

## Supporting Information

### Synthesis of $\text{CaCO}_3@C$ yolk-shell particles for $\text{CO}_2$ adsorption†

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## Materials and methods

### Materials

Hexadecyltrimethylammonium bromide (CTAB,  $\geq 99.0\%$ ), formaldehyde (37% solution), anhydrous calcium chloride ( $\text{CaCl}_2$ ,  $>95\%$ ), anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ,  $\geq 99.5\%$ ), aqueous ammonia (25% solution), poly(4-styrenesulfonic acid) sodium salt (PSS, MW~70,000 and 30% solution), ethanol (undenatured, 95-100%), resorcinol (99%) and tetraethyl orthosilicate (TEOS,  $\geq 99.0\%$ ) were purchased from Sigma-Aldrich and used as received without any further purification. Washing was achieved with ultrapure water and reagent grade ethanol where required. Ultrapure water was used for solution preparations.

### Synthesis of calcium carbonate ( $\text{CaCO}_3$ ) nano-spheres

18 mL of 0.1M  $\text{CaCl}_2$  solution containing 20 g  $\text{L}^{-1}$  PSS was quickly added to 6 mL of 0.1M  $\text{Na}_2\text{CO}_3$  solution also containing 20 g  $\text{L}^{-1}$  PSS. The mixture was vigorously agitated using a magnetic stirrer for 15 minutes. The solid was washed 3 times with ultrapure water and collected by centrifugation followed by air-drying at 60°C for 24 hours.

### Synthesis of $\text{CaCO}_3@SiO_2$ spheres

The synthesis of  $\text{CaCO}_3@SiO_2$  core-shell spheres was performed according to the Stöber method reported elsewhere<sup>1</sup>. In a typical experiment, 0.25 g of  $\text{CaCO}_3$  was mixed with 40 mL of ultrapure water, 160 mL of undenatured ethanol and 2 mL aqueous ammonia. The mixture

was sonicated for 30 minutes and transferred to a magnetic stirrer. 1 mL of TEOS was added dropwise and the mixture was allowed to mix for 6 hours at 30°C. The solid was washed 3 times with a mixture of ultrapure water and ethanol and collected by centrifugation followed by air-drying at 60°C for 24 hours.

### **Synthesis of CaCO<sub>3</sub>@SiO<sub>2</sub>@C spheres**

A carbon shell was added to the CaCO<sub>3</sub>@SiO<sub>2</sub> core-shell spheres by using the following method. In a typical experiment 0.40 g of as-synthesised CaCO<sub>3</sub>@SiO<sub>2</sub> spheres was mixed with 92 mL ultrapure water, 3.6 mL of 0.01M CTAB solution and 0.34 mL aqueous ammonia. The mixture was sonicated for 30 minutes and then transferred to a magnetic stirrer. After stirring for 30 minutes, 0.17 g of resorcinol was added. The mixture was allowed to mix for 30 more minutes after which 0.2 mL formaldehyde solution was added. The mixture was allowed to mix overnight to coat a resorcinol-formaldehyde (RF) layer on the CaCO<sub>3</sub>@SiO<sub>2</sub> spheres. The solid CaCO<sub>3</sub>@SiO<sub>2</sub>@RF spheres was washed 3 times with ultrapure water and collected by centrifugation followed by air-drying at 60°C for 24 hours.

A carbon shell was obtained by carbonising the CaCO<sub>3</sub>@SiO<sub>2</sub>@RF solid in a tube furnace (LABEC, model: HTF40/12) under N<sub>2</sub> flow of 33 mL min<sup>-1</sup>. The solid was heated from ambient temperature to 350°C at 1°C min<sup>-1</sup>, held at 350°C for 2 hours, heated to 600°C at 1°C min<sup>-1</sup> and held at 600°C for 4 hours.

