

Access to Porous Substructure of Block Copolymer-Derived Nanomaterials via Reactive Ion Etching (RIE)

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Primary CNF Tools Used: Oxford 81 Etcher

Abstract:

The use of block copolymers (BCPs) as structure-directing agent offers a facile pathway toward nanomaterials with tunable mesostructures and functional properties. However, the surface energy often disrupts the thermodynamics of block copolymer self-assembly and results in a different surface morphology from the bulk substructure. In this report, we demonstrate the use of reactive ion etching (RIE) in the CNF cleanroom as a simple technique to access the substructure in block copolymer-derived carbon materials. RIE removes the dense capping layer on the surface so that we can make use of the internal structure with massive meso- and nano-porous surface areas. These carbon monoliths with open pore structures may be promising candidates for electrode materials in the design of 3D continuous electrochemical energy storage devices.

Summary of Research:

With high interfacial areas and a low areal footprint, three-dimensionally (3D) continuous nanostructured electrode materials have gained interest as the demand for increasingly efficient electrochemical energy storage devices grows. As a result, nanostructured carbon materials with 3D network architectures are under active investigation for routes to 3D functional composite materials, e.g., via straightforward backfilling, for the eventual incorporation into energy storage devices.

In our work, ultralarge molar mass diblock copolymers are employed as structure-directing agents for carbon precursors to prepare carbons with ultralarge pore sizes. The unfavorable interaction between the large blocks forces them to segregate from each other at the nanoscale and the carbon precursors preferentially mix with the more hydrophilic block. Upon heat treatment in the furnace to high temperatures of up to 1600°C, nonperiodically ordered co-continuous network structures are derived with an average pore sizes of around 100 nm (Figure 1).

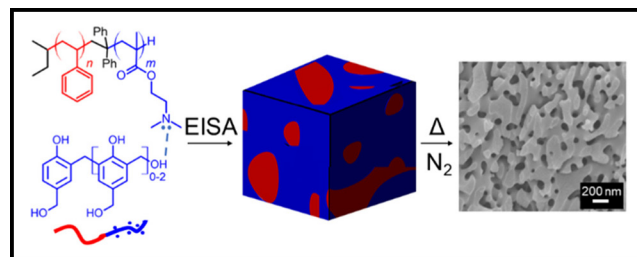


Figure 1: Schematic of the self-assembly of BCPs and carbon precursors (left) via evaporation-induced self-assembly (EISA) into mesostructured hybrids (middle) and the mesoporous carbon materials after high-temperature treatments (right). The SEM images show representative cross sections of the final monoliths.

After subsequent carbon activation processes, the porous carbons with continuous 3D network structures are a promising candidate as the cathode materials for the intercalation of lithium. However, since the self-assembled mesostructures are formed from a solution in

a dish, the solution-air and solution-container interfaces experience different thermodynamic driving forces for the microphase segregation of the BCPs. The scanning electron microscopy (SEM) image in Figure 2a shows that the surface of an as-made hybrid that has gone through the heat treatment is capped by a dense layer, which renders the porous understructure inaccessible.

In order to realize the potential of the porous 3D network structure, Oxford 81 Etcher was utilized with oxygen plasma. Each side of the as-made hybrid is subject to 30 min of oxygen plasma at 150 W forward power, 50 sccm flow rate, and 60 mTorr pressure. Figure 2b shows the carbon structure derived from heat treating the etched hybrid, whose underlying pores in the substructure are now fully accessible from the surface.

Conclusions and Future Steps:

In summary, a one-pot route to co-continuous porous carbons is demonstrated via ultralarge molar mass block polymer self-assembly with carbon precursors. Aided by reactive ion etching (RIE), open and accessible 3D co-continuous pore network structures of carbon materials make them appealing for applications that require fast kinetics through the large 3D continuous pore network or backfilling processes, e.g., required for producing 3D nanoarchitecture-based energy storage devices.

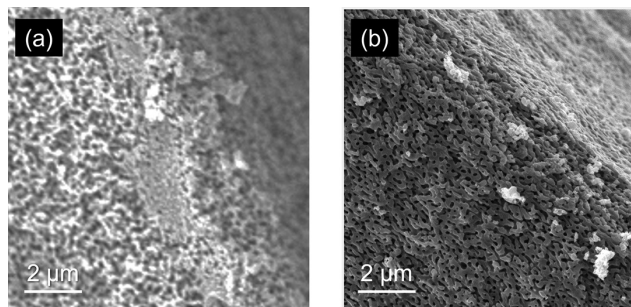


Figure 2: Scanning electron microscopy (SEM) images of carbon monoliths derived from heat treating BCP-carbon precursor hybrids (a) without and (b) with oxygen plasma etching.

References:

- [1] Tait, W.R., Thedford, R.P., Chapman, D.V., Yu, F., Freidl, J.W., Sablina, E.S., Batsimm, G.M. and Wiesner, U.B. One-Pot Structure Direction of Large-Pore Co-Continuous Carbon Monoliths from Ultralarge Linear Diblock Copolymers. *Chemistry of Materials* 2021, 33(19), 7731-7742.