

One-pot Synthesis of Hierarchically Macro- and Mesoporous Carbon Materials with Graded Porosity

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Supporting Information

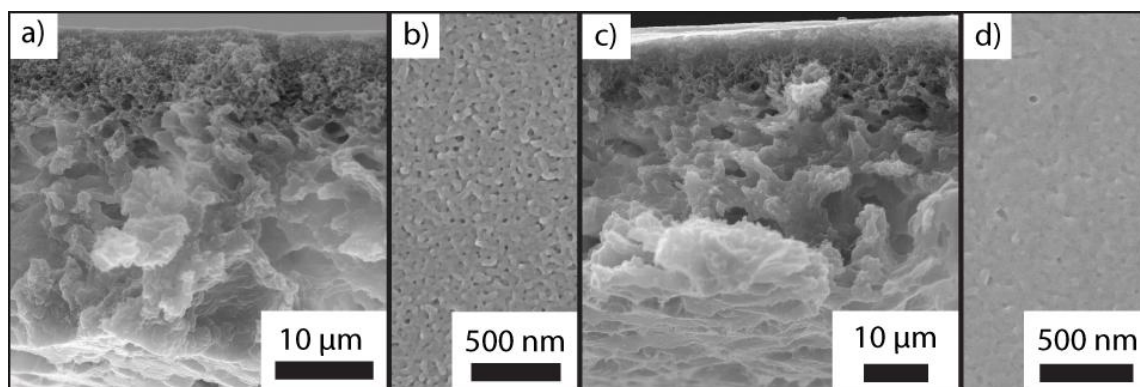


Figure S1: SEM images of membranes cast from 12 wt% polymer and resols (2:1 wt ratio) solutions evaporated for 33 sec and immersed in a non-solvent deionized water bath overnight. (a,b) cross section and surface structure of membrane at as-cast stage, (c,d) cross section and surface structure at the post-90 °C cross-linking stage. The membranes did not carbonize (no materials could be recovered after pyrolysis at 1100 °C), most likely because the resols were dissolved out during overnight immersion in the DI water bath.

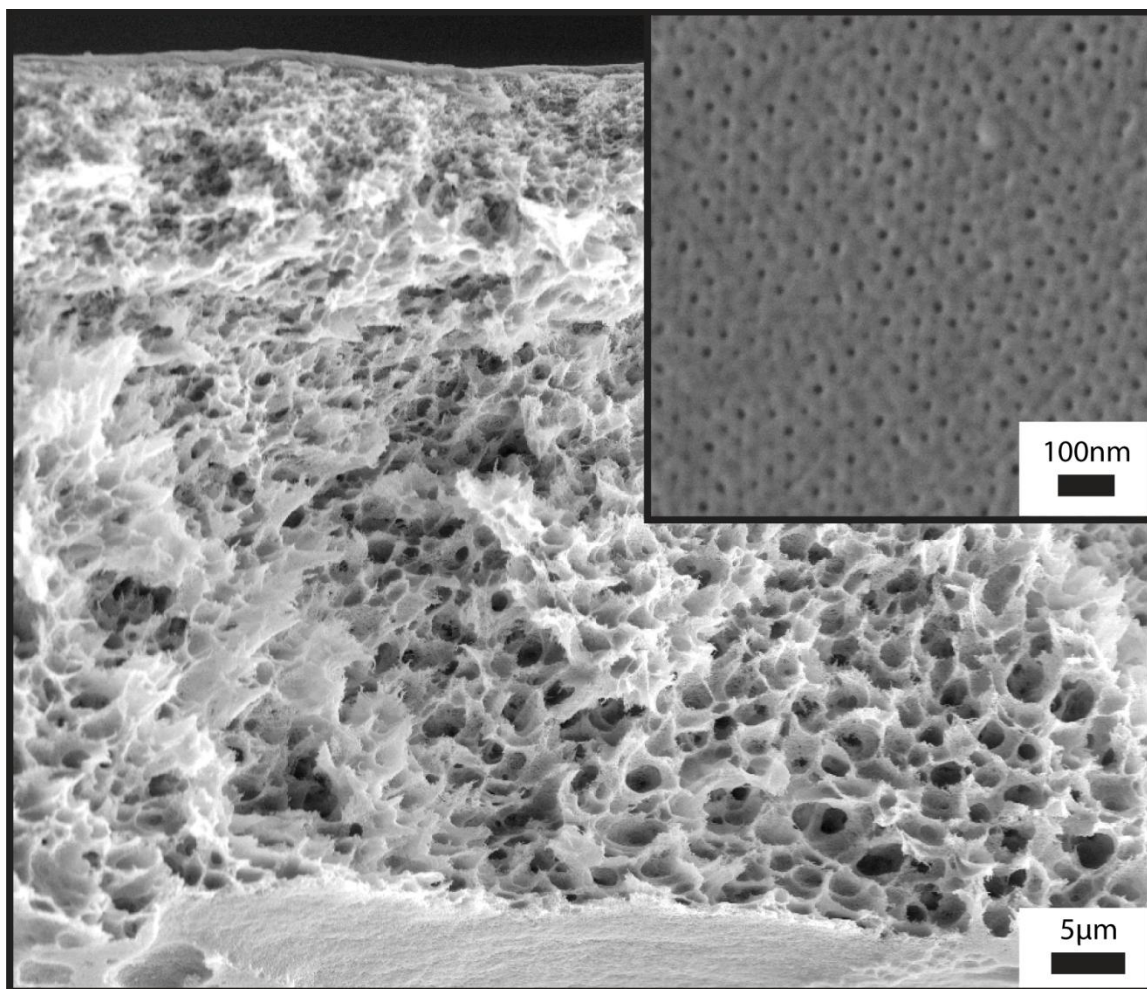


Figure S2. SEM images of the cross-section and top surface (inset) of the neat ISV terpolymer membrane (i.e. without resols) cast from a 12 wt% ISV solution evaporated for 45 sec.

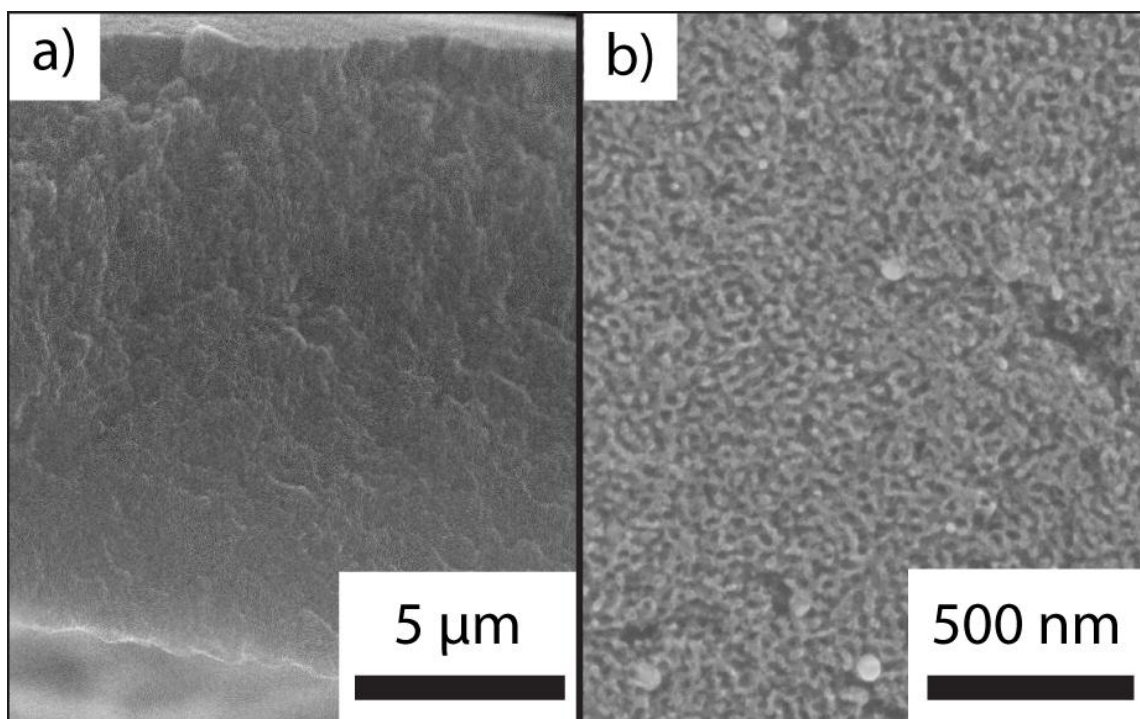


Figure S3: SEM images of the carbonized film cast from a 12 wt% polymer - resols solution (2:1 wt ratio) and completely dried for approximately 2.5 mins before immersion in water. Disordered mesoporosity without macroporosity is evident in this film.

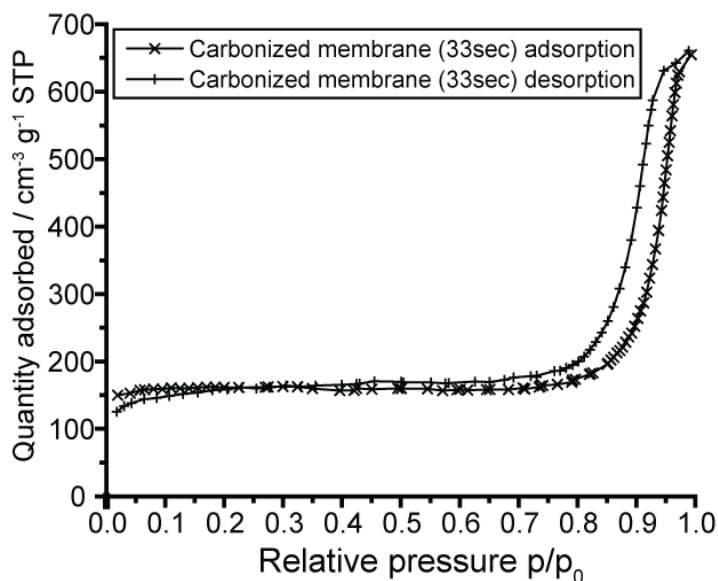


Figure S4. Nitrogen sorption isotherms of a carbonized membrane (1100 °C) cast from a 12 wt% polymer and resols solution (2:1 wt ratio) and evaporated for 33 sec.

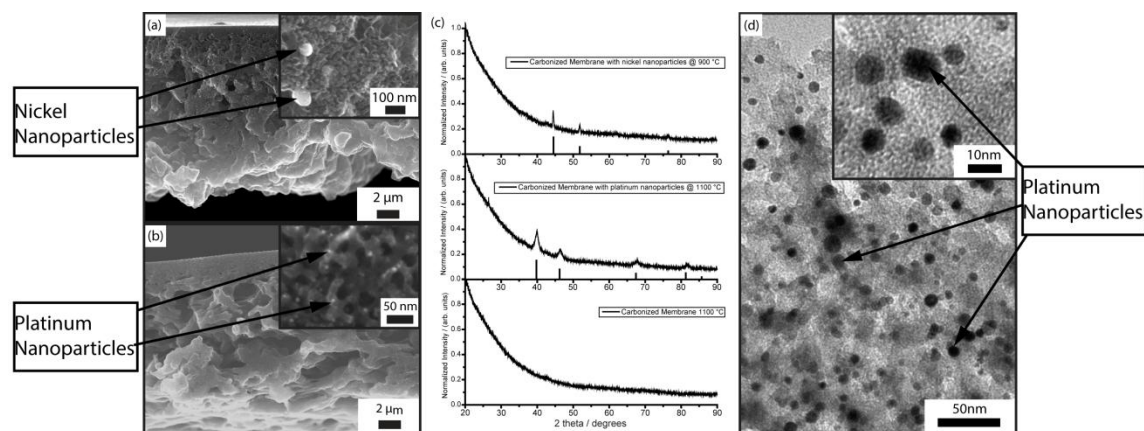


Figure S5. Copy of Figure 5 with labeled nickel and platinum nanoparticles.

Detailed Experimental Procedure

Synthesis. The Poly(isoprene)-*block*-poly(styrene)-*block*-poly(4 vinylpyridine) (ISV) triblock terpolymer was synthesized *via* sequential anionic polymerization, as has previously been described.¹ The polymer had an overall molar mass of 103 kg mol⁻¹, a polydispersity index of 1.11, and weight fractions of 25%, 57%, and 18% for poly(isoprene) (PI), poly(styrene) (PS) and poly(4-vinylpyridine) (P4VP), respectively.

Phenol-formaldehyde resols were synthesized with a molar mass of <500 g mol⁻¹ *via* the well-known polymerization of phenol and formaldehyde under basic conditions as previously described.² Briefly, phenol, formaldehyde, and sodium hydroxide were combined at 45 °C in a molar ratio of 1:2:0.1 and polymerized at 75 °C. After neutralizing with *para*-toluene sulfonic acid, the resols solution was freeze-dried, dissolved in a 1:1 wt mixture of tetrahydrofuran (THF) and chloroform as a 25 wt% solution and filtered to remove precipitated sodium *para*-toluene sulfonate. The resols were freeze dried again and dissolved as a 25 wt% solution in THF or dioxane (DOX).

Film casting. For the casting solution, ISV and resols were dissolved as a 12 wt% solution with a 2:1 ISV to resols weight ratio, in a 7:3 (by volume) mixture of 1,4 dioxane (DOX) and tetrahydrofuran (THF). The solutions were stirred overnight to dissolve the polymer and subsequently left without stirring for about 2 hours to allow for gas bubbles to dissipate. For the synthesis of nickel nanoparticles on graded, hierarchically porous carbon, bis(cyclopentadienyl) nickel(II) was added to a 14 wt% ISV-resols solution that was stirred over night, with a 1:10 weight ratio of nickel precursor to resols and stirred for two more hours. For the synthesis of platinum nanoparticles on graded, hierarchically porous carbon, (1,5-cyclooctadiene) dimethyl platinum(II) was added to a 12 wt% ISV-resols solution that was stirred over night, with a 1:4 weight ratio of platinum precursor to resols and stirred for three more hours.

To create the organic-polymeric hybrid membranes, the solutions were cast onto a glass slide using a doctor blade (Testing Machines, Inc., K Control Coater) with a gate height of 229-254 μm . Part of the solvent was allowed to evaporate for 33 or 45 sec (see text), followed by plunging the film into the non-solvent bath (deionized water). After about 30 sec, the phase-separated hybrid membrane was removed from the water bath. All membranes were cast at humidity ranging between 40-50%.

Carbonization. The membranes were dried, placed onto graphoil, and heated in a convection oven to crosslink the resols. The temperature profile was 50 °C for 12 hours, followed by 90 °C for 5 days. The hybrids were carbonized by further heating under inert atmosphere (nitrogen) at 1 °C min⁻¹ to 600 °C for 3 h, then at 5 °C min⁻¹ to 1100 °C for 3 h (900 °C for nickel containing films), and subsequently cooled to room temperature.

Characterization. The ISV triblock terpolymer was characterized with a combination of ¹H-nuclear magnetic resonance (¹H-NMR) spectroscopy using a Varian Mercury spectrometer at 300 MHz and gel permeation chromatography (GPC) on a Waters ambient-temperature GPC at 23 °C (flow-rate 1 mL min⁻¹) with a Waters 2410 differential refractive index (RI) detector.

Scanning electron micrographs were obtained using either a Zeiss LEO 1550 FE-SEM with an in-lens detector and an accelerating voltage of 10-20 kV or a TESCAN MIRA3 LM FE-SEM using an in-lens detector and an accelerating voltage of 5-15 kV. The as-cast and post-90 °C samples were coated with gold-palladium prior to imaging, which accounts for the surface patterning.

Thermogravimetric analysis was conducted on a Q50 TGA from TA instruments under argon flow (90 mL min^{-1}) with a heating rate of $1 \text{ }^{\circ}\text{C min}^{-1}$.

Raman spectroscopy was performed on a Renishaw InVia confocal Raman microscope with backscattering geometry at room temperature using a 785nm or diode laser as excitation source at 50x magnification.

Small-angle X-ray scattering (SAXS) on the membranes was performed on a custom-built lab-sized X-ray line using Cu K α radiation (wavelength 1.5418 \AA).

X-ray diffractograms were obtained using a Rigaku Ultima IV multipurpose X-ray diffractometer equipped with a D/teX Ultra detector using Cu K α radiation (40V, 44mA, wavelength 1.5418 \AA) in a 2θ range between 10 and 90 degrees with a speed of $4 \text{ degrees min}^{-1}$.