### **Synthesis of CaCO<sub>3</sub>@C spheres**

The middle SiO<sub>2</sub> layer was etched by vigorously stirring the CaCO<sub>3</sub>@SiO<sub>2</sub>@C solid in ca. 20 mL concentrated NaOH solution (2.5M) at 51°C for 3 hours to obtain the final CaCO<sub>3</sub>@C solid product. The solid was washed 3 times with ultrapure water and collected by centrifugation followed by air-drying at 60°C for 24 hours.

### **Characterisation**

The sample morphology was characterized by using a transmission electron microscope (TEM, JEOL EM-2011) and a scanning electron microscope (SEM, TESCAN MIRA 3). High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging and element mapping were carried out using a FEI Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at 200 kV. The element maps were obtained by energy dispersive X-ray spectroscopy using the Super-X detector on the Titan

with a probe size  $\sim 1$  nm and a probe current of  $\sim 0.4$  nA. The nitrogen adsorption isotherm, BET surface area, BJH total pore volume and pore size distribution were obtained at 77K using a nitrogen sorption instrument (Micromeritics TriStar II Surface Area and Porosity Analyser). Prior to measurements in the nitrogen sorption analysers, the samples were degassed at 200 °C overnight. XRD patterns were measured using a Bruker-AXS D8 Advance Diffractometer with copper radiation (40 kV, 40 mA) and a LynxEye position sensitive detector. Crystalline phases were identified by using the Search/Match algorithm, DIFFRAC.EVA 3.1 (Bruker-AXS, Germany) to search the Powder Diffraction File (PDF4+, 2013 edition). The density of the CaCO<sub>3</sub> nanoparticles and CaCO<sub>3</sub>@C were estimated by the ratio of the weight of the geometric volume, including the weight of entrapped air.

### **CO<sub>2</sub> adsorption**

The carbon dioxide adsorption isotherm was obtained at room temperature using a carbon dioxide sorption instrument (Micromeritics Gemini 2360 Surface Area Analyser). Prior to measurements in the carbon dioxide sorption analysers, the samples were degassed at 200 °C overnight.

## Figures

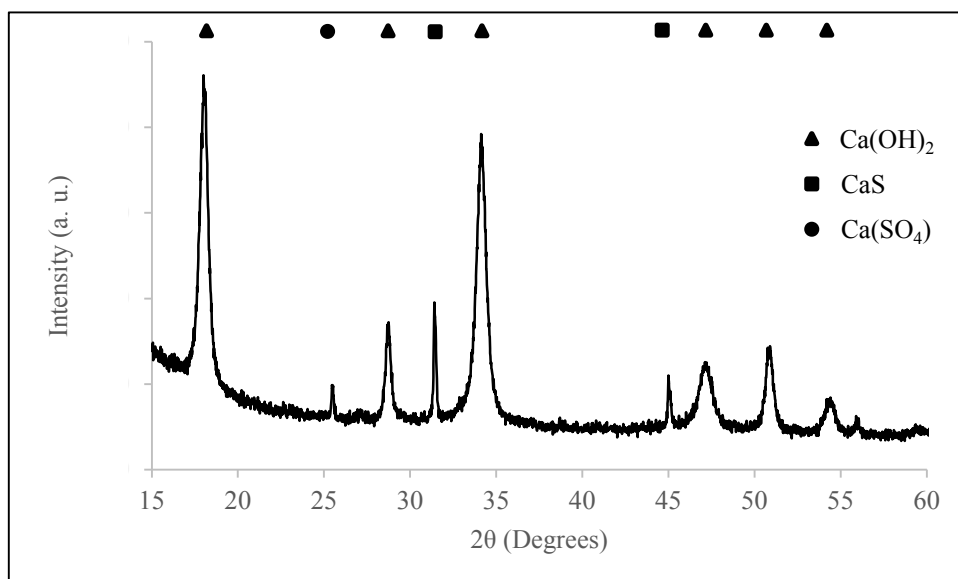


Figure S1: XRD data for calcined CaCO<sub>3</sub> nanoparticles. Presence of CaS and CaSO<sub>4</sub> attributed to the reaction of surfactant PSS with CaO.

