

Hierarchically Porous Carbon Materials from Self-Assembled Block Copolymer/Dopamine Mixtures

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Abstract

Hierarchically porous carbon materials with interconnected frameworks of macro- and mesopores are desirable for electrochemical applications in biosensors, electrocatalysis, and supercapacitors. In this study, we report a facile synthetic route to fabricate hierarchically porous carbon materials by controlled macro- and mesophase separation of a mixture of polystyrene-block-poly(ethylene) and dopamine. The morphology of mesopores is tailored by controlling the co-assembly of PS-*b*-PEO and dopamine in acidic THF-water co-solvent. HCl addition plays a critical role via enhancing the charge-dipole interactions between PEO and dopamine, and suppressing the clustering and chemical reactions of dopamine in solution. Dopamine polymerization induced by solvent annealing in NH₄OH vapor enables formation of percolating macropores. Subsequent pyrolysis to selectively remove the PS-*b*-PEO template from the complex can produce hierarchically porous carbon materials with interconnected frameworks of macro- and mesopores when pyrolysis is implemented at a low temperature or when DA is a minor component.

Keywords - Self-assembly, Block Copolymer, Dopamine, Hierarchically Porous Materials

Introduction

Hierarchically porous carbon materials (HPCMs) which contain three different scales of pores, such as micropores (<2nm), mesopores (2-50 nm) and macropores (>50nm), offer various remarkable properties.¹ Combination of the three different pore regimes enables materials with high mass transport, high specific surface area, and abundant reaction sites for guest molecules.¹ They can serve a wide range of applications such as catalytic nanomaterials,² energy conversion and storage,³ CO₂ sorbents,⁴ and molecular sensing.⁵

In recent studies, block copolymers (BCPs) have been demonstrated as good candidates for designing HPCMs with dimensional tunability and morphological diversity through self-assembly.⁶ For BCP self-assembly in solution, additional factors, such as solvent quality, polymer concentration, additives, and water content, can increase the level of complexity in comparison with BCP self-assembly in bulk.⁷ Benefiting from the merits mentioned above, BCP materials have attracted significant interest and shown a great promising platform to directing morphologies of HPCMs. Much work in recent years has focused on using dopamine (DA) molecules as carbon and nitrogen precursors to synthesize nitrogen-doped mesoporous carbon through templating of BCP micelles.² However, compared to spherical shape, other kinds of morphologies have been rarely reported. Furthermore, the self-assembly and phase behavior of PS-*b*-PEO/DA in solution still remain unclear, and structural evolution from a liquid to solid phase still needs in-depth understanding. In this study, we attempted to synthesize HPCMs with interconnected frameworks of macro- and mesopores. This approach combines the self-assembly behavior of PS-*b*-PEO BCP in THF-water and DA-polymerization in dried films. To simultaneously polymerize DA and trigger formation of macropores within a PS-*b*-PEO/DA binary mixture, solvent annealing in NH₄OH vapor was used. Thermal pyrolysis at elevated temperatures selectively degrades PS-*b*-PEO and converts polydopamine to carbon and hierarchically porous carbon materials can be achieved.

Experiments

11.69 mg of PS_{36k}-*b*-PEO_{15k} was dissolved in 0.29 ml THF. Aqueous dopamine (DA) solutions were prepared by dissolving 50.27 mg DA in 0.13 ml DI water. DA solution was gradually poured into PS-*b*-PEO in THF under mild stirring. For acidic solution, 0.027 ml HCl was added to the mixture. To understand effects of DA on the morphology we prepared the mixture with low DA content (PEO-to-DA molar ratio, 1:0.25) and high DA content (1:3.3). The mixtures were aged and stored in a dark environment. The mixture was deposited onto Si substrates by solution casting and dried. The as-casted films were exposed to solvent vapor annealing (SVA) of NH₄OH (33%) in a closed chamber at 50 °C to trigger DA polymerization. After complete polymerization, the samples were pyrolyzed at T_p=500 or 700 °C for 1 h under argon gas.

Results

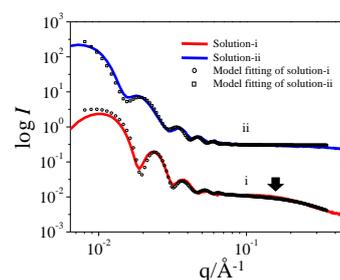


Fig. 1. Experimental SAXS data (lines) as well as fitted curves (symbols) of two mixed solutions containing both PS-*b*-PEO and DA in THF-water co-solvent (i) without and (ii) with HCl addition.

SAXS profiles show three prominent features (Fig. 1.). The first prominent feature is that several broad scattering maxima corresponding to the form factor scattering of micelles are present (line curves i and ii). Second, solution-i shows an asymptotic behavior of intensity decay at high q (indicated by an arrowhead). Such an asymptotic behavior is absent for solution-ii. The result suggests a second phase composed of small DA clusters coexisting with the phase of micelles in solution-i. The

third feature is that the scattering maxima shift to low q values for solution-ii. The downshifting suggests that the size and shape of PS-*b*-PEO/DA micelles may change after HCl addition. The SAXS profiles were quantitatively analyzed via model simulation by SASview and Scatter. For solution-i, a best fit (open circles) was obtained by a combination of two shape models: core-shell-sphere model for micellar structure and solid-sphere model for small structure. Structural parameters extracted from the best fit reveal that the core radius of PS is 23.6 ± 2.1 nm, the shell thickness of PEO/dopamine is 14.1 ± 5 nm and the diameter of small clusters is 1.7 nm.

In solution-ii, the PS-*b*-PEO/dopamine mixture only formed micelles. A best fit (open squares) was obtained with the shape model of short polydisperse cylinders with a core-shell structure. Structural parameters extracted from the best fit reveal that the cylindrical core radius is 7.7 ± 0.1 nm, the shell is 17.1 ± 1.5 nm and the cylindrical length is 22.3 ± 6 nm. This result indicates that in solution-ii, added HCl can prohibit formation of clusters, enable more DA molecules to swell the PEO shells, and eventually result in the morphological change from core-shell spheres to core-shell cylinders.

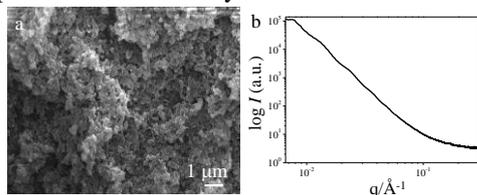


Fig. 2. Top view of SEM image and (d) SAXS profile of a PS-*b*-PEO/polydopamine (PDA) film that was casted from solution-ii and then treated by SVA.

SVA in NH_4OH vapor was carried out at 50°C , at which DA polymerization started from the free surface and extended into the interior through a series of reactions in the presence of O_2 under an alkaline environment.³ The self-assembled nanodomains with SVA retain a morphological fidelity. SVA not only triggers DA polymerization but also results in formation of macropores. The SAXS profile of the SVA-treated sample displays a series of scattering modulations correspond to the form factor scattering of micelles. The result indicates that the sample retains morphological integrity at the mesoscale.

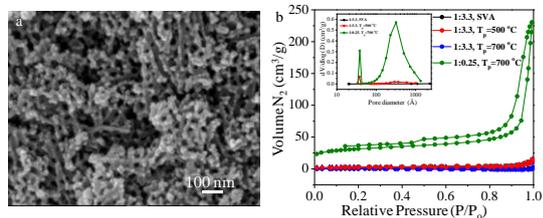


Fig. 3. (a) SEM image of a carbonized sample obtained from 700°C -pyrolysis of a PS-*b*-PEO/PDA mixture with low DA. (b) BET results of PS-*b*-PEO/PDA mixtures and the pore size distributions as an inset.

SEM result as shown in Fig. 3a displays the carbonized PS-*b*-PEO/PDA mixture with low DA ratio has interconnected networks filled with uniformly distributed pores, indicating that the morphology of hierarchical pores can be significantly preserved even under harsh pyrolysis. Nitrogen adsorption/desorption isotherms were measured and analyzed to understand the

porosity of carbonized mixtures that initially contained a low or high DA content. For the PS-*b*-PEO/PDA-lean mixture, hierarchically porous structures could be preserved to a large extent (green curve). Therefore, it clearly shows a typical type H4 adsorption/desorption isotherm contributed from a high total surface area of $101.5 \text{ m}^2/\text{g}$. The hierarchical porous structures existing in a major amount cover meso- and macro-meter scales in size for the carbonized PS-*b*-PEO/PDA-lean material.

Discussion

The aforementioned SAXS data suggest that the self-assembly of PS-*b*-PEO micelles was influenced by the addition of DA, and HCl. DA can be selectively incorporated in the PEO block of PS-*b*-PEO by charge-dipole interactions. HCl addition plays a critical role via enhancing the charge-dipole interactions between PEO and DA, thereby suppressing the clustering and chemical reactions of neat DA aggregates in solution. As a result, subsequent drying can produce interpenetrated PS-*b*-PEO/DA complex without forming phase-separated DA micro-sized crystallites. In a dry state, the SVA process in NH_4OH not only triggers DA polymerization but also induces three-dimensionally interconnected macropores after removal of NH_4OH . Consequently, removal of PS-*b*-PEO by thermal pyrolysis leads to the formation of mesopores and the carbonization of PDA produced the carbonized matrix with an interconnected framework. When DA was a major component in a PS-*b*-PEO/PDA mixture, Ostwald ripening process led to the collapse of interconnected porous structures. In contrast, when the DA content was minor, an interconnected framework could be preserved to a large extent under pyrolysis at $T_p=700^\circ\text{C}$. As a result, the hierarchically porous structures could remain intact. These results point out that the DA content should be carefully adjusted in tailoring HPCMs with the approach.

Acknowledgments

Financial supports from the Ministry of Science and Technology (MOST 107-2221-E-008-034-MY3) are gratefully acknowledged.

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