

Hierarchically Porous Carbon Monoliths with High Surface Area from Bridged Polysilsesquioxanes without Thermal Activation Process

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Supplementary Information

Experimental Procedure

The precursor silane 4,4'-bis(triethoxysilyl)-1,1'-biphenyl (BTEBP) was purchased from Sigma-Aldrich Co. (USA). The solvent *N,N*-dimethylacetamide (DMA) and sodium hydroxide (NaOH) were purchased from Kishida Chemical Co., Ltd. (Japan). Aqueous solution of nitric acid (HNO₃) in 65 wt % and urea were purchased from Hayashi Pure Chemical Industry Ltd. (Japan). Pluronic F127 (PEO₁₀₆-PPO₇₀-PEO₁₀₆) was obtained from BASF Co. (Germany). All reagents were used as received and distilled water was used in all experiments.

In a typical synthesis, 1.4 g of Pluronic F127 was dissolved in 8 mL of DMA, and 0.5 mL of 1 M HNO₃ aq. was added. After the complete mixing, BTEBP was added to the obtained homogeneous solution followed by mixing for 3 min at room temperature. The resultant sol was then stood at 60 °C for 24 h for gelation and aging. The wet gels thus obtained were washed with ethanol (EtOH) followed by the gradual solvent exchange to pure ethanol, EtOH/H₂O = 9/1, EtOH/H₂O = 8/2, EtOH/H₂O = 7/3, EtOH/H₂O = 6/4, EtOH/H₂O = 5/5, EtOH/H₂O = 4/6, EtOH/H₂O = 3/7, EtOH/H₂O = 2/8, EtOH/H₂O = 1/9, and pure H₂O in this sequence at 60 °C for 8 h each. This solvent exchange process is indispensable to obtain the crack-free monoliths because the monoliths are cracked when the gels are directly immersed in pure H₂O due to the osmotic pressure. The obtained gels were then hydrothermally treated in 1 M urea aq. at 200 °C for 24 h. The dried gels were obtained after slow evaporative-drying at 40 °C. The dried gels were subsequently heat-treated at 800 °C or 1200 °C for 2 h with a heating rate of 4 °C min⁻¹ under an argon flow at 1.0 L min⁻¹. The resultant carbon/silica composites were immersed in 1 M NaOH aq. at 60 °C for 12 h for three times to remove silica. The obtained carbon monoliths were washed with H₂O at 60 °C for 4 h for three times followed by drying at 60 °C. The carbon/silica composites are denoted as CS-*x*, while the carbon samples which are obtained after the removal of silica are denoted as C-*x*. Here, *x* represents the heat-treatment temperature.

Observation of the microstructures of the fractured surfaces of the samples and the elemental analysis were conducted under scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (JSM-6060S, JEOL, Japan). A mercury porosimeter (Pore Master 60-GT, Quantachrome Instruments, USA) was used to characterize the macropores and the bulk densities of the samples, while nitrogen adsorption-desorption (Belsorp mini II, Bel Japan Inc., Japan) was employed to characterize the meso- and micropores of the samples. Before nitrogen adsorption-desorption measurements, the samples were degassed at 300 °C under vacuum for more than 6 h. Specific surface areas of the samples were calculated by the *t*-plot method. The thermogravimetric analysis (TGA) was performed on Thermo Plus TG 8120 (Rigaku Corp., Japan) at a heating rate of 5 °C min⁻¹ while continuously supplying air at a rate of 100 mL min⁻¹. The crystal structure was confirmed by powder X-ray diffraction (XRD) (RINT Ultima III, Rigaku Corp., Japan) using Cu K α (λ = 0.154 nm) as an incident beam. Raman spectroscopy was employed to analyze the molecular structure with a laser Raman spectrophotometer (RMP-210, Jasco Corp., Japan). Helium pycnometry (Accupyc 1330, Micromeritics,

USA) was employed to determine the true densities of the heat-treated samples. Porosity (%) of each sample was calculated as $(1 - [\text{bulk density}]/[\text{skeletal density}]) \times 100$.

