Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information of the Manuscript

Block Copolymer Assisted Synthesis of Carbon Aerogels Exhibiting High Conductivity and Remarkable Capacitance

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Experimental Part.

Materials: Resorcinol, triethyl orthoacetate (EOA), formaldehyde, poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) (PPO_{15}-PEO_{22}-PPO_{15}) were purchased from Sigma-Aldrich and used as received. Water was distilled and deionized.

Preparation of monolithic carbon aerogel (CA): The synthesis followed for preparation of CA1-800 was as follows: 0.661 g of resorcinol was dissolved in 0.81 mL of deionized distilled water, 2.9 mL of ethanol and 0.06 mL of HCl (5 M). PPO_{15}-PEO_{22}-PPO_{15} (0.20 g) was added to the resulting resorcinol solution. Once PPO_{15}-PEO_{22}-PPO_{15} was dissolved, 0.570 mL of triethyl orthoacetate and 1.35 mL of a formaldehyde solution (37% in water) were also added, stirred at 30ºC for 20 min. Hydrolysis and condensation of resorcinol and formaldehyde (RF) was conducted at 90ºC for 5 h for the achievement of a monolithic phenolic resols (PR). CA monoliths were obtained by PR carbonization; e.g., 4 hours at 250 ºC followed for 4 additional hours at 800 ºC under nitrogen atmosphere (heating ramp 1.8 ºC min^{-1}). The synthesis followed for preparation of CAq-800, CA2-800 and CA3-800 was identical to that described above for CA1-800, except for the use of different amounts of PPO_{15}-PEO_{22}-PPO_{15} (e.g. 0, 0.28 and 0.32 g,

respectively). The synthesis followed for preparation of CA1-600 and CA1-1100 was identical to that described above for CA1-800, except for the use of a different final temperature during the thermal treatment; e.g. 600 and 1100 ºC, respectively.

Characterization: The morphology of the different CA monoliths was investigated by scanning electron microscopy (SEM) using a Zeiss DSM-950 instrument and transmission electron microscopy (TEM) using a JEOL 2000 FXII (200-KeV). Bulk and skeletal density, and porosity data were obtained using a Micromeritics Autopore II 9220 mercury porosimeter. The BET surface area was measured on an Omnisorp-100 (Coulter) on samples thermally treated at 250 °C overnight prior to nitrogen-gas adsorption. Raman spectrum was recorded on a Renishaw InVia upon irradiation at 514 nm. X-ray Photoelectron Spectroscopy (XPS) experiments were performed in an ultrahigh vacuum system at a base pressure of $6 \cdot 10^{-10}$ mbar equipped with a SPECS Phoibos 150 electron spectrometer and a delay-line detector in the nine-segment mode, using monochromatized Al Kalpha radiation. High resolution C1s and O1s core level spectra were recorded at normal emission take-off angle, using an energy step of 0.05 eV and a pass energy of 14 eV, which provides an overall energy resolution of 0.48 eV as measured at the Fermi edge of a silver reference sample. The line shape of XPS spectra was fitted using the XPSPeak4.1 processing program.[1] This fitting procedure uses a mixed percentage of Gaussian and Lorentzian curves with for each component, keeping the fwhm and the Gaussian/Lorentzian ratio constant and fitting the energy of the peaks and their heights using a LLS algorithm. A Shirley function was used to subtract the background. A Gaussian(80)-Lorentzian(20) function component line shape was found to provide a satisfactory fit to the C1s spectra, while those of O 1s spectra were fitted with a single a 100% Gaussian function. Quantitative analysis was done considering the sensitivity factors of S(C1s) = 1.00 and S(O1s) = 2.93 from the SPECS

[1] http://www.phy.cuhk.edu.hk/~surface/XPSPEAK/

instrument. The DC conductivity (σ_{DC}) of cylindrical CA monoliths and of pellets (obtained after compacting at 38 MPa a mixture of finely ground CA monolith and PVDF in a 20 wt%) was measured using a typical four-probe method.

CONDUCTIVY MEASUREMENTS:

A current was applied at the two outer electrodes and voltage drop was measured at the two inner ones. Conductivity was calculated according to equation:

$$\sigma_{DC} = \frac{L}{RA}$$

where L is the length between the two inner electrodes and A is the geometrical area defined by the electrodes length and the dimension perpendicular to the electrodes (*i.e.* the monolith thickness or pellet thickness).

