508d Directly Patterned Mesoporous Carbon Film Prepared Using Block Copolymer Templates in Supercritical Co_2

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Porous carbon films have wide ranging applications in separations, sensors, catalysis and other fields. Here we report the synthesis of mesoporous carbon films via phase selective reaction in block copolymer templates dilated with supercritical carbon dioxide. The technique can be used to fabricate directly patterned unsupported carbon films and metal containing carbon films.

Porous carbon films have conventionally been synthesized by arc discharge, sputtering, chemical vapor deposition (CVD) or simple carbonization of suitable precursor. The films synthesized using these approaches mostly contain disordered micropores in the size range of ~ 2 nm, which renders them suitable for separation and adsorption of small gas molecules but limits their applicability for large molecules including biomolecules and bulky organics. Recently, mesoporous carbon films having pores in the size range of 10-50 nm have been prepared using mesoporous silicates as templates for the infusion and polymerization of carbon pre-polymers. The templates are then removed by acid etching after the carbon film synthesis. While this approach enables the preparation of ordered mesoporous carbons, it requires a sacrificial silica template, offers limited connectivity of the mesoporous carbon pores, and presents challenges for film formation and for pore orientation. Moreover, synthesizing patterned carbon films and metal-doped carbon films is difficult using this approach.

Here we report supercritical fluid-assisted infusion and phase selective reaction within pre-organized block copolymer and block copolymer/homopolymer templates as alternatives to existing synthesis techniques that can overcome the limitations mentioned above. In this approach, a block copolymer template of Pluronic F127 $(PEO)_{105}$-$(PPO)_{70}$-$(PEO)_{105}$ or a template blend of Pluronic F127/homopolymer – poly(acrylic acid) (PAA)(2k) is spin coated onto planar or patterned silicon wafers from solutions containing para-toluene sulfonic acid (pTSA). Upon evaporation of the solvent, the pTSA segregates preferentially in hydrophilic domain of the template. The templates are then exposed to supercritical carbon dioxide solutions of furfuryl alcohol resulting in acid-catalyzed polymerization of furfuryl alcohol within the PEO domains. After removal from the reactor, the as-infused template is heated to 200 ^{o}C to promote further polymerization. The film is then subjected to a slow carbonization cycle at temperatures up to 400 ^{o}C in vacuum during which the block copolymer template decomposes, leaving a porous carbon film. The approach can be extended to produce unsupported patterned carbon films by simple pattern transfer and metal containing carbon films prepared by doping the templates with metal salts prior to carbon precursor infusion. The films are characterized using Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray diffraction (XRD) and Atomic Force Microscopy (AFM).