Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supplemental Information

Experimental Details

Conversion of silica diatom frustules into micro/mesoporous carbon replicas. The conversion of SiO_2 diatom frustules into MgO/Si replicas was conducted by sealing the frustules with Mg granules (molar Mg:SiO_2 ratio = 2.5:1) inside mild steel ampoules and then heating to 900˚C for 1.5 h. The MgO/Si specimens were then immersed in a 3M HCl solution for 3 h to allow for selective MgO dissolution. The resulting porous Si specimens were exposed to a flowing gas stream of 10% CH_4/90% Ar at 950˚C for 2.5 h, followed by annealing in flowing Ar at 1200˚C for 12 h, to allow for conversion into SiC. The SiC frustule replicas and commercial SiC powder (8.7 μm ave. particle size, Alfa Aesar, Ward Hill, MA) were then exposed to a flowing Cl_2 gas stream at 950˚C for 2 h. The resulting porous C microparticles were then immersed in a 4% aqueous HF solution for 3 h, followed by washing in DI water and then drying at 75˚C overnight. The porous carbon frustule replicas and carbide-derived carbon microparticles were then exposed to a flowing hydrogen gas stream for 0.5 h at room temperature to remove residual adsorbed chlorine.

Deposition of platinum nanoparticles. Pt deposition onto/within the C frustule replicas, commercial C black (Vulcan XC-72R, Cabot Corp., Billerica, MA), and SiC-derived C microparticles was conducted with the aid of $Pt(CO)_2Cl_2$ vapor. A 250 mg batch of $PtCl_2$ powder (99.9% purity, Alfa Aesar) was placed within an alumina combustion boat. After placing porous alumina cloth (Item No. E01C01, Zircar Zirconia, Inc., Florida, NY) over the $PtCl_2$ powder, 130 mg of a given batch of C microparticles was placed on the alumina cloth, and the assembly was heated in a flowing CO atmosphere for 0.5 h at 230˚C to allow for $Pt(CO)_2Cl_2$ formation. The specimens were then washed with DI water, dried at 110ºC overnight, and then heated to 300˚C in flowing H_2 gas for 1 h to ensure complete reduction of the deposited Pt.

Structural, thermal, chemical characterization. Scanning electron microscopy was conducted with a field emission scanning electron microscope (Leo/Zeiss 1530, Cambridge, UK) operating at an accelerating voltage of 10 kV and equipped with an energy dispersive x-ray spectrometer (INCA EDS, Oxford Instruments, Bucks, UK). Transmission electron microscopy was conducted with a JEOL 4000 EX microscope operating at an accelerating voltage of 400 kV. Cross-sections of specimens were obtained via focused ion beam (FIB) milling (Nova Nanolab 200 FIB/SEM, FEI, Hillsboro, OR, USA). Nitrogen adsorption measurements (Quantachrome Autosorb 1-C, Boynton Beach, FL) were used to evaluate the specific surface area (Brunauer-Emmett-Teller, BET, analysis) and the specific volumes of micropores and mesopores (non-local density functional theory, NLDFT, analysis). Thermogravimetric analysis (Netzsch STA 449 C, Burlington, MA) was conducted in flowing air at a heating rate of 5ºC/min up to 1000ºC. X-ray diffraction analyses (X-Pert Pro Alpha 1 diffractometer, PANalytical, Almelo, The Netherlands) were conducted with Cu Kα radiation with an incident beam Johannsen monochromator and an Xcelerator linear detector.

