Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

High surface area metal salt templated carbon aerogels via a simple subcritical drying route: Preparation and CO_2 uptake properties

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Material Synthesis

The following chemicals were used as supplied without any modification; 2,4,6-Triamino-1,3,5-triazine (Melamine), hydrochloric acid and sodium carbonate from Fischer Scientific while 37% Formaldehyde and calcium chloride were obtained from Sigma-Aldrich. The carbon aerogels were synthesized as follows; 4.2 g of melamine and 19.4 g of 37% formaldehyde were added to 15 ml of water under stirring, followed by the addition of 0.44 g (0.007 moles) of 0.1M sodium carbonate solution. The resulting mixture, which had a pH of 8.5 was heated at 40 ^{o}C until a clear solution of hexamethylomelamine (MF) was formed. Metal salt templating was via addition of 33.6 g of $CaCl_2$ to the MF solution to a $CaCl_2$/MF ratio of 2. A condensation reaction was then initiated by adjusting the pH of the salt containing MF solution to 4.5 by addition of 1M HCl. The solution was then heated at 60 °C for 1 h, during which a MF resin/calcium chloride composite was formed. The composite was dried and cured at 180 °C for 6 h then carbonised at 700, 800 and 900 °C for 2 h under nitrogen gas flow. The products were washed with water to remove the metal salt template. The washed products (carbon aerogels) were denoted as Ca-CAMFx (where x = temperature of carbonisation), i.e., the resultant carbon aerogels carbonised at 700, 800 and 900 °C were designated as Ca-CAMF700, Ca-CAMF800 and Ca-CAMF900 respectively.

Chemical activation of the Ca-CAMF800 aerogel was performed by mixing the carbon with KOH at a carbon/KOH weight ratio of 1:4. The carbon/KOH mixture was ground together to attain a homogeneous sample which was loaded on an alumina boat and placed in a flow-through tube furnace followed by heat-treatment at heating ramp rate of 3 °C/min under nitrogen gas flow to the activation temperature (600 or 800 °C) and held for 1 h. After cooling down under nitrogen flow, the activated templated carbon aerogels were obtained and washed with 2 M HCl under stirring at room temperature to remove any inorganic salts formed during the activation stage, followed by copious deionise water until a neutral pH was attained. Solid materials were obtained by filtration and finally dried in the oven at 120 °C. The obtained templated activated aerogels were denoted as 14AC-CAMF800-x (where x is 6 or 8 corresponding to activation at 600, or 800 °C respectively).

In order to assess the effect of salt templating a set of activated carbon aerogels were prepared from conventional non-metal salt templated melamine-formaldehyde resin (designated as CAMF). The carbons were designated as 12AC-CAMFx (where x is the activation temperature of 600, 700, 800 or 900 °C while 12 means carbon:KOH ratio of 1:2).

For porosity analysis, each sample was pre-dried in an oven and then degassed overnight at 200 ˚C under high vacuum. The textural properties were determined by nitrogen sorption at -196 ^{o}C using a Micromeritics ASAP 2020 volumetric sorptometer. The surface area was calculated by using the BET method applied to adsorption data in the relative pressure (P/Po) range of 0.06 – 0.22. The total pore volume was determined from the amount of nitrogen adsorbed at P/Po = 0.99. The micropore surface area and pore volume were determined via *t*-plot analysis. The pore size distribution was determined via two methods, which were applied to adsorption data; the BJH method and a non-local density functional theory (NLDFT) method.

CO_2 uptake measurements:

CO_2 uptake was measured using a TA Instruments SDT Q600 analyzer at atmospheric pressure. Prior to uptake measurements, the carbon samples were heated to 250 ^{o}C under static nitrogen and then cooled to 25 ^{o}C under a flow of nitrogen. The samples were then purged with CO_2 (50 mL min^{-1}) for 3 h, and then the CO_2 uptake determined repeatedly at 25 ^{o}C. Between measurements, desorption of CO_2 was undertaken by heating the sample to 250 ^{o}C under nitrogen gas flowing at the rate of 100 mL min^{-1}.

