A Facile Approach for the Synthesis of Monolithic Hierarchical Porous Carbons - High Performance Materials for Amine Based CO_2 Capture and Supercapacitor Electrode

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Materials employed

Commercially available colloidal silica suspensions in water with different average size silica: 4 nm (15 wt% , Alfa Aesar) 8 nm (LUDOX SM-30, 30 wt%, Sigma Aldrich), 12 nm (LUDOX HS-30, 30 wt%) 20 nm (40 wt%, Alfa Aesar) were used as received. The carbon precursor was D-(+)-Glucose, ACS reagent grade, purchased from Sigma Aldrich.

In a typical synthesis, 10 g of a 15 wt% suspension of 4 nm colloidal silica and 1.5 g of glucose D is added to a 50 mL centrifuge tube and mixed well. Next the centrifuge tube (uncapped) is plunged into liquid nitrogen. Once the ice front (traveling radially from outside in) meets at the center of the suspension, the whole tube is submerged in the liquid nitrogen bath. The frozen sample is then subjected to freeze drying until the sample is completely dry. The freeze-dried glucose-silica composite is then pyrolyzed at 1000 ºC at a ramp rate of 3 ºC/min for a dwell time of 3 h under a nitrogen or argon environment, resulting in a carbon-silica composite. This carbon-silica composite is then placed in a 3M NaOH solution at 80 ºC overnight under medium stirring to etch out the silica. The sample is finally washed with deionized water until a neutral pH is reached and dried at 80 ºC for at least 12 hours before use. For convenience the samples are denoted by KCU-C *x-y*, where *x* represents the average colloidal silica size (nm) and *y* represents the ratio of silica to glucose (by weight) in the original suspension. To introduce significant microporosity, CO_2 activation is used. Specifically for the CO_2 activation, the sample (after silica etching) is heated first under an inert atmosphere up to a temperature of 950 ºC, whereupon the inert gas is replaced by CO_2 at a flow rate of 50 cc/min. The time for activation varies from 1 – 4 h. CO_2 activated samples are denoted by KCU-C *x-y-z*, where *z* represents the time (h) for CO_2 activation.

Characterization Methods

Scanning Electron Microscopy (SEM). The microstructure of the samples was investigated by a LEO 1550 FESEM operating between 2-20 keV. SEM sample preparation involved polishing the sample's surface by a cryo-microtome (Leica EM FC7). The sample was placed in the microtome's cryo-chamber, which was kept at a temperature below -80 °C to ensure sufficient stiffness. Then using a diamond knife Trimming tool (Diatome Cryotrim 45), progressively thinner slices of material were removed starting from a thickness of 5 microns until reaching a final polishing thickness of 30-50 nm. This approach allowed the sample to be examined at various depths.

Transmission Electron Microscopy (TEM). TEM images were obtained using an FEI T12 Spirit TEM/STEM. The T12 is a 120 kV field emission TEM, equipped with a LaB_6 filament and an SIS Megaview II CCD camera. The sample was grounded and then added into a vial with ethanol. The sample was then sonicated and physically mixed by shaking the vial. After roughly 45 s, with the larger particles settling to the bottom of the vial, the top of the vial was pipetted out and placed on a carbon coated copper TEM grid.

Dynamic Mechanical Analysis (DMA). Compression measurements were carried out using a TA Instruments DMA Q800 Dynamic Thermal Mechanical Analyzer. Cylindrical samples (all approximately 8 mm in diameter and 10 mm in length) were preloaded at 0.001 N. Stress-strain measurements were taken at a compression rate of 0.5 N/min until a maximum force of 18 N was reached. Measurements were taken at ambient temperature and pressure.

Electrical conductivity measurements. Electrical conductivity measurements were obtained by way of a four point probe setup. The probe was set up so that the sample (in powder form) was in an insulating cylinder with two conductive pistons on either end able to squeeze the powder together. By using a spring the amount of force applied to the pistons and thus, the pressure on the powder could be measured. Two small pinholes in the side of the cylinder allowed for two narrow conductive pins to contact the KCU-C powder. The pins allowed the voltage drop to be measured in the compacted powder as a current was applied through the conductive pistons. The pressure applied to the KCU-C powder was above 8000 psi, to minimize the void space of the material measured.

Electrochemical Measurement. The electrodes were prepared by mixing 92.5 wt% KCU-C 4-1-4 and 7.5 wt% polytetrafluoroethylene (PTFE) (60 wt% PTFE obtained from Sigma Aldrich) with ethanol to form a slurry. The slurry was grounded using a mortar and pestle and dried by placing in an oven at 80 ºC for an hour to obtain a dough like paste. The paste was then rolled into a film and then pressed onto a stainless steel mesh (Alfa Aesar). The electrochemical performance was characterized by cyclic voltammetry (CV). The CV experiments were carried out using a three-electrode configuration with Pt as the counter electrode, Ag/AgCl as the reference electrode and with 1M H_2SO_4 as the electrolyte in the potential range between 0-1V. Different sweep rate values ranging from 2 to 200 mV/s were used. The galvanostatic charge-discharge measurement was carried out using a two electrode configuration at different current densities (*I/m*, where *m* is the mass of a single electrode) ranging from 1-80 A/g. The electrochemical impedance spectroscopy measurement was performed using a sinusoidal signal of 10 mV over the frequency range from 100 kHz to 2 mHz. The specific capacitance, energy density and power density are calculated using the following formula:

$$E = \frac{1}{8} C_S \left(V - V_{drop}\right)^2$$

$$P = \frac{1}{2}\left(V - V_{drop}\right)\left(\frac{I}{2m}\right)$$

$$C_s = 2\left(\frac{I}{m}\right)\left(\frac{dt}{dV}\right)$$

where

m is the mass of single electrode
I is the current
V is the maximum applied potential (1V)
V_{drop} is the IR drop
dV/dt is the rate of potential decline during the discharge (excluding IR drop)
C_s is the specific capacitance of the material
E is the specific energy density
P is the specific power density

