deng JG, Ding XB, Zhang WC, Peng YX, Wang JH, Long XP, et al. Polymer 2002;43(8):2179–84.