Nanopatterned Carbon Films with Engineered Morphology by Direct Carbonization of UV-Stabilized Block Copolymer Films

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ABSTRACT

Nanopatterned thin carbon films were prepared by direct and expeditious carbonization of the block copolymer polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) without the necessity of slow heating to the process temperature and of addition of further carbon precursors. Carbonaceous films having an ordered “dots-on-film” surface topology were obtained from reverse micelle monolayers. The regular nanoporous morphology of PS-b-P2VP films obtained by subjecting reverse micelle monolayers to swelling-induced surface reconstruction could likewise be transferred to carbon films thus characterized by ordered nanopit arrays. Stabilization of PS-b-P2VP by UV irradiation and the concurrent carbonization of both blocks were key to the conservation of the film topography. The approach reported here may enable the realization of a broad range of nanoscaled architectures for carbonaceous materials using a block copolymer ideally suited as a template because of the pronounced repulsion between its blocks and its capability to form highly ordered microdomain structures.

Mesoporous carbonaceous materials,1–3 which combine high mechanical, thermal, and chemical stability as well as tunable semiconducting properties with a high specific surface, have been employed as catalyst support,4,5 separation medium,6,7 energy storage and conversion system,8 and as a platform for nanoelectronic devices.9 Its fabrication is commonly based on the replication of shape-defining hard templates such as mesoporous silica5 or on the self-assembly of amphiphilic soft templates such as block copolymers (BCPs). In the latter case, a mesoscopic fine structure consisting of phases of different polarities forms. A carbon precursor segregates to the phase with similar polarity and is repelled from that with opposite polarity. The mesoscopic morphology is fixated by gelation prior to a high-temperature carbonization step, in which the precursor-rich domains are converted into a scaffold consisting of carbonaceous material, whereas the precursor-depleted domains define the positions of mesopores.10–12 A peculiar advantage of BCP soft templates is the possibility to utilize them for the synthesis of low-dimensional carbonaceous materials that do not only exhibit a mesoscopic fine structure but are nano-objects themselves, such as spheres,13 nanorods,14,15 nanotubes,16 and thin films.17–21

In BCPs containing polyacrylonitrile (PAN) blocks, the latter act as carbon precursors preorganized into a nanostructure generated by microphase separation. Hence, no additional low-molecular-mass carbon precursors need to be added, and cross-linking the PAN along with subsequent high-temperature carbonization yields nanopatterned carbon.13,17,19 However, the use of PAN-containing BCPs as templates is driven by the fact that PAN is a well-known carbon precursor rather than by their aptitude for forming well-developed, ordered microdomain structures. To this end, polystyrene-block-poly(x-vinylpyridine) (PS-b-PxVP; x = 2 or 4) would be much better suited. The Flory–Huggins interaction parameter for PS and PxVP is given by χ = 91.6/T − 0.095.22 Independent of the temperature T, PS and PxVP show pronounced repulsive interactions, in turn resulting in a strong driving force for microphase separation even if the molecular weights are so low that periods in the sub-30 nm range are obtained. Thus, PS-b-PxVP exhibits significantly better long-range ordering than PAN-based BCPs and has
thus been used as a nanoporous BCP template. However, only little efforts have been made to employ PS-b-P4VP as a template for the preparation of nanostructured carbonaceous materials. Kondyurin et al. prepared ordered carbonized nanostructured thin films from supramolecular assemblies of PS-b-P4VP and a low-molecular-weight additive by extraction of the latter and subsequent plasma immersion ion implantation. Here, we report the direct fabrication of highly ordered nanostructured carbon films by carbonizing hexagonally ordered monolayers of reverse PS-b-P2VP micelles having a P2VP core surrounded by a PS shell without the need of adding low-molecular mass carbon precursors or additives.