The capacitive frequency response was calculated from the EIS data using the following formula:

$$C = \frac{1}{j\omega Z} = \frac{1}{j\omega\left(\mathrm{Re}(Z) + j\,\mathrm{Im}(Z)\right)}$$

$$|C| = \left[\{\mathrm{Re}(C)\}^2 + \{\mathrm{Im}(C)\}^2\right]^{1/2}$$

$$\omega = 2\pi f$$

Sorbent preparation for amine based CO_2 capture: Polyethylenimine (PEI) (average M_w ~800, from Sigma Aldrich) was mixed with absolute methanol to obtain a 20 wt% solution. The sorbents were prepared by adding a fixed amount of this 20 wt% solution to 25 mg of KCU-C 4-3. The mixture was then sonicated and kept under 70 mbar at 40 ºC for at least 12h. The CO_2 sorption measurement was performed using a TA Instruments Q500 thermal graphic analyzer. Sorption tests were performed with 1atm of dry CO_2. For the sorption tests, 5-10 mg of the PEI-carbon composite was placed in a platinum pan, heated to 100 ºC @ 10 K/min under N_2 (40 ml/min flow rate) and held at 100 ºC for 40 min to remove any moisture and CO_2 sorbed from air. The sorbent was then cooled to 75 ºC @ 10 K/min and the gas was switched over to CO_2 and held at 75 ºC for 45 min. The CO_2 capacity of the sorbents (in mmol g^{-1}) was calculated based on the weight gain of the sorbent during the adsorption. Tests were also conducted with 10% CO_2-90% N_2, under dry and moist (by passing the gas through a water bubbler maintained at room temperature) conditions.

Mercury porosimetry: Monolithic samples were analyzed using mercury intrusion via a Micromeritics AutoPore IV (9500 Series) porosimeter. The cylindrical monolith samples were cut in half (axially) to fit into the penetrometer sample holder. Care was taken to analyze the data up to a pressure of 3617.27 psia, ensuring that pores with size below 50 nm were not analyzed. The apparent density was calculated by the AutoPore IV by measuring the volume of the sample at 0.60 psia and using the weight measured by the operator.

BET

Nitrogen adsorption-desorption tests were carried out at 77K using a Micromeritics ASAP 2020 analyzer. Prior to gas adsorption measurement, the samples were degassed at 180 ºC under vacuum for at least 12 hours. The specific surface area was calculated using the Brumauer-Emmett-Teller (BET) method. The pore volume was estimated from single point adsorption at a relative pressure of 0.994. The pore diameter was determined from the adsorption branch, according to the Barrett-Joyner-Halanda (BJH) method.

Microporosity characterization via CO_2 adsorption:

CO_2 adsorption-desorption tests were carried out at 273K using a Micromeritics ASAP 2050 Xtended Pressure Sorption Analyzer. Prior to gas adsorption, the samples were degassed at 180 ºC for 16 hours, under vacuum. The absolute pressure range used was roughly 0.03 bar to 10 bar. The pore size distribution was calculated using density functional theory, using CO_2 at 273K on carbon and the pores represented as slits for modeling purposes.