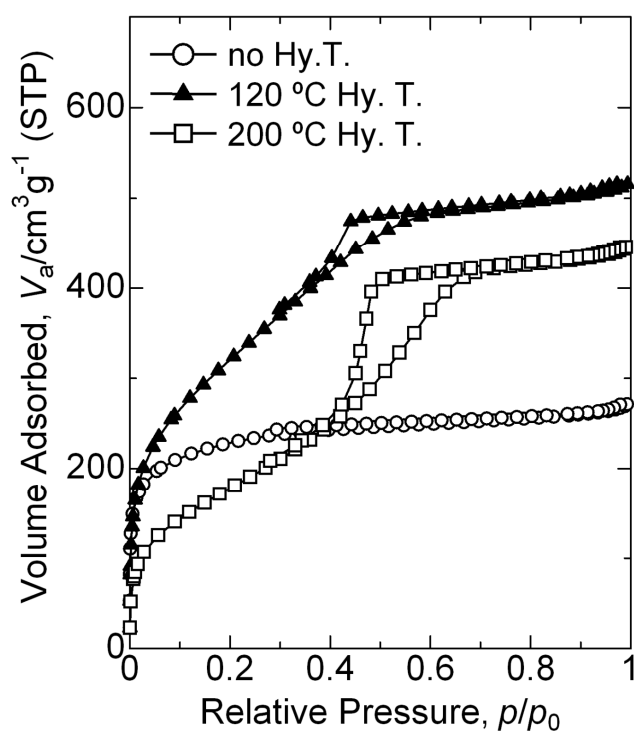


Figure S1 Nitrogen adsorption-desorption isotherms of the samples hydrothermally-treated in 1 M urea solution at different temperatures (120 and 200 °C Hy.T.) as well as the untreated sample (no Hy.T.).

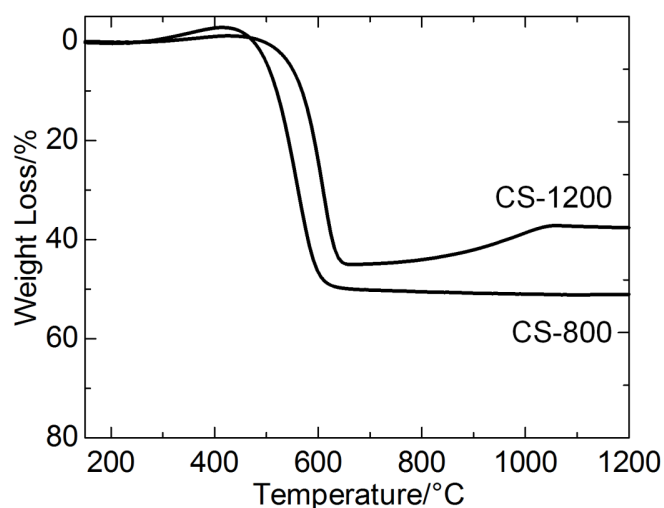


Figure S2 Results of thermogravimetric analysis of CS-800 and CS-1200 in air.

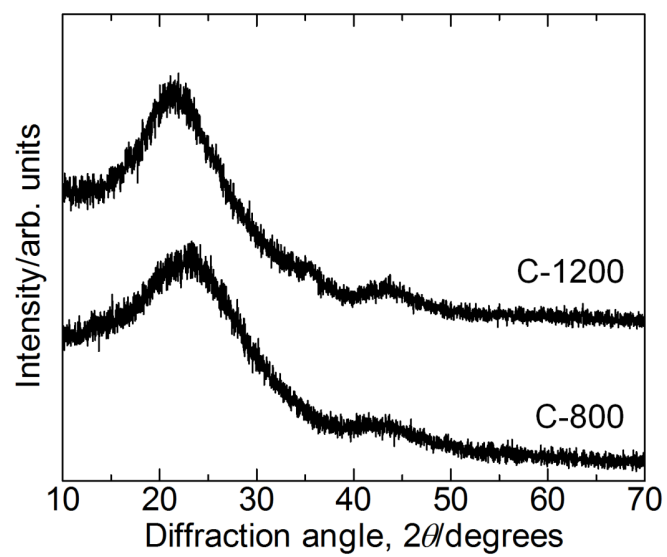


Figure S3 X-ray diffraction patterns of C-800 and C-1200.

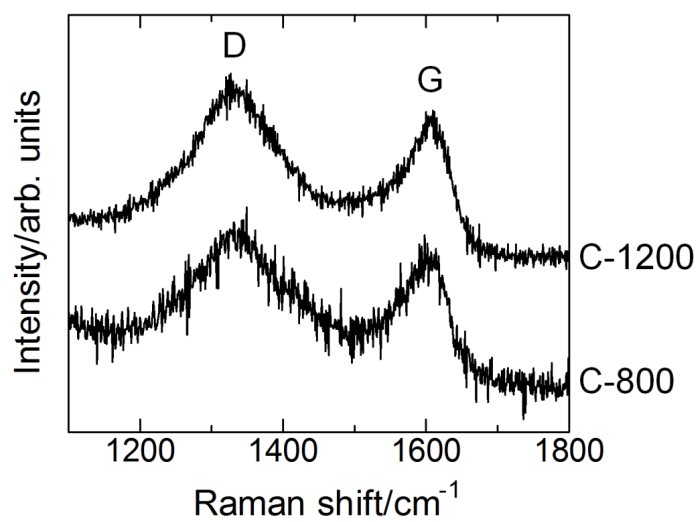


Figure S4 Raman spectra of C-800 and C-1200.