The reverse micelle monolayers were deposited on silicon wafers through spin coating of solutions containing 0.5 wt % PS-b-P2VP ($M_n$ (PS) = 102 000 g/mol, $M_n$ (P2VP) = 97 000 g/mol, $M_n$/$M_n$(PS-b-P2VP) = 1.12, obtained from Polymer Source Inc.) in toluene. While the P2VP cores are glassy, the solvated PS blocks are highly flexible. Hence, the initially spherical reverse micelles partially deform upon deposition, and their PS coronas partially merge, whereas their P2VP cores form a densely packed, quasi-hexagonal monolayer. After vitrification caused by the evaporation of the toluene, PS resides at both the polymer/air and polymer/substrate interfaces and surrounds the P2VP spheres. However, at the positions of the P2VP spheres the film is thicker than in between so that a characteristic “dots-on-film” topography results (Figure 1a). Key to the conservation of topographic and morphological features of the reverse micelle films in the course of the carbonization is the stabilization of the PS-b-P2VP by exposure to UV light (Figure 1b). It is well known that UV irradiation leads to the formation of cross-links in PS as well as P4VP homopolymers and stabilizes nanostructures consisting of BCPs containing PS blocks. Control experiments revealed that thin films of PS and P2VP homopolymers had a yellowish color after exposure to UV light and showed a markedly slower dissolution rate in good solvents such as tetrahydrofuran and ethanol, respectively, than corresponding native homopolymers.

We directly carbonized stabilized PS-b-P2VP reverse micelle films in argon atmosphere by heating them to 600 °C at a rate of about 40 K/min and keeping them at this temperature for 1 h. Note that a faithful pattern transfer to the carbonized films could be achieved despite the rapid heating. Carbonization of cross-linked PS cores in micelles with sacrificial shells reported previously yielded discrete spherical and rodlike, partially graphitic carbon nanoobjects. However, in the process reported here both PS and P2VP are converted to carbon so that less mass loss occurs as compared to the carbonization of BCPs with a sacrificial block. Thus, a faithful pattern transfer from the reverse micelle monolayers acting as templates to continuous carbon films bearing ordered arrays of carbon nodots, which exhibit the high degree of order of the initial BCP template, could be achieved (Figure 1c).

Reverse PS-b-P2VP micelle monolayers can easily be reorganized into films containing hexagonal arrays of nanopores by surface reconstruction upon exposure to selective solvents as previously shown for micellar polystyrene-block-poly(acrylic acid) films. A treatment of reverse PS-b-P2VP micelle monolayers for 60 min at room temperature with ethanol, a selective solvent for P2VP, results in the formation of a nanoporous film (Figure 1d). Subsequent stabilization with UV light (Figure 1e) and carbonization as described above yields carbon films containing ordered arrays of nanopits (Figure 1f).

Figure 2a1 displays a scanning electron microscopy (SEM) image. Figure 2b1 shows an atomic force microscopy (AFM) topography image, and Figure 2c1 displays a typical topographic profile of as-cast reverse PS-b-P2VP micelle films corresponding Figure 1a. The P2VP spheres, which appear in bright contrast, have a diameter of about 50 nm. They form a hexagonally ordered array with a period, corresponding their center-to-center distance, of approximately 60 nm. The apparent peak-to-valley height determined
from the topographic AFM profile shown in Figure 2c1, which was measured along the line seen in Figure 2b1, is about 3 nm, and the thickness of the entire PS-b-P2VP film, measured at the positions of the dots, is about 24 nm. Figure 2a2 shows an SEM image, and Figure 2b2 shows an AFM topography image of carbonized reverse PS-b-P2VP micelle films corresponding to Figure 1c. Well-ordered hexagonal arrays of nanodots that presumably formed at the positions of the P2VP spheres can be seen. The diameter of the former is reduced to around 35–40 nm, while their center-to-center distance of about 60 nm corresponds to that of the P2VP spheres in the native PS-b-P2VP template. The topographic AFM profile seen in Figure 2c2 measured along the line seen in Figure 2b2 reveals an apparent peak-to-valley height of approximately 1 nm, while the overall thickness of the carbonized film at the positions of the carbon nanodots was around 7 nm. These findings suggest that the carbon nanodots discernible in Figure 2a2,b2 are connected to an underlying continuous carbon film. Therefore, the “dots-on-film” topography of the native PS-b-P2VP templates was conserved. A comparison between the thickness of the PS-b-P2VP templates and that of the carbon films revealed volume shrinkage in the direction perpendicular to the substrate surface of about 70%. The conservation of the “dots-on-film” topography upon carbonization is in line with the assumption that both the PS and the P2VP were converted into carbonaceous material.