Figures

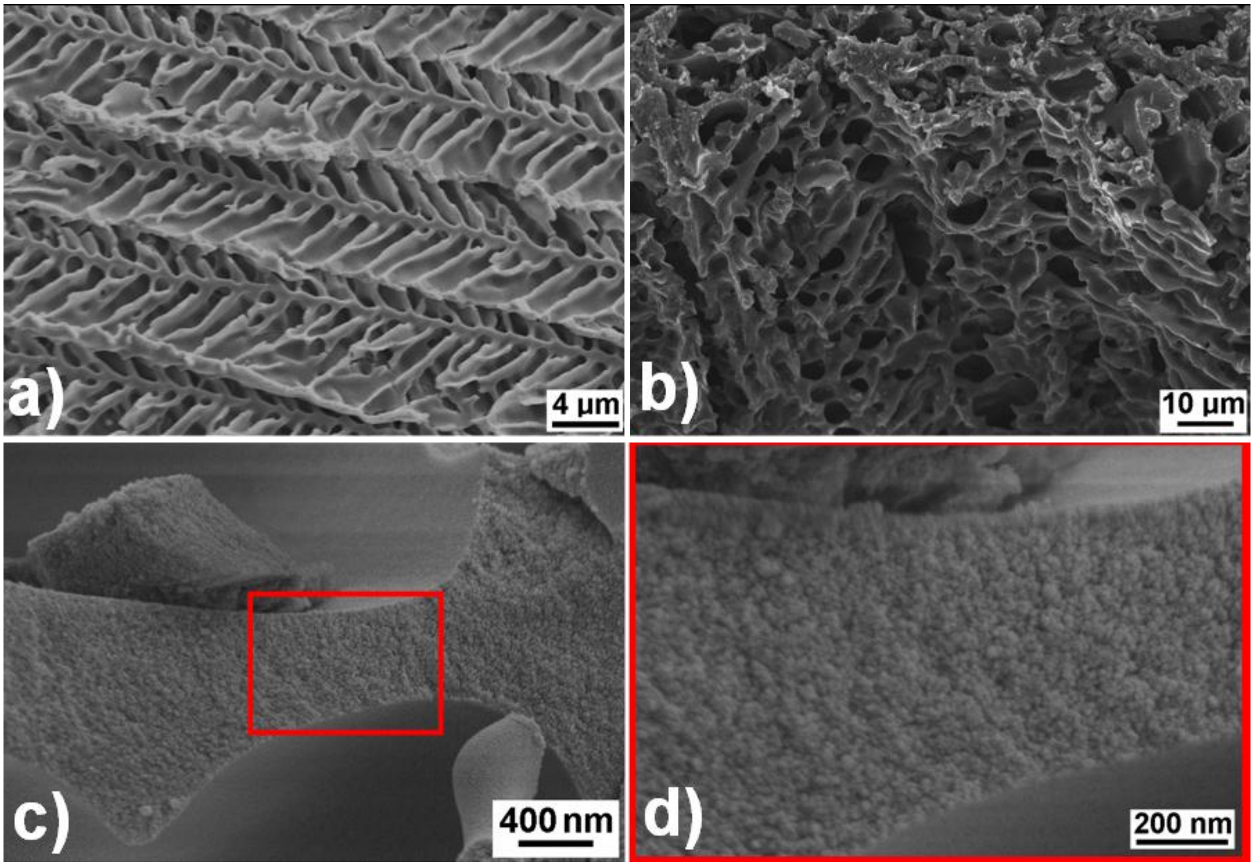

Figure S1. SEM images where the sample was cut and polished via microtome as described previously. The SEM images reveal (a) a fishbone like structure in the glucose-silica composite that is also seen in the (b) carbonized HPC material. HR-SEM images show (c) the macroporous walls of the glucose-silica hybrid material, in which the (d) colloidal silica can clearly be seen.

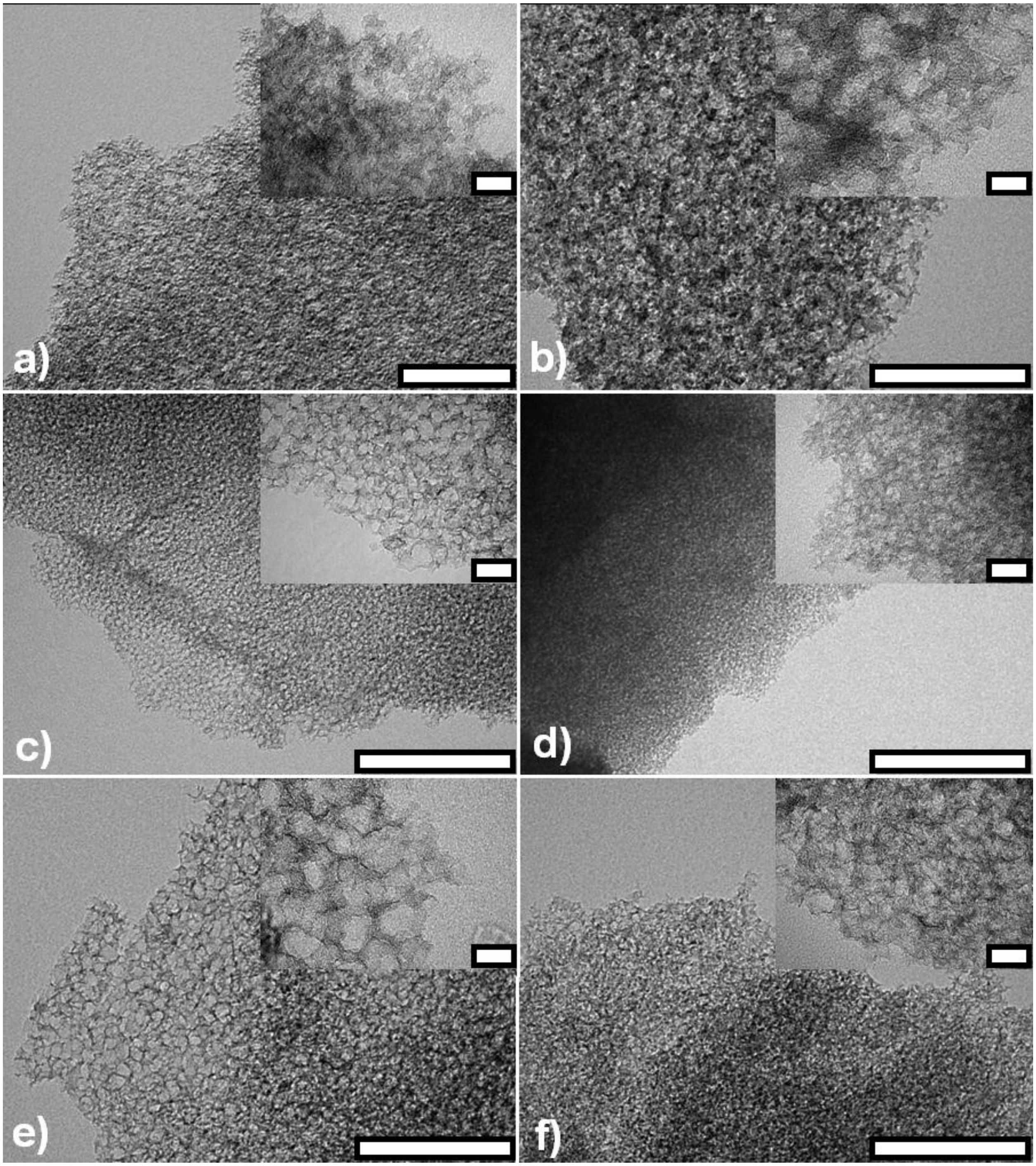

Figure S2. TEM images of KCU-C x-y samples. Scale bars for all images are 200 nm for the larger images and 20 nm for the inset images. a) KCU-C 4-1 b) KCU-C 4-2 c) KCU-C 8-1 d) KCU-C 8-2 e) KCU-C 20-1 f) KCU-C 20-2.

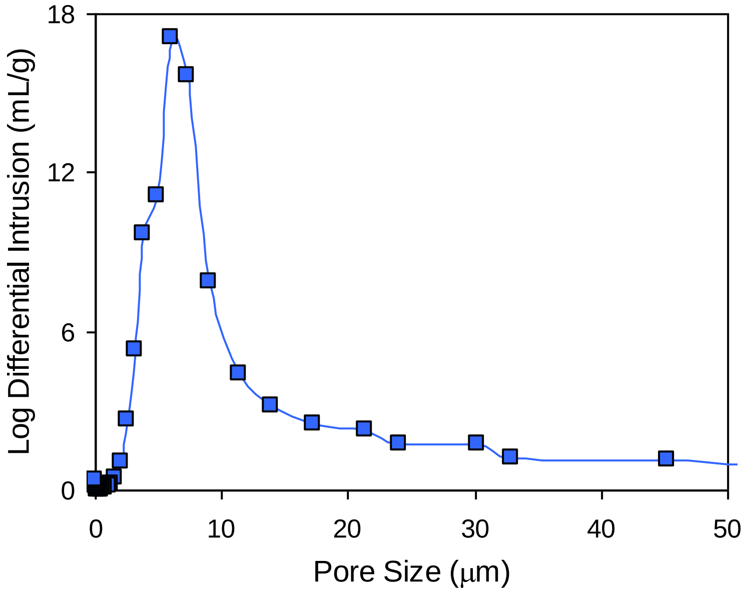

Figure S3. Pore size distribution via mercury porosimetry for the KCU-C 4-1 monolith sample. The pore size distribution shows macropores present mostly in the range from 3-12 microns. Some larger (above 15 μm) macropores are present, but to a relatively small degree. The analysis reveals the monoliths have a porosity of 83% and a bulk density of 0.09 g/mL (at 0.60 psia).

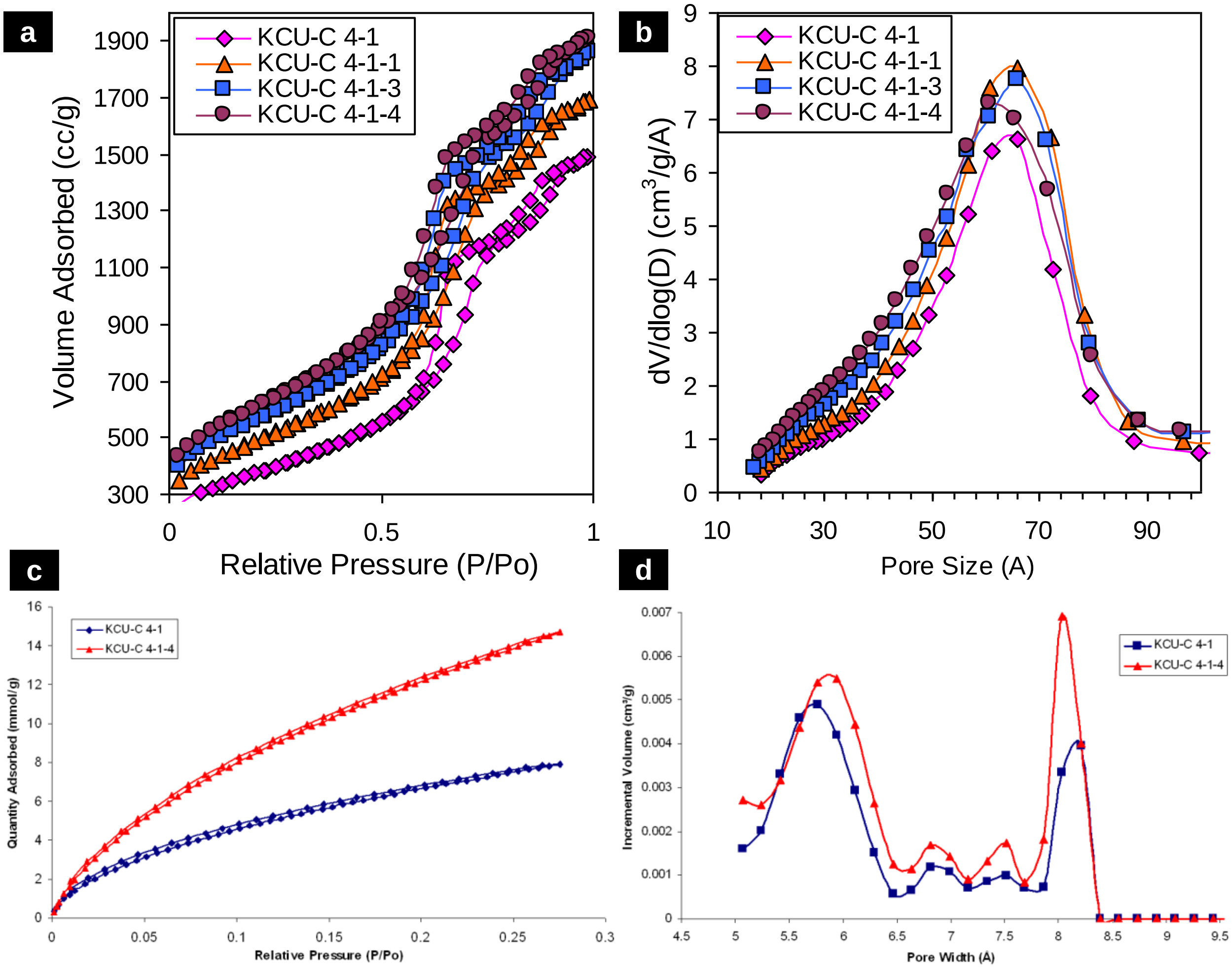

Figure S4. (a) N2 sorption isotherms and (b) BJH pore size distributions, for KCU-C 4-1 samples that underwent physical activation for 0, 1, 3 and 4 hours at a CO_2 flow rate of 50 cc/min. The curves show how the 1.8-4.0 nm (small mesopore/large micropore) shoulder present in the KCU-C 4-1 sample increases with increased activation time. (c) CO_2 sorption isotherms for both activated and non activated KCU-C 4-1 samples; and (d) the resultant micropore size distribution via density functional theory (slit pores) model. Both the CO_2 sorption curves and the DFT pore size distribution show a substantial increased microporosity in the KCU-C 4-1-4 sample. This increased microporosity correlates directly with the increased surface areas for increasing activation times seen in table S1 (below).

Table S1. BET surface area and mesopore volume of KCU-C 4-1 samples under various physical activation times. As the activation times increase, the surface area and pore volume increase.