Supercapacitor consisted of two cylindrical CA monoliths of 10 mm diameter and 1 mm height assembled in Swagelok^{TM}-type cells. The two electrodes (of ca. 50 mg each) were separated by a glassy microfibre paper (Whatman 934-AH). Aqueous 6M KOH and 2M H_2SO_4 solutions were used as electrolytes. Two tantalum rods acted as current collectors. Charge and discharge of the supercapacitor cells were followed by voltammetry and galvanostatic measurements at room temperature with potentiostat/galvanostat PGSTAT30 Autolab. The specific capacitance (C) expressed in farads per gram of carbon material (F/g) was obtained from the discharge galvanostatic plots recorded for different current densities. The voltage drop V_1 accounts for the equivalent series resistance, *ESR,* associated with the cell ($V_1=2\cdot I\cdot ESR$, where I is the current applied). From the voltage drop V_2 and the discharge time (t_d), the cell capacitance, $C=I\cdot t_d/V_2$, can be calculated. Specific capacitance of the CA monoliths were calculated as $2\cdot I\cdot t_d/V_2\cdot m_c$; where m_c is the CA monolith mass of one electrode.

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Figure S1: SEM micrographs of a CA1-800 monolith synthesized in absence of EOA. Bar is 10 µm.

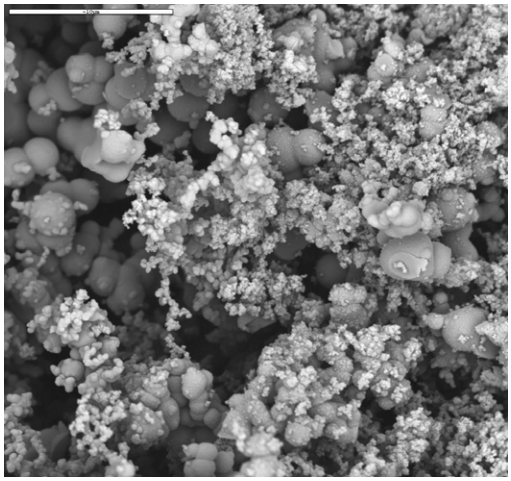

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Figure S2: SEM micrographs of CA0-800 (a), CA2-800 (b) and CA3-800 (c). Bars are 2 μm for (a) and 20 μm for (b) and (c).