Electrochemical characterization. The electrocatalytic activity toward the oxygen reduction reaction (ORR) was measured at room temperature in an oxygen-saturated 0.5M H_2SO_4 electrolyte solution using a rotating disk apparatus (MSR analytical rotator, Pine Research Instrumentation) operating at 2000 rpm and a voltage sweep rate of 10 $mVsec^{-1}$. The working electrode consisted of Pt-loaded C microparticles on a glassy carbon electrode (geometric area = 0.196 cm^2) embedded in a PTFE holder (RDE, Pine Research Instrumentation, Raleigh, NC). The counter electrode was comprised of platinum (99.95% purity, wire of 0.5 mm outer dia. X 152 mm length, AFCTR1, Pine Research Instrumentation). For the working electrode, an ink of Pt-loaded C frustule replicas was prepared by ultrasonification of a 30 mg batch of the replicas in 5 ml of an aqueous perfluorosulfonic acid (Nafion®)-bearing solution (2 vol% of a 20 wt.% aqueous Nafion® solution, 70 vol% distilled water, 28 wt% isopropyl alcohol) for 0.5 h. A 10 ul aliquot of the catalyst ink suspension was placed onto the glassy carbon working electrode and the coating was dried in air at 80°C for 0.5 h. A similar procedure was followed for the Pt-loaded C black (Vulcan XC-72R) and Pt-loaded C derived from SiC, except that the starting concentration of these microparticles in the ink was adjusted so that the amount of platinum deposited on the glass carbon electrode was maintained at 0.1 $mgcm^{-2}$. Oxygen was bubbled through the 0.5M H_2SO_4 solution for 30 minutes before starting the ORR measurements. The applied voltage was controlled with a potentiostat (Solartron SI 1286, Oak Ridge, TN). All potentials were measured versus a Saturated Calomel Electrode (SCE) as the reference electrode, but converted to values with respect to a Normal Hydrogen Electrode (NHE). Electrochemical impedance spectroscopic (EIS) analysis was conducted with a frequency response analyzer (Solartron SI 1255) under the influence of an ac voltage of 10 mV in the frequency range of 0.001 Hz to 1 MHz. EIS and chronoamperometric analysis (CA) were conducted at 0.8 V at a rotation rate of 2,000 rpm to ensure sufficient mass (dissolved oxygen) transfer to the electrodes during measurement.