Sample name	**CO_2 activation time (h)**	**BET surface area (m^2/g)**	**N_2 adsorption pore volume (cm^3/g)**
KCU-C 4-1	0	1316	2.3
KCU-C 4-1-1	1	1703	2.6
KCU-C 4-1-3	3	1935	2.9
KCU-C 4-1-4	4	2096	3.0

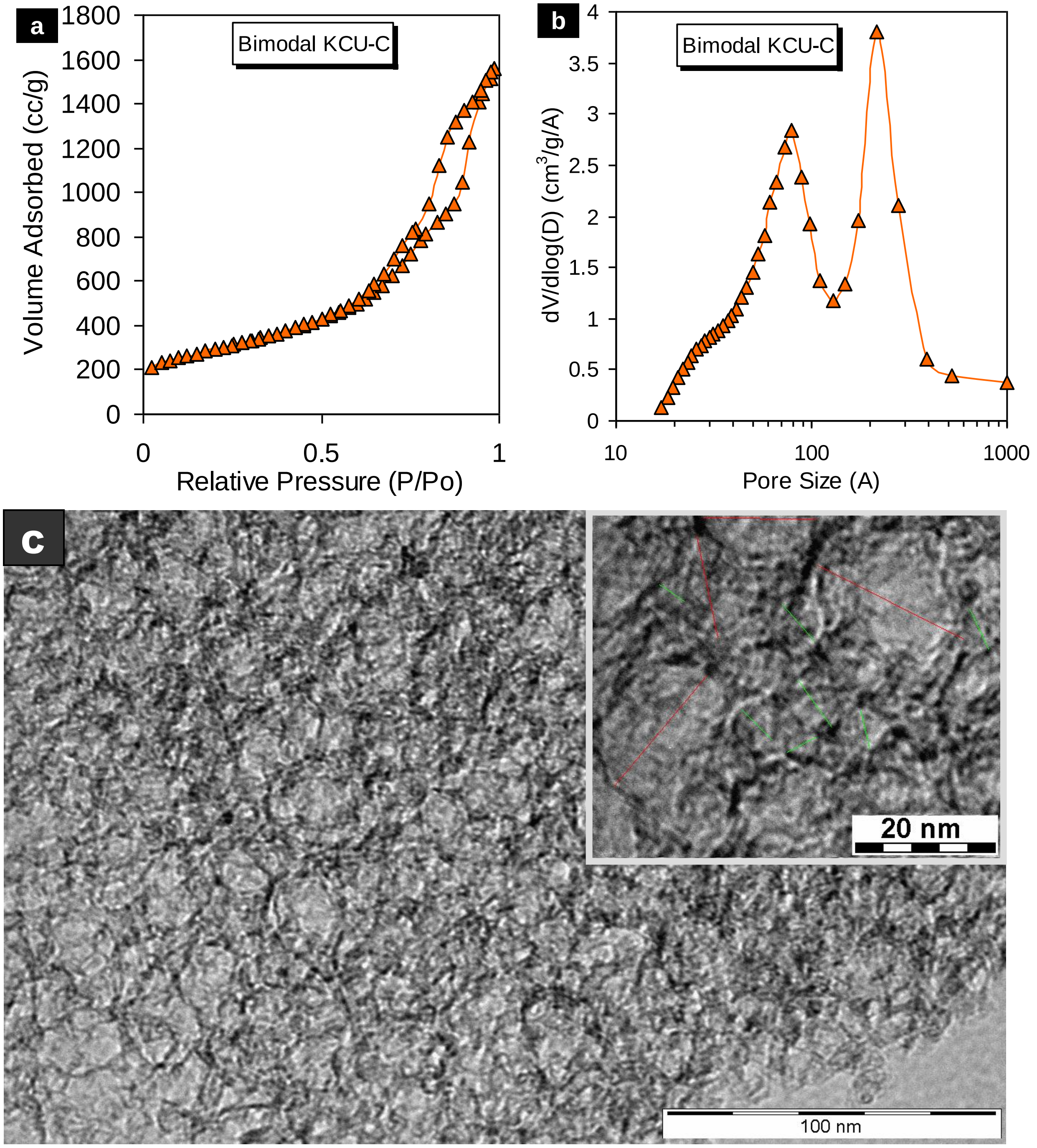

Figure S5. (a) N_2 sorption isotherm and (b) BJH pore size distribution for a KCU-C synthesized using both 4 and 20 nm sized colloidal silica (as specified by the manufacturer). The sample was prepared using equal parts (by weight) of each colloidal silica and adding glucose to the suspension until the glucose to the combined silica weight ratio was 1:1. The sample has a BET surface area of 1025 m^2/g and a mesopore volume of 2.4 cm^3/g. (c) TEM image of the bimodal HPC sample with a bimodal pore size distribution consistent with the peaks seen in S5b (8 and 20 nm). Inset image is a higher resolution TEM image that denotes the diameters of the smaller 8 nm pores with green lines and the larger 20 nm pores with red lines.

