Preparation of Highly Ordered Mesoporous Thiophene–Silica with Spherical Macrostructure

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Highly ordered mesoporous thiophene–silica powder was prepared using nonionic PEO–PLGA–PEO triblock copolymer templates and a 2,5-bis(triethoxysilyl)thiophene organosilica precursor under acidic conditions. The mesoporous thiophene–silica materials prepared with the $EO_{16}(L_{29}G_7)EO_{16}$ template were observed to have a well-defined spherical-like external morphology with a diameter of 2–5 µm, and a 2D hexagonal (*p*6*mm*) array of mesopores with a lattice constant of 9.55 nm. The thiophene–silica also displayed a large surface area of up to 1410 $m^2\,g^{-1}$.

Periodic mesoporous organosilicas (PMO) have been developed using several organo-bridged silsesquioxane precursors in order to distribute the organic moieties homogeneously inside the framework wall.[1] Periodic mesoporous materials with aromatic bridging groups have attracted particular attention owing to their versatile functionalities, surface properties, and so on.[2] However, only a few works have been published about the preparation of mesoporous thiophene–silica using conventional surfactant templates.[3] In this paper, we report a more facile procedure and the characterization of highly ordered periodic mesoporous thiophene–silica hybrid materials using poly(ethylene oxide)–poly(DL-lactic acid-*co*-glycolic acid)–poly(ethylene oxide) (PEO–PLGA–PEO) block copolymers having different interaction parameters from those of typical PEO–PPO–PEO triblock copolymers. The PLGA chain is approximately four times as hydrophobic as the PPO chain, which is less hydrophobic than the polyisoprene and poly(butylene oxide) chains.[4] Moreover, the amorphous PLGA chain has better mobility and solubility than crystalline poly(D-lactic acid) and poly(L-lactic acid) with their orthorhombic and pseudo-orthorhombic unit cells, respectively.[4]

The purpose of this study is to present highly ordered mesoporous thiophene–silica materials with a spherical external morphology, which is useful for the host material and the adsorbent of special applications, using a new nonionic block copolymer template.

Ring-opening metathesis polymerization was employed from mixtures of recrystallized 3,6-dimethyl-1,4-dioxane-2,5-dione (DL-lactide) (Aldrich) and glycolide (Polyscience) onto distilled monomethoxypoly(ethylene oxide) ($M_n = 750$ $g\,mol^{-1}$, $d = 1.094\,g\,cm^{-3}$, Aldrich) using stannous 2-ethyl hexanoate (Sigma) as a catalyst and hexamethylene diisocyanate (Sigma) as a coupling agent.[5] The number-average molecular weight of the $EO_{16}(L_{29}G_7)EO_{16}$ triblock copolymers obtained was determined to be 5310 Dalton, and their polydispersity index was 1.28 by GPC. The volume fraction of the PEO blocks (Φ_{PEO}) was calculated to be 0.38 using the group contribution method.

$EO_{16}(L_{29}G_7)EO_{16}$ triblock copolymers and 2,5-bis(triethoxysilyl)thiophene (BTET) (JSI Silicone) were used as received for preparing the periodic mesoporous thiophene–silica materials. In a typical synthesis, 0.5 g of $EO_{16}(L_{29}G_7)EO_{16}$ was dissolved in 0.5 g of ethanol and 21.9 g of distilled water. Then, 0.1 g of HCl (37 wt %) and 0.73 g of BTET were added to the solution. Precipitates were obtained after the mixture was stirred for about 1 h at 313 K, and the solid products were then aged for 24 h at 368 K. Residual block copolymer was removed by stirring the mesoporous materials (0.5 g) in an HCl (4 g of 37 wt %)/ethanol (120 mL) mixed solvent for 10 h.

The synchrotron SAXS data of the mesoporous thiophene–silica powder prepared with the $EO_{16}(L_{29}G_7)EO_{16}$ block copolymer template and BTET precursor is shown in Figure 1a. It was found that the block copolymer-free thiophene–silica powder has a highly ordered 2D hexagonal (*p*6*mm*) mesophase with four well-resolved peaks indexed as the (100), (110), (200), and (210) reflections. The most intense (100) peak represents the large lattice spacing of $d = 8.27$ nm corresponding to the 2D hexagonal unit cell parameter, $a = 9.55$ nm. The well-defined 2D hexagonal (*p*6*mm*) of the thiophene–silica powder is also clearly observed in the transmission electron microscope (TEM) images. Figure 1b shows the TEM images of the mesoporous thiophene–silicas prepared with the $EO_{16}(L_{29}G_7)EO_{16}$ template, which are perpendicular and parallel to the channel, respectively.

The FE-SEM image in Figure 1c shows the external morphology of the mesoporous thiophene–silicas prepared with the $EO_{16}(L_{29}G_7)EO_{16}$ template. The mesoporous thiophene–silica assumes the form of spherical-like particles with a uniform diameter of 2–5 µm. The end-capped PEO chains in the PEO–PLGA–PEO make the macrostructure of the mesoporous materials spherical, as the attractive forces are not strong between

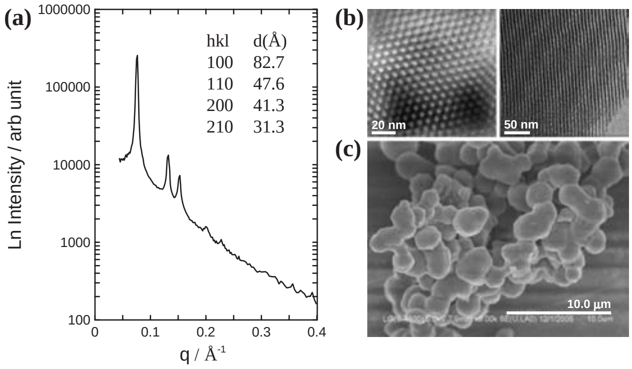

Figure 1. (a) Synchrotron small angle X-ray scattering patterns, (b) TEM images, and (c) SEM image of block copolymer-free mesoporous thiophene–silica prepared with the $EO_{16}(L_{29}G_7)$-EO_{16} block copolymer template.

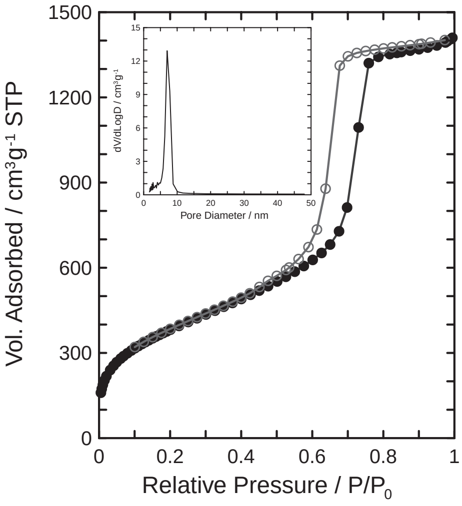

Figure 2. N_2 adsorption–desorption isotherm of mesoporous thiophene–silica materials. The pore size distributions shown in the insets and pore diameter are determined by BJH method.

the block copolymer micelles containing silsesquioxane precursors during the cooperative self-assembly. This spherical external morphology is particularly useful in applications such as catalysis and microelectronics, because spherical particles can be formed as densely packed layers and mixed well with other particles.

The nitrogen adsorption–desorption isotherms of the polymer-free mesoporous thiophene–silica powder are shown in Figure 2. The typical type-IV adsorption isotherms show a steep increase at $P/P_0 = 0.65$–0.70 due to the capillary condensation of nitrogen in the mesopores. The Brunauer–Emmet–Teller (BET) surface area and pore volume of the thiophene–silica powder are determined to be $1410\,m^2\,g^{-1}$ and $2.155\,cm^3\,g^{-1}$, respectively, from the nitrogen adsorption isotherm, as shown in Figure 2. A uniform pore size distribution with a maximum pore diameter of 7.0 nm was obtained from the adsorption isotherm based on the BJH method, as shown in the inset of Figure 2, and the wall thickness was found to be 2.6 nm by subtracting the pore diameter from the lattice unit parameter (*a*), which is in good agreement with the value estimated from the TEM image. The physicochemical properties of the mesoporous thiophene–silica prepared in this study are characterized by a high surface area and mesopore volume.

Solid-state ^{13}C and ^{29}Si CP-MAS NMR experiments were performed on the polymer-free thiophene–silica powder to verify the composition of the covalently bonded thiophene–silica framework. The ^{13}C CP-MAS NMR spectrum shows a resonance peak at 137 ppm assigned to the carbons on the thiophene ring and another resonance due to spinning sidebands. The ^{29}Si CP-MAS NMR spectrum also shows the characteristic signals assigned to $CSi(OSi)_3$ (T^3, δ −82), $CSi(OSi)_2(OH)$ (T^2, δ −74), and $CSi(OSi)(OH)_2$ (T^1, δ −66), confirming the presence of thiophene moieties inside the thiophene–silica framework and the high degree of condensation of the silanol groups. The Q peaks, such as $Si(OSi)_4$ and $Si(OSi)_3(OH)$ between −90 and −120 ppm, are negligible, which confirms that the carbon–silicon bond cleavage of the BTET precursors is not likely to occur through sol–gel synthesis under very low acidic conditions. The solid-state ^{13}C and ^{29}Si NMR spectra clearly show that the carbons on the thiophene ring and silica are bonded covalently inside the thiophene–silica pore wall network. The T^3/T^2 peak intensity ratio is lower than that of other periodic mesoporous silica with bridged aromatic group such as benzene–silica prepared with a cationic surfactant under basic conditions.[2] The low T^3/T^2 peak intensity ratio and low molecular-scale periodicity obtained from the WAXD measurements suggest that the interactive forces among the BTET precursors and those between the PEO chain and BTET precursors function weakly under acidic conditions using a nonionic block copolymer template. The TGA thermogram demonstrates high thermal stability up to 673 K.

In conclusion, a highly ordered 2D hexagonal (*p*6*mm*) mesoporous thiophene–silica hybrid material with large pores was successfully prepared using a new $EO_{16}(L_{29}G_7)EO_{16}$ triblock copolymer template. The mesoporous thiophene–silica materials prepared with the PEO–PLGA–PEO triblock copolymer templates displayed a spherical external morphology which differed from that of the materials prepared with a Pluronic P123 (PEO–PPO–PEO) template. The pore size and specific surface area were found to be about 7 nm and $1400\,m^2\,g^{-1}$, respectively, which clearly demonstrate the usefulness and versatility of the final mesoporous material, as well as the PEO–PLGA–PEO triblock copolymer templates used in this study, in a wide range of applications.

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