Table S1. Textural properties and CO_2 uptake of $CaCl_2$-templated carbon aerogel Ca-CAMF800 before and after activation (14AC-Ca-CAMF800-X, where X is activation temperature; 6 or 8 for 600 or 800 °C respectively) at KOH/carbon ratio = 4.

Sample	Surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]	Pore size (Å)[c]	CO_2 uptake (mmol/g)[d]
Ca-CAMF800	1090 (611)	1.37 (0.28)	1.2/3/9	2.1
14AC-Ca-CAMF800-6	1504 (1272)	0.83 (0.60)	1.2/2.7	2.5
14AC-Ca-CAMF800-8	3343 (803)	2.65 (0.36)	1.2/3.1	2.6

The values in the parentheses refer to; [a]micropore surface area, [b]micropore volume. [c]Maxima of pore size obtained from PSD curves. [d]CO_2 uptake at 298 K and 1 bar.

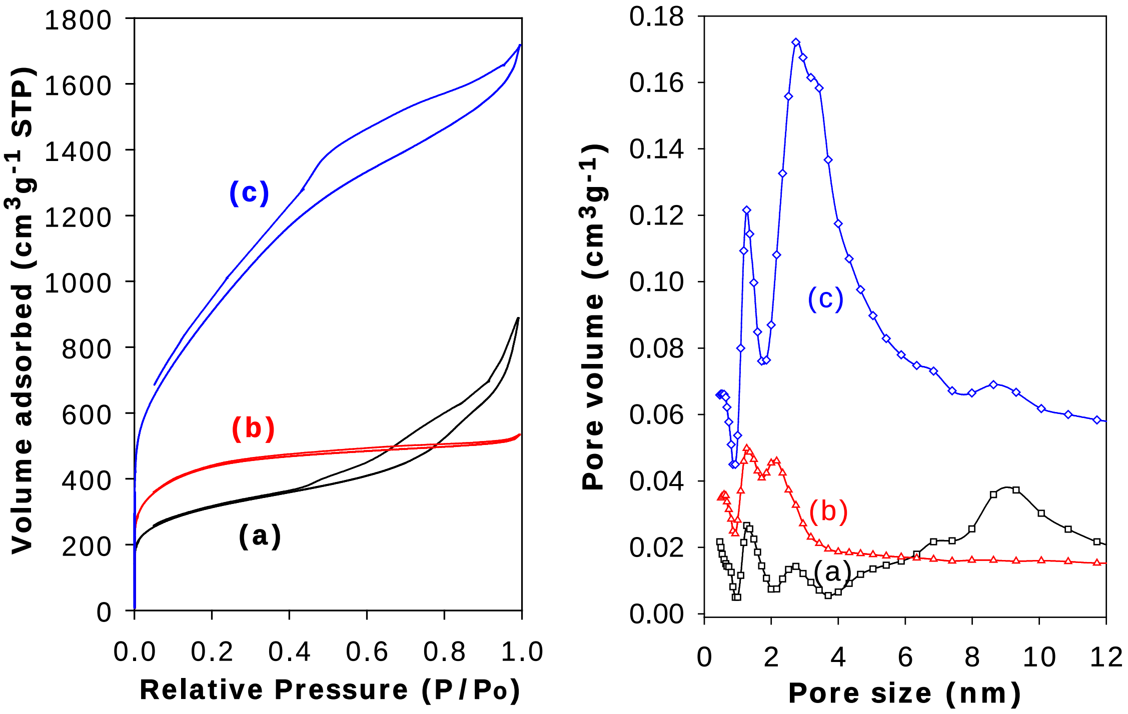

Fig. S1. Nitrogen sorption isotherms (left panel) and pore size distribution curves (right panel) for (a) $CaCl_2$-templated carbon aerogel (Ca-CAMF800) and after activation (14AC-Ca-CAMF800X, where X is activation temperature; 6 or 8 for 600 or 800 ^{o}C respectively) at KOH/carbon ratio = 4; (b) 14AC-Ca-CAMF800-6 and (c) 14AC-Ca-CAMF800-8.