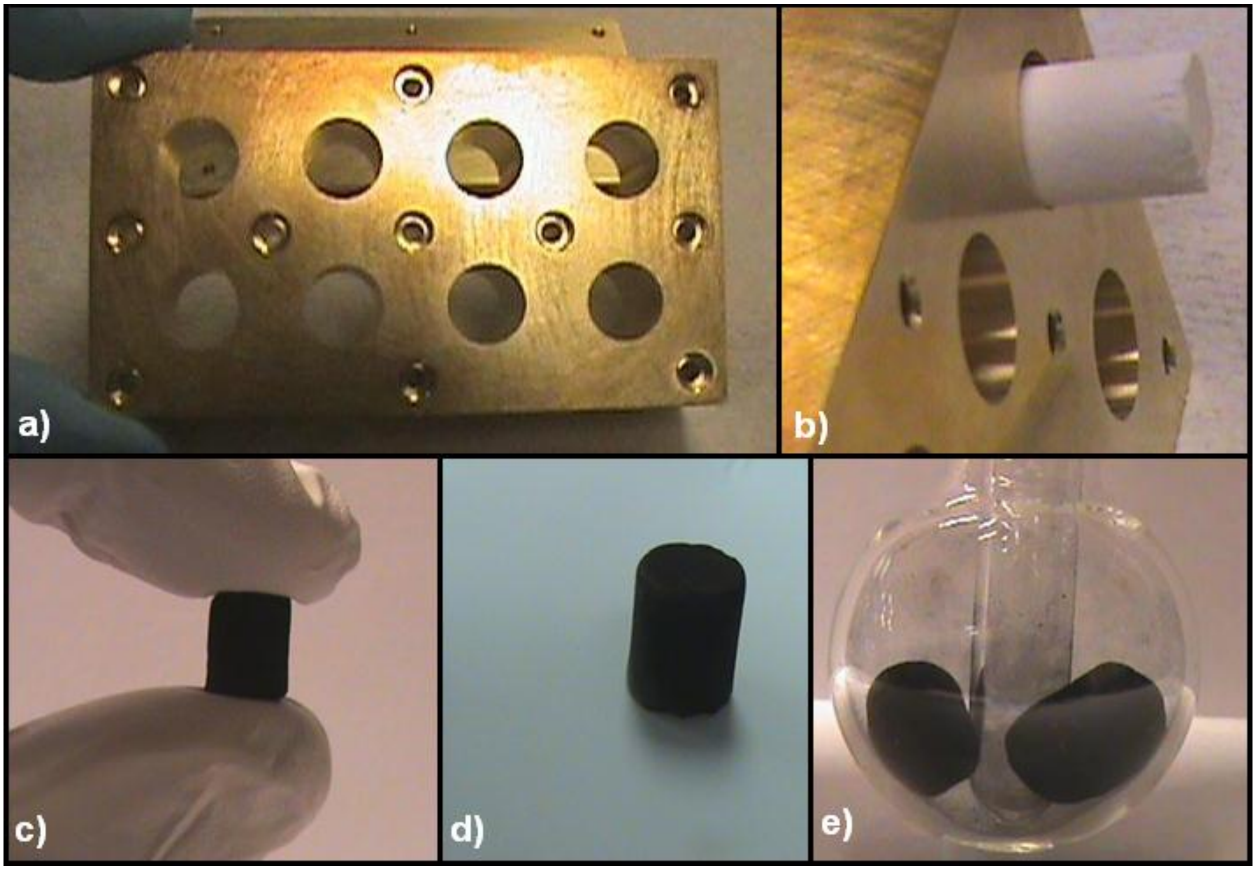

Figure S6. Photographic images of: (a) the brass mold employed to fabricate monolithic cylindrical samples with (b) a KCU-C 4-1 monolith shown in the mold before carbonization. The finished cylindrical monoliths (c, d) were approximately 8 mm in diameter and 10 mm in length after being pyrolyzed. The monoliths (e) are shown as they were measured under nitrogen sorption.

Figure S7 below shows a typical compressive stress/strain plot. In general, the stress/strain curves exhibit a behavior typical of porous cellular solids. At small strains the material behaves elastically and the slope of the curve equals the compressive modulus of the porous material. At higher strains the material collapses in brittle failure until it starts to reach a maximum compacted state, whereupon the stress starts to increase sharply.

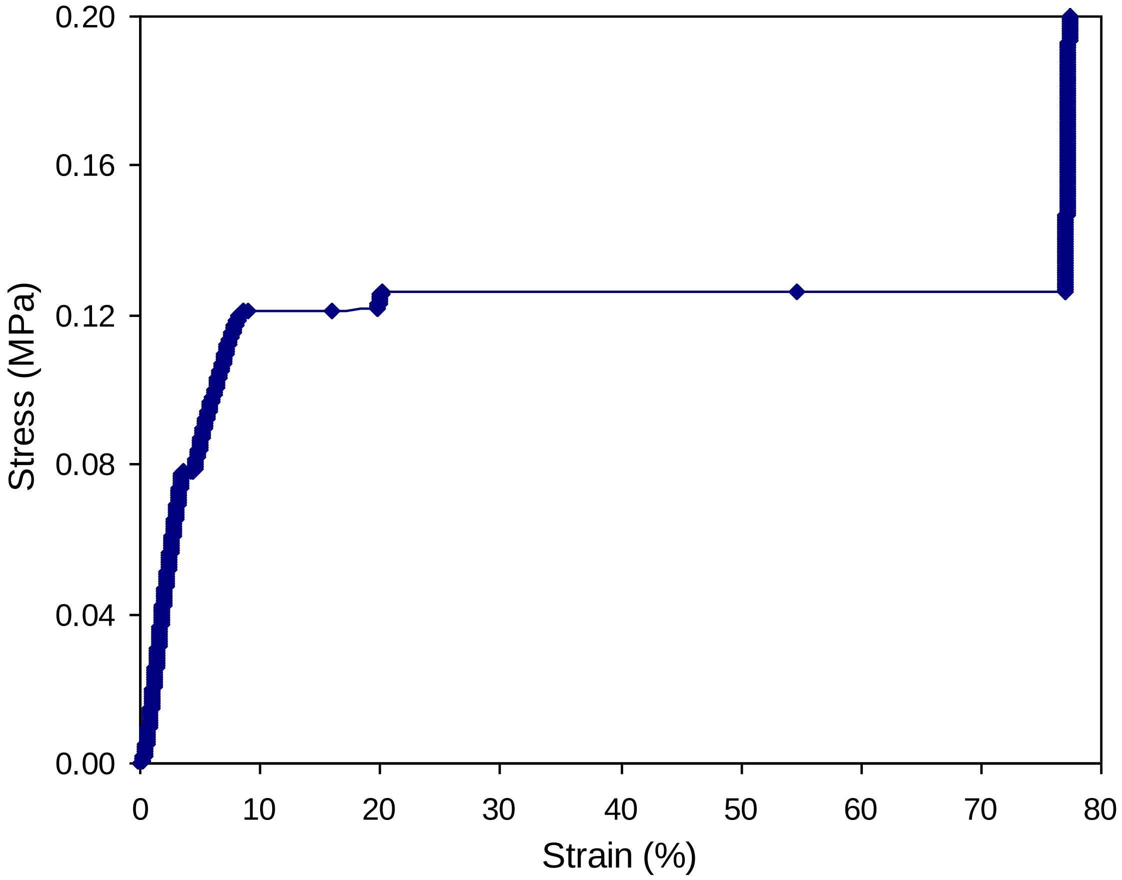

Figure S7. Stress strain curve representative of KCU-C 4-1 cylindrical monoliths. The modulus was obtained by measuring the slope of the curve before the collapse of the material under brittle failure.