Figure 3a1 displays an SEM image and Figure 3b1 shows an AFM topography image of an ethanol-treated PS-b-P2VP film corresponding to Figure 1d with a thickness of about 23 nm. Note the inversion in contrast in comparison with Figure 2a1 and 2b1 showing native reverse PS-b-P2VP micelle films. The diameter of the holes formed upon exposure to ethanol amounts to ≈25 nm, while their center-to-center distance of 60 nm again corresponds to that between the P2VP spheres before exposure to ethanol. The AFM topography image seen in Figure 3b1 and the topographic AFM profile seen in Figure 3c1, which was measured along the line in Figure 3b1, moreover reveal that the film thickness is largest at the circular rims of the holes with an apparent depth of 3–4 nm, whereas depressions are seen in between the holes.

Figure 3a2,b2 shows SEM and AFM images of carbon films with a thickness of about 7 nm obtained by UV-exposure and carbonization of ethanol-treated PS-b-P2VP films. Clearly, hexagonal arrays of nanopits were preserved, and no noticeable change in the period occurred in the course of the carbonization. The apparent depth of the nanopits amounts to approximately 1 nm, as obvious from the topographic AFM profile displayed in Figure 3c2 measured along the line in Figure 3b2. The diameters of nanopores in surface-reconstructed BCP films are much smaller than the period of the BCP. Hence, it is reasonable to assume that, because of the geometry of the AFM tips, the pore mouths are probed rather than the nanopits themselves in the topographic AFM profiles seen in Figure 3c1,c2. However, the properties of the carbonaceous films obtained from surface-reconstructed reverse PS-b-P2VP micelle films indicate again that both PS and P2VP were converted to carbon.

Raman spectroscopy confirmed the formation of partially graphitic carbon. Raman spectra of carbonaceous materials...
commonly exhibit two peaks referred to as $D$ and $G$ bands. Ferrari and Robertson$^{42}$ suggested a phenomenological three-stage model to classify carbonaceous materials along an “amorphization trajectory” comprising perfectly ordered graphite and amorphous carbons predominantly containing $sp^3$ hybridized carbon atoms as limiting cases, as well as three intermediate stages ranging from graphite to nanocrystalline graphite (stage 1) to amorphous carbon with less than 20% $sp^3$ hybridized carbon atoms (stage 2) to amorphous carbon predominantly containing $sp^3$ hybridized carbon atoms (stage 3). All three stages are characterized by specific shifts of the $G$ band and changes in the intensity ratios of the $D$ and $G$ bands. Most of the carbon atoms constituting the PS and P2VP blocks of the native BCP template are $sp^2$ hybridized and located in the phenyl and pyridyl moieties. Therefore, it is reasonable to assume that the carbonization products of PS-$b$-P2VP predominantly contain $sp^2$-hybridized carbon and fall in stages 2 or 3 of the Ferrari–Robertson scheme. The Raman spectra of a carbonized reverse PS-$b$-P2VP micelle monolayer with dots-on-film topography and its counterpart obtained from an ethanol-treated PS-$b$-P2VP monolayer (Figure 4(a)) are identical and show $D$ bands at $\approx1360$ cm$^{-1}$. The $G$ bands contain not only a larger peak at $\approx1560$ cm$^{-1}$, but also a smaller one at $\approx1590$ cm$^{-1}$. It is reasonable to assume that the nitrogen of the pyridyl moieties is completely incorporated into the carbonaceous films, but the presence of nitrogen as such does not directly modify vibration modes and thus the shape of the Raman spectra.$^{43}$ We speculate that the unusual splitting of the $G$ band originates from the presence to two different phases in the carbonized films. A comparison of the Raman spectra with the Ferrari–Robertson scheme reveals that the $G$-band peak at $1590$ cm$^{-1}$ could be ascribed to ordered regions containing nanocrystalline graphite, for which the phenyl groups of the PS blocks can be considered as potential precursors. The nitrogen in the pyridyl groups acts as a defect site impeding the formation of graphitic structures.$^{43}$ Thus, the $G$-band peak at $1560$ cm$^{-1}$ possibly originates from regions with amorphous character in which nitrogen is enriched. Remarkably, the Raman spectrum of a thicker carbonaceous film obtained by carbonization of a PS-$b$-P2VP film consisting of ten successively deposited and stabilized reverse micelle monolayers (Figure 4(b)) shows $D$-band and $G$-band peaks at the same positions than the spectra of single monolayers but with an inverted $G$-band peak height ratio. Apparently, the peak height ratios in the $G$ band do not exclusively depend on the relative concentrations of the phenyl and pyridyl groups. Moreover, it seems that spatial confinement and interfacial effects impede, to some extent, the formation of nanocrystalline graphite in the single monolayer films.

In conclusion, thin nanostructured films consisting of PS-$b$-P2VP, a widely used BCP template able to form highly ordered microdomain structures, can directly be converted to likewise nanostructured carbon films with engineered surface topographies. Whereas carbonization of monolayers of reverse PS-$b$-P2VP micelles yields hexagonal arrays of carbon dots on continuous carbonaceous films, carbonaceous films characterized by hexagonal arrays of nanopits are obtained from modified reverse PS-$b$-P2VP micelle monolayers subjected to swelling-induced surface reconstruction. The patterns imposed by the PS-$b$-P2VP templates are retained even if heating rates much higher than in conventional protocols are applied in the course of the carbonization, thus reducing the process time. Stabilization of the PS-$b$-P2VP by UV irradiation and the concurrent...
carbonization of both blocks ensure faithful pattern transfer from the native template to the carbonaceous films. Exploiting the broad range of microdomain structures accessible with PS-b-P2VP templates should enable the fabrication of tailored carbonaceous nanoarchitectures.

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(38) For scanning electron microscopy investigations the samples were coated with Au/Pd alloy and probed with a JEOL 6340F scanning electron microscope operated at 10 keV.
(39) Atomic force microscopy was performed with a Digital Instruments Dimension 5000-1 Nanoscope IIIA apparatus (Veeco Instruments) equipped with silicon cantilevers (NSC15, MikroMasch, resonant frequency 325 kHz) in the tapping mode.
(40) The thickness of both PS-b-P2VP films and carbonaceous films was measured as follows. We scratched the films with tweezers consisting of poly(tetrafluoroethylene). The film thickness was determined by measuring topographic AFM profiles across the scratches. The film thickness was assumed to correspond to the apparent step height.
(41) Raman spectra were measured in reflection with a Horiba Jobin Yvon LabRAM HR high resolution Raman microscope. The system was configured with the 514.5 nm emission line of an Ar+ ion laser, a HR800 spectrometer, and a thermoelectrically cooled CCD array detector. The laser with a power of ~5 mW was focused on the sample, the laser spot was ~3 µm in diameter, and the integration time was set to 500 s.

Figure 4. Raman spectra of carbonaceous films obtained by carbonization of PS-b-P2VP. (a) Spectra of a carbonaceous dots-on-film structure prepared by carbonizing a reverse micelle monolayer (orange) and of a carbonaceous film containing ordered nanopit arrays prepared by carbonizing an ethanol-treated reverse micelle monolayer (black). (b) Raman spectrum of a thicker carbonaceous film obtained by carbonization of a PS-b-P2VP film consisting of ten successively deposited and stabilized monolayers of reverse micelles.