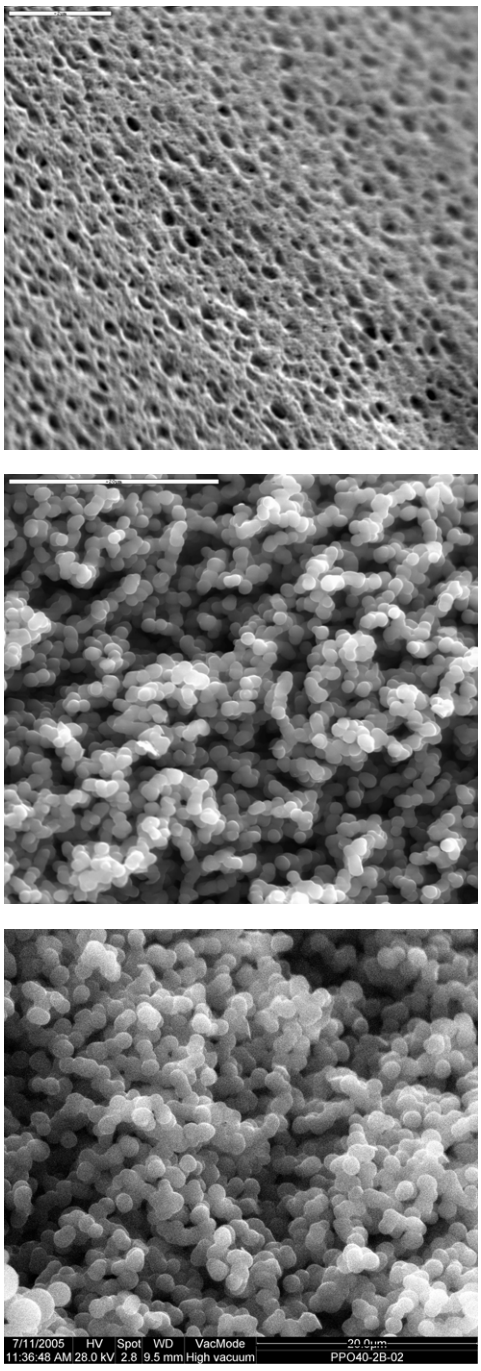

Figure S3: Raman spectra of CA1-800 and CA1-1100 monoliths (blue and red lines, respectively). The band at 1350 cm^{-1} (D band) is related to disordered graphitic structures (e.g. defects and sp3-hydridized bonds), while that at 1590 cm^{-1} (G band) is related to the in-plane vibrations of carbon atoms placed at the hexagonal well-ordered carbon sheets.

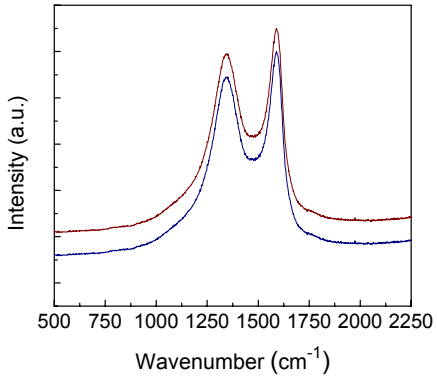

Figure S4: XPS O1s spectra of CA1-800 and CA1-1100 monoliths. Every spectrum was presented as-acquired with data points represented as black symbols, and Shirley background and component peaks using solid lines. The fitting curve (red line) resulted from four contributions; carboxylic groups (grease line), epoxyde/carbonyl groups (red line), hydroxyde groups (dark yellow line) and chemisorbed O_2 and/or H_2O (blue line).

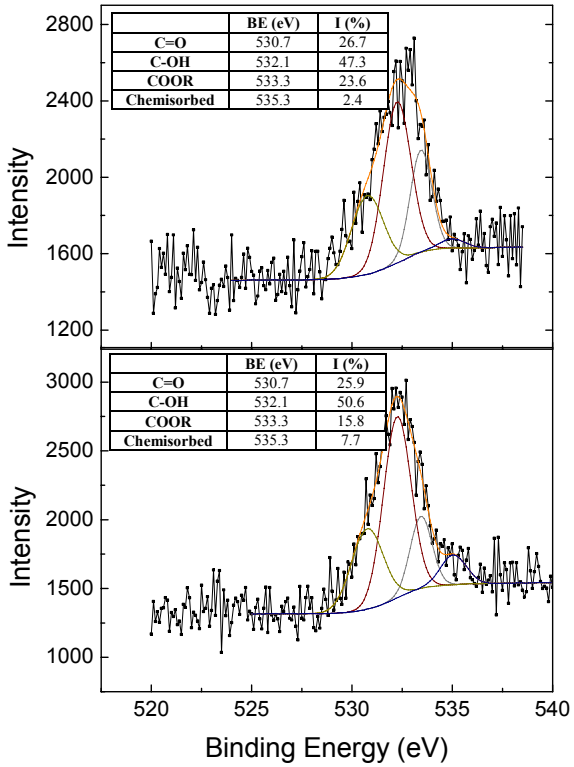

Figure S5: Nitrogen sorption isotherm of CA monoliths.

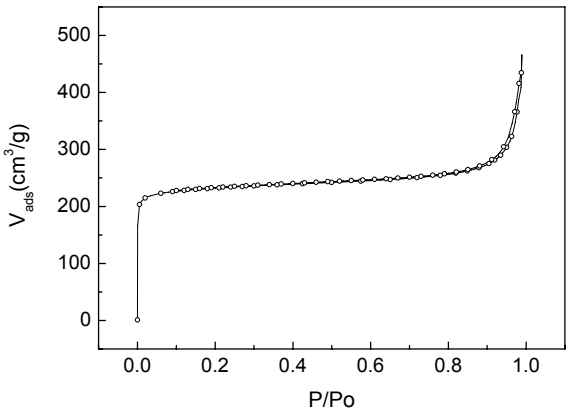

Figure S6: Charge/discharge galvanostatic plot recorded at 10 mA for a supercapacitor cell made with two identical CA1-800 monoliths as electrodes and 6M KOH solution as electrolyte.