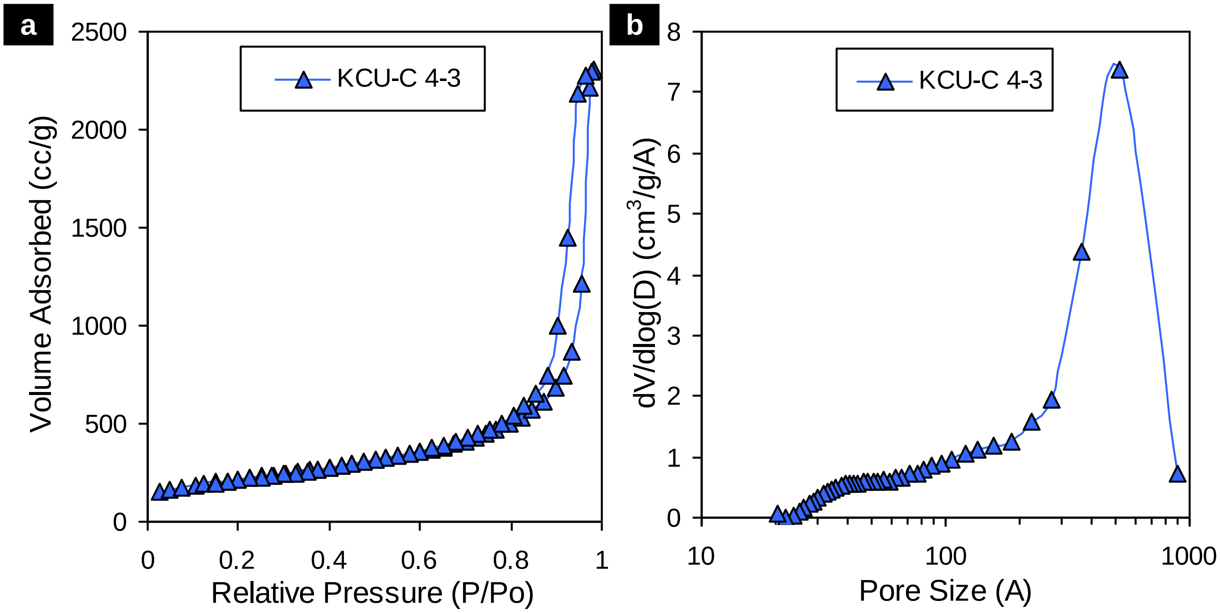

Figure S8. (a) N_2 sorption isotherm and (b) BJH pore size distribution for KCU-C 4-3 synthesized using 4nm colloidal silica and silica/glucose ratio of 3. The sample has a BET surface area of 760 m^2/g and a mesopore volume of 3.6 cm^3/g. KCU-C 4-3 sample was impregnated with amine and used for CO_2 capture.