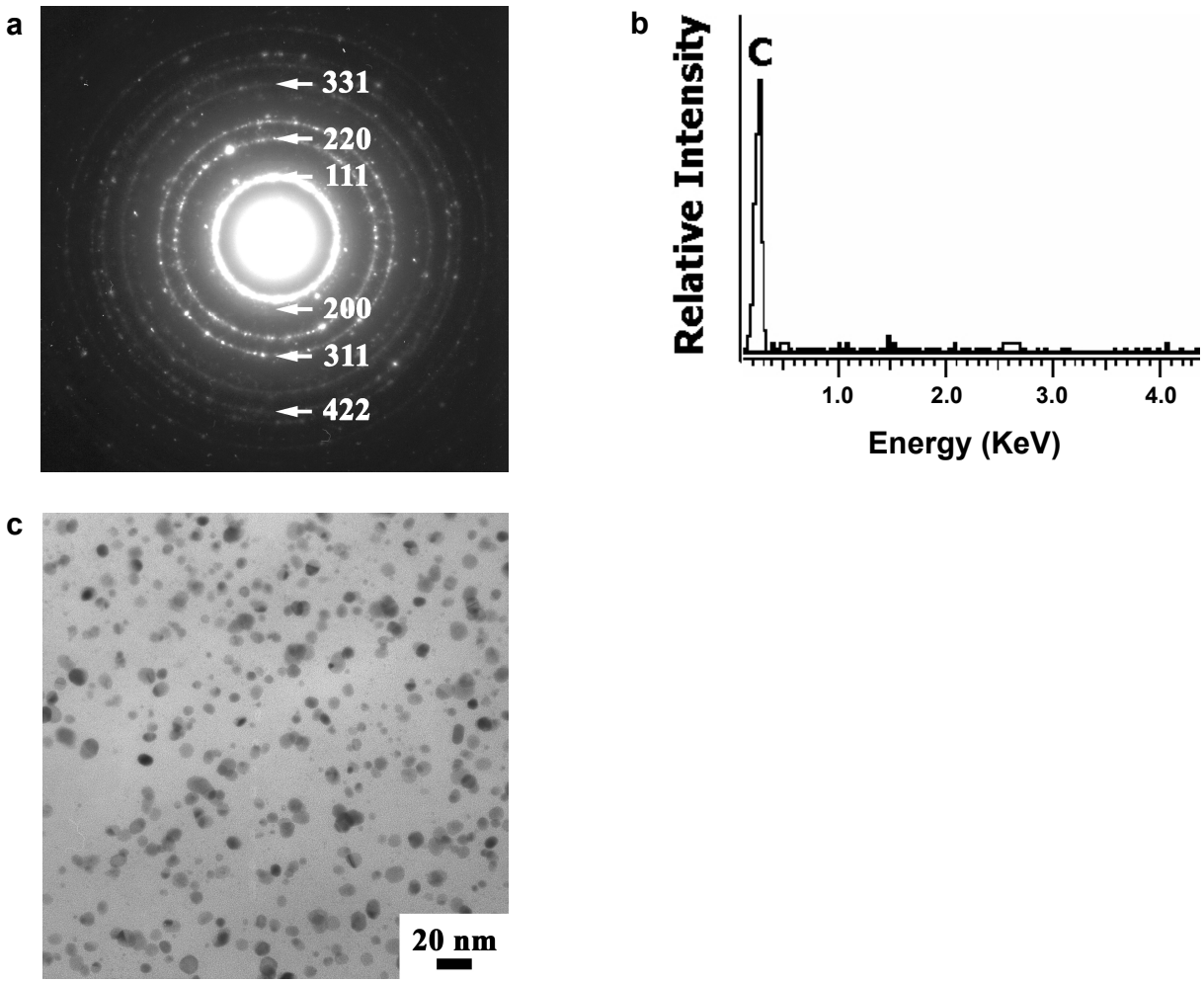

Fig. S1 Additional structural and chemical analyses of SiC, C, and Pt-loaded C frustule replicas. a Selected area electron diffraction (SAED) pattern, consistent with β-SiC, obtained from a cross-section of a SiC replica of an *Aulacoseira* diatom frustule. **b** EDX pattern obtained from a C replica of an *Aulacoseira* diatom frustule, **c** Low magnification bright field transmission electron image of a cross-section of a Pt-loaded C replica of an *Aulacoseira* diatom frustule.

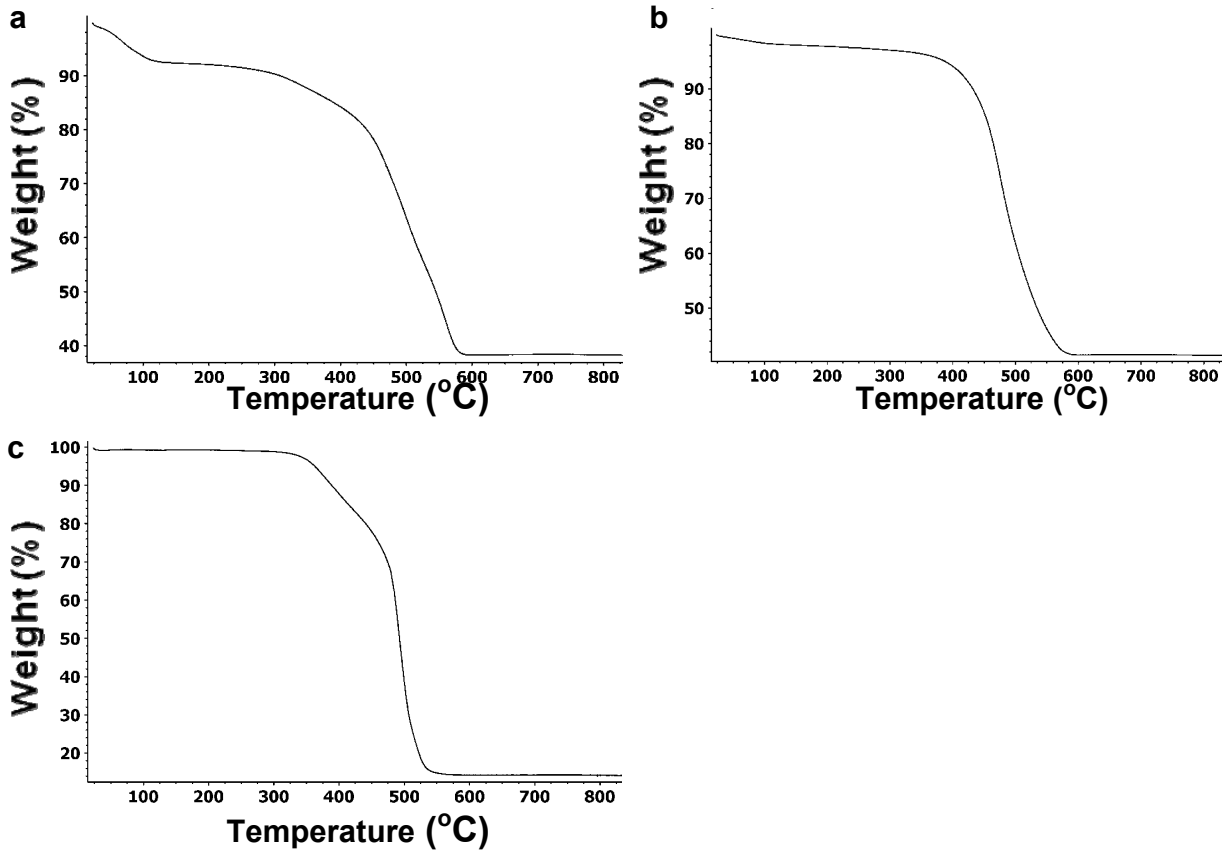

Fig. S2 Platinum loading of porous C microparticles. Thermogravimetric (TG) analysis (with heating at 5°C/min in air) of: **a** Pt-bearing C replicas of *Aulacoseira* diatom frustules, **b** Pt-bearing SiC-derived C microparticles, **c** Pt-bearing C black (Vulcan XC-72R).

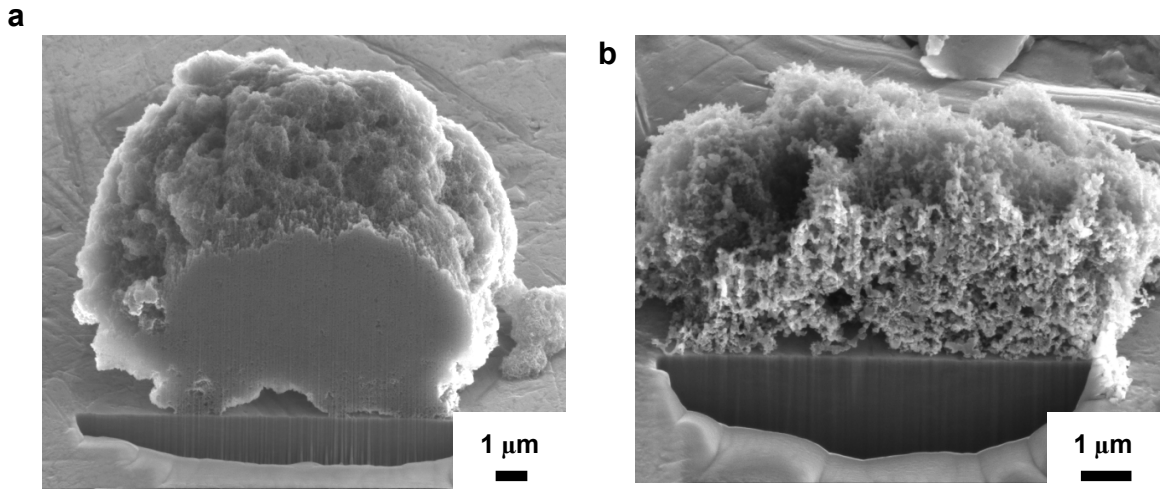

Fig. S3 Cross-sections of carbide-derived carbon microparticles and carbon black particles. a Secondary electron (SE) image of an ion-milled cross-section of a silicon carbide-derived carbon microparticle. **b** SE image of an ion-milled cross-section of a carbon black (Vulcan XC-72R) particle.