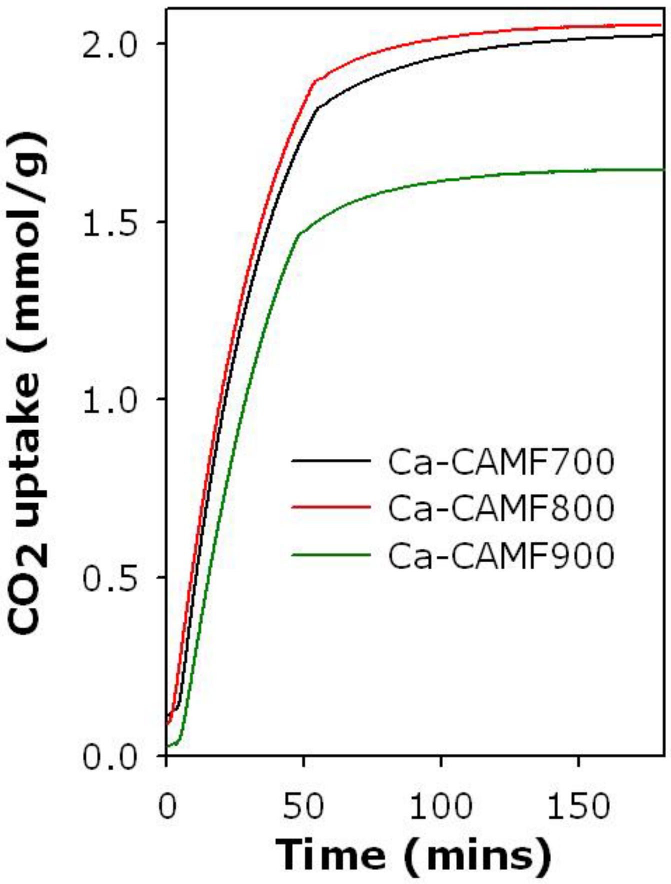

Fig. S2. CO_2 uptake as a function of time under ambient conditions for Ca-CAMFx samples carbonised at 700, 800 or 900 °C. Uptake was from flowing CO_2.

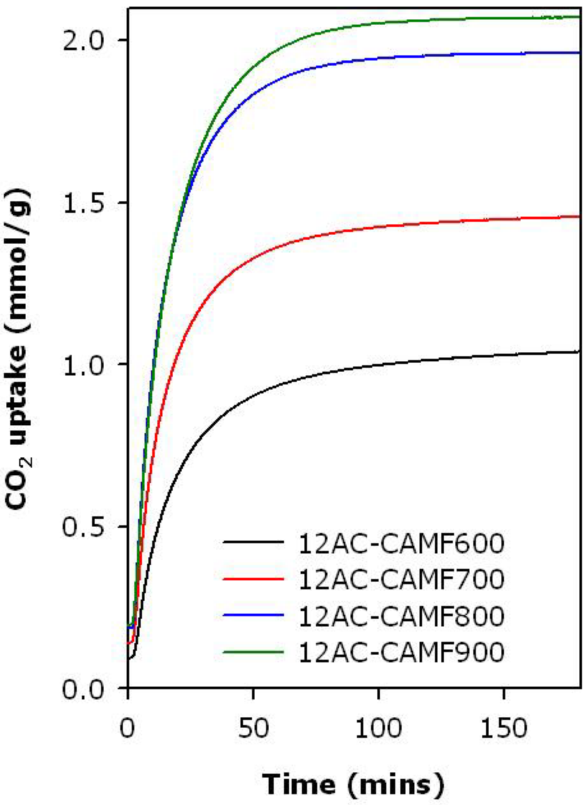

Fig. S3. CO_2 uptake under ambient conditions (25 °C and 1 bar) for activated non-templated carbon aerogels (12AC-CAMFX, where X is activation temperature, and at KOH/carbon ratio = 2.