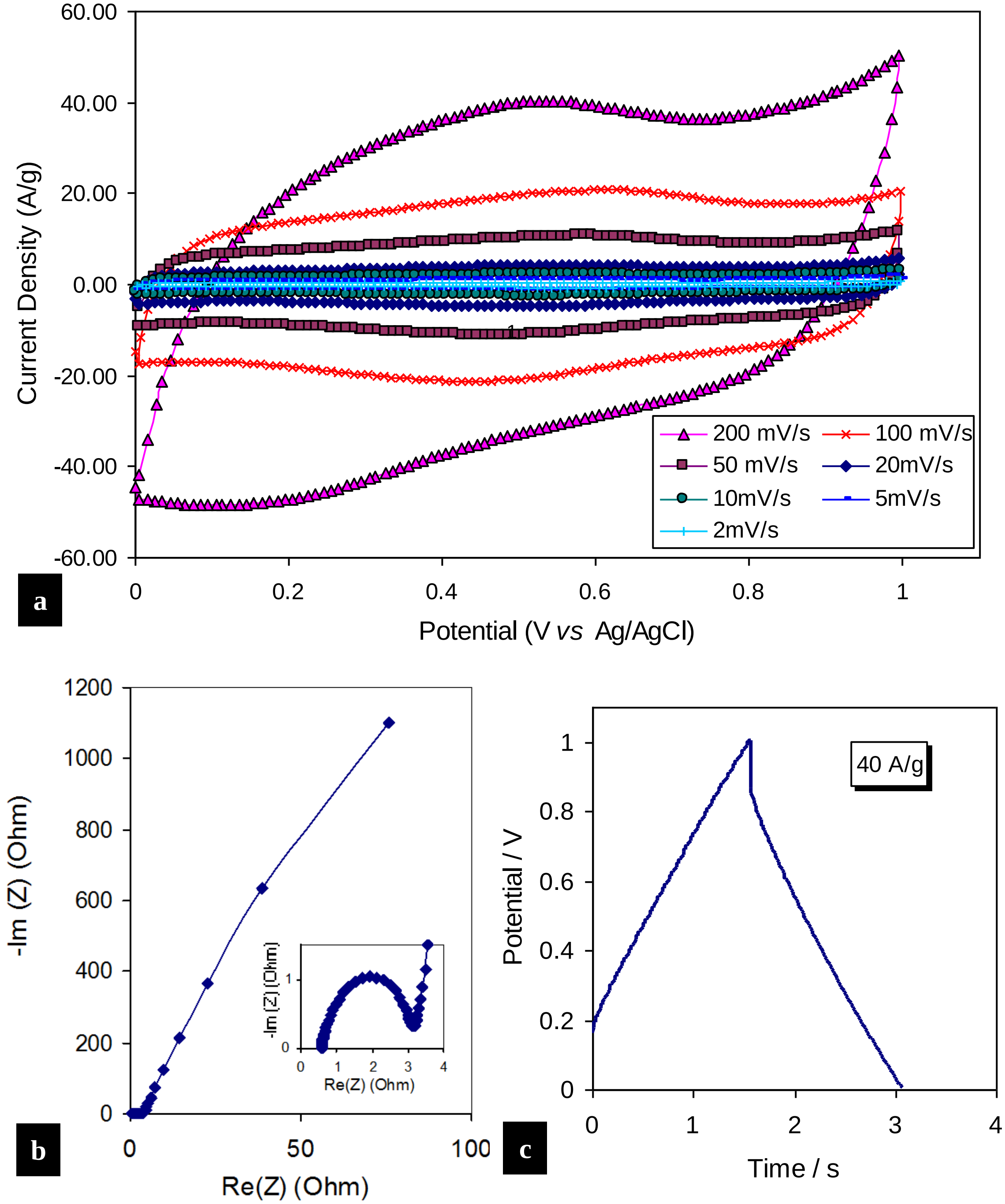

Figure S9. (a) Cyclic voltammetry results (b) Nyquist plot for KCU-C 4-1-4 using a sinusoidal signal of 10 mV over the frequency range from 100 kHz to 2 mHz. Re(Z) represents the real impedance and Im(Z) represents the imaginary impedance, (c) Galvanostatic charge-discharge curve for KCU-C 4-1-4 measured using symmetrical two electrode configuration in 1M H_2SO_4 within the potential range 0-1 V

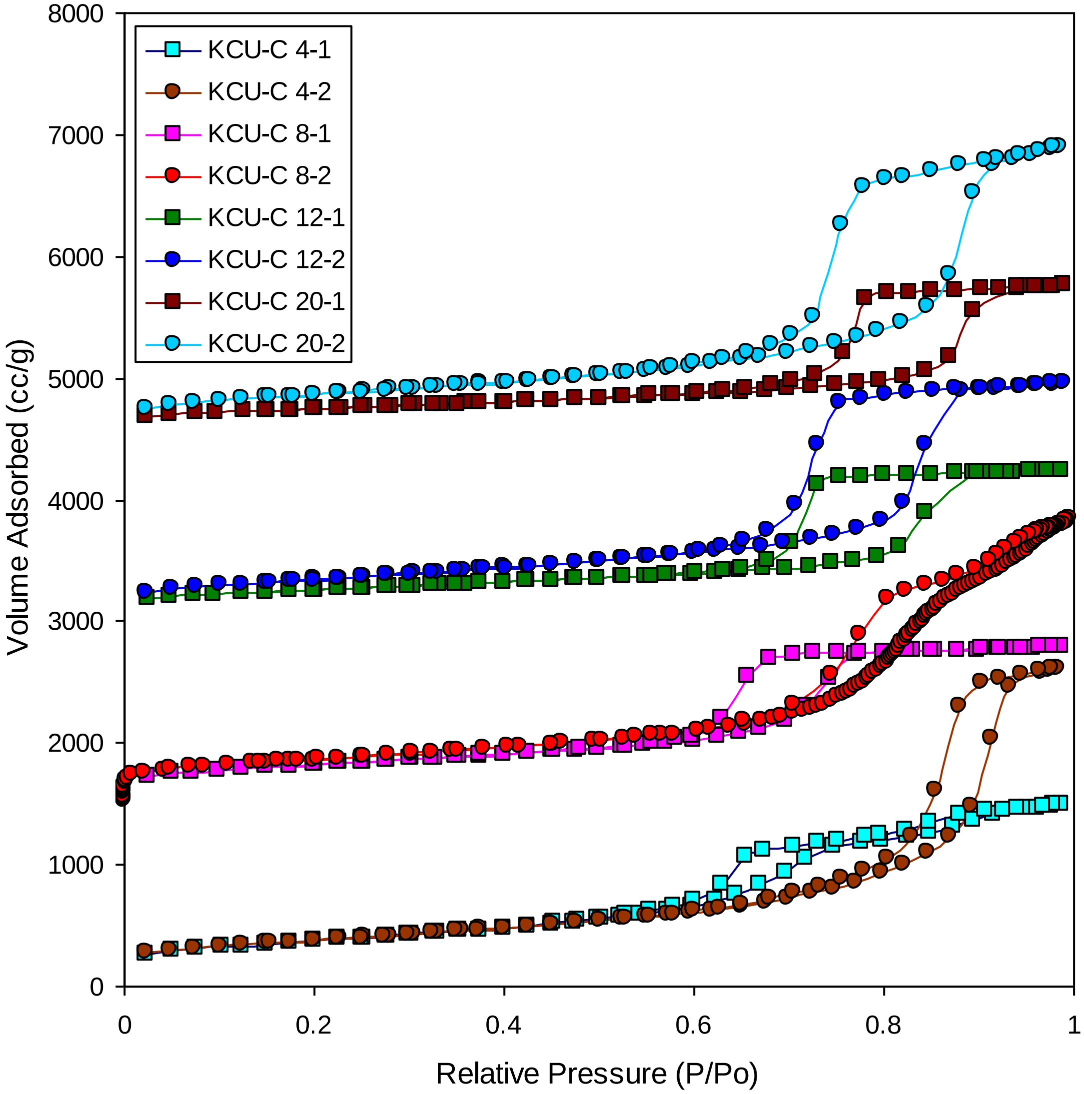

Figure S10. Nitrogen sorption isotherms for the KCU-C samples. The curves for KCU-C 8-y, KCU-C 12-y, KCU-C 20-y are offset vertically by 1500, 3000, 4500 cc/g respectively.