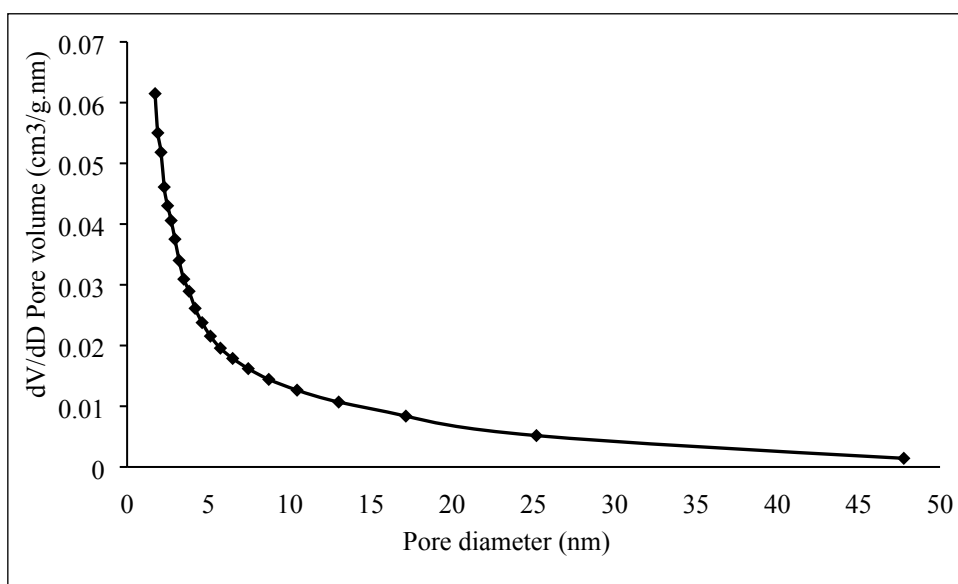
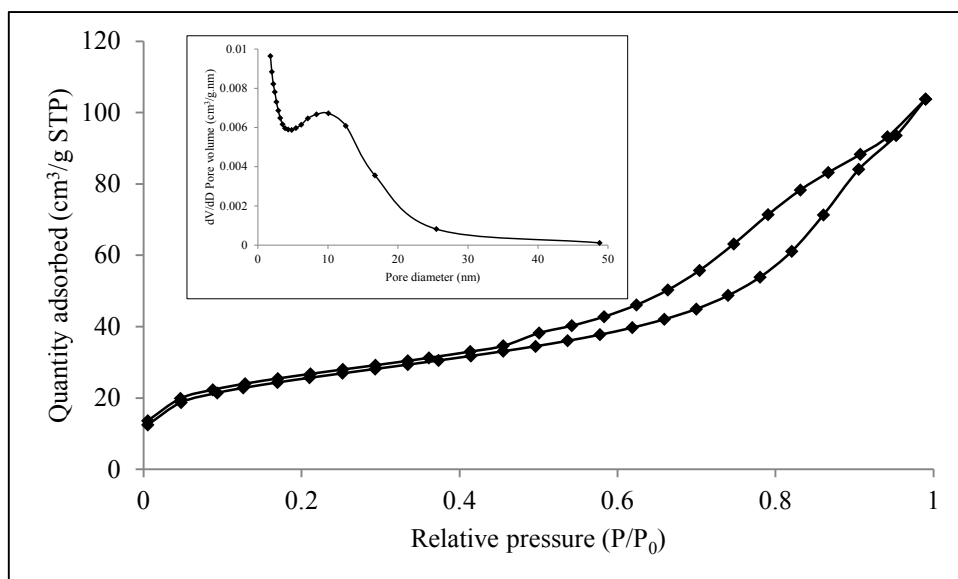
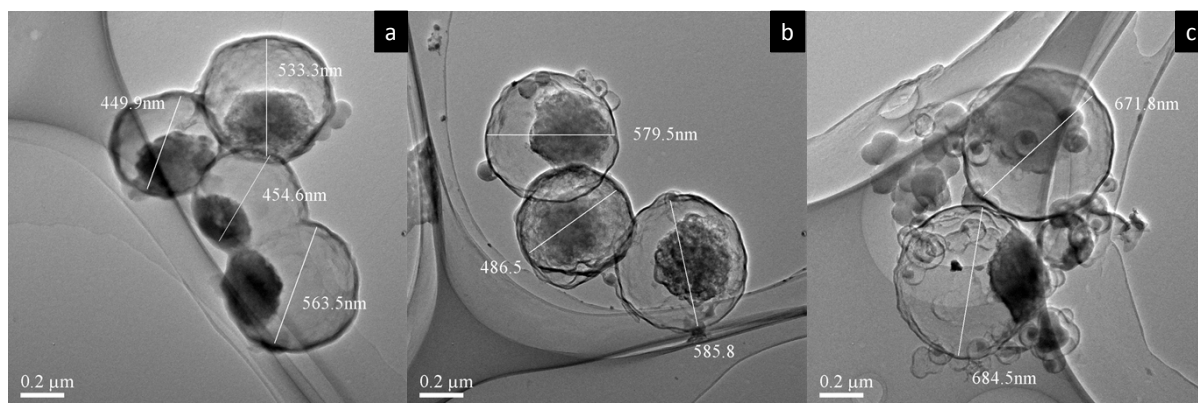


Figure S2: Pore size distribution of CaCO<sub>3</sub>@C particles. TEOS concentration = 2 mL g<sup>-1</sup> CaCO<sub>3</sub>, RF ratio = 0.5 and etching time = 3 hours.



**Figure S3:**  $N_2$  adsorption isotherm for the  $CaCO_3$  precursor nanoparticles. Pore size distribution shown in the inset.



**Figure S4:** Effect of TEOS concentration on cavity size of  $CaCO_3@C$  particles; a) TEOS = 2 mL  $g^{-1}$   $CaCO_3$ , b) TEOS = 4 mL  $g^{-1}$   $CaCO_3$  and c) TEOS = 6 mL  $g^{-1}$   $CaCO_3$ . RF ratio = 0.5 and etching time = 3 hours.

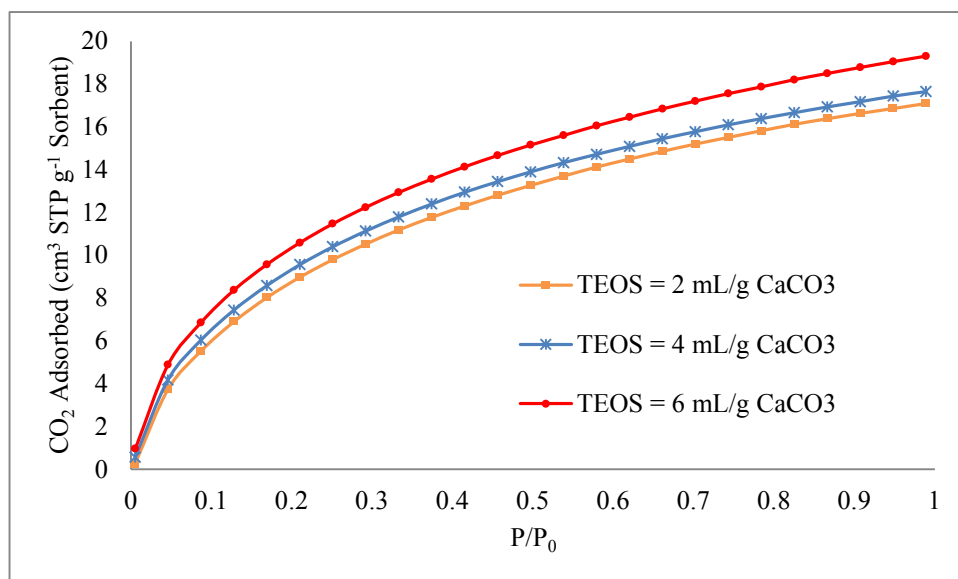


Figