Fabrication of a novel polypyrrole/poly(methyl methacrylate) coaxial nanocable using mesoporous silica as a nanoreactor†

Jyongsik Jang,* Byungkwon Lim, Jinwoo Lee and Taeghwan Hyeon*

School of Chemical Engineering, Seoul National University, Seoul 151-742, Korea.
E-mail: jsjang@plaza.snu.ac.kr and thyeon@plaza.snu.ac.kr

Received (in Cambridge, UK) 31st July 2000, Accepted 15th November 2000
First published as an Advance Article on the web 14th December 2000

We report on the fabrication of a polypyrrole/poly(methyl methacrylate) coaxial nanocable through the sequential polymerization of methyl methacrylate and pyrrole monomers inside the channels of mesoporous SBA-15 silica, followed by the removal of the silica template.

There has been tremendous interest in the development of conducting structures with nanometer dimensions. These nanostructured conducting materials could find many attractive applications such as electromagnetic interference shielding, electrochromic devices, supercapacitors, polymeric electrolytes and sensors.† Recently, many nanotubes and nanowires of polymers, metals and carbons have been produced through template approaches with various membranes,‡ layered inorganic solids,§ zeolites and mesoporous materials.¶ Generally conducting polymers themselves, however, possess poor mechanical properties, and are very difficult to process. To overcome these drawbacks, much research effort has been focused on the development of processes to combine conducting polymers and polymer matrices with good tractability.1 Recently, many different conducting polymer composites have been developed, no nanostructured conducting polymer/polymer composites have, as yet, been reported. Herein, we report the preparation of polypyrrole/poly(methyl methacrylate) coaxial nanocable using mesoporous silica as a template.§

In the synthesis, mesoporous SBA-15 silica was utilized as a template. Mesoporous SBA-15 silica with regular hexagonal pores of 7.5 nm was prepared by the reported method.4 To synthesize tubular PMMA within the pores of SBA-15, methyl methacrylate (MMA) was incorporated into the pores of SBA-15 silica and MMA was subsequently polymerized. The amount of MMA was precisely controlled so that the polymerization of MMA occurs, PMMA might fill these micropores in addition to partial filling of the mesopores. Therefore, the actual amount of PMMA derived solely from the partial filling of mesopores.

Small angle X-ray scattering (SAXS) patterns were obtained at various times during the synthesis. The diffraction pattern of SBA-15 showed typical h0l reflections (100, 110 and 200) from the hexagonal arrangement of pores. The peak intensity in the SAXS of PMMA/SBA-15 and PPY/PMMA/SBA-15 decreased compared with that in SBA-15 silica, but the peak positions of the XRD patterns were nearly identical. These results show that the SBA-15 structure remained intact during the synthesis, demonstrating the usefulness of SBA-15 silica as a nanoreactor.

The PPY/PMMA nanocomposite was obtained by HF etching of the SBA-15 silica template. It has been reported that acid treatment does not decrease the electrical conductivity of PPY.8 The resulting polymer/polymer nanocomposite was dried at 100 °C under vacuum to obtain the dry powder which was analyzed by FTIR spectroscopy. The IR spectrum of the nanocomposite exhibited characteristic peaks from both PMMA and PPY. One very unusual observation is that there are two carbonyl peaks associated with PMMA. The curve-fitted

† Electronic supplementary information (ESI) available: FTIR spectra, XRD patterns and TEM images. See http://www.rsc.org/suppdata/cci/b0/b006197m/

‡ Organic solids, 3 zeolites and mesoporous materials. 4 Generally nanostructured conducting materials could find many attractive applications such as electromagnetic interference shielding, electrochromic devices, supercapacitors, polymeric electrolytes and sensors. 5

Fig. 1 The pore size distribution curves of SBA-15, PMMA/SBA-15 and PPY/PMMA/SBA-15. The curves were obtained from the adsorption branch of the nitrogen isotherm calculated by the BJH method. The isotherms were collected at 77 K on a Micrometrics ASAP2010 Gas Adsorption Analyzer after degassing at 250 °C at 30 μTorr for 5 h.

DOI: 10.1039/b006197m


This journal is © The Royal Society of Chemistry 2001
The Korean Ministry of Education for the financial support.

The PPy chains.

exposure of the conducting surface of PPy, the conductivity is

are surrounded by insulating PMMA tubules, limiting full

shoulder at 1700 cm$^{-1}$ [Fig. 2(a)]. The carbonyl peak at 1700 cm$^{-1}$ indicates hydrogen bonding interactions between PMMA carbonyl groups and PPy N–H groups. On the other hand, the peak at 1727 cm$^{-1}$ arise from the free carbonyl groups of PMMA. Such a strong interaction between PPy and PMMA has not been reported before in the micrometer-sized PPy/PMMA composites. Judging from these data, it seems that the outer PMMA layer is intimately mixed with PPy at the nanometer-scale [Fig. 2(b)].

The PPy/PMMA nanocomposite could be easily molded by compression under 25 kN cm$^{-2}$ at 220 °C for 10 min using a pelletizer. Interestingly, the AFM image of the compression-molded PPy/PMMA composite revealed highly oriented and unidirectional structures (Fig. 3). The well aligned structure was observed nearly all over the sample, which seems to result from template synthesis inside regular hexagonally arranged mesopores of SBA-15. The compression-molded PPy/PMMA nanocomposite exhibited an electrical conductivity of 1.7 S cm$^{-1}$.

Considering that the typical conductivity of chemically synthesized PPy lies in the range 1-10 S cm$^{-1}$, the conductivity of our PPy/PMMA composite seems to be low. However, when we consider that the PPy wires in the PPy/PMMA nanocomposite are surrounded by insulating PMMA tubules, limiting full exposure of the conducting surface of PPy, the conductivity is relatively high which might result from the good alignment of the PPy chains.

We are grateful to the Brain Korea 21 Program supported by the Korean Ministry of Education for the financial support.

Notes and references


8 M. Forsyth and V. T. Truong, Polymer, 1995, 36, 725.

Fig. 2 (a) Curve-fitted IR spectra of the PMMA carbonyl peak for the PPy/PMMA nanocomposite. (b) A schematic illustration of coaxial nanocable of PPy/PMMA.

Fig. 3 AFM images of PPy/PMMA nanocomposite: (a) height image and (b) phase image. The film was fabricated by compression-molding of the PPy/PMMA nanocomposite at 220 °C under 25 kN cm$^{-2}$ for 10 min. The images were obtained with Nanoscope Illa Dimension 3100 SPM (Digital Instruments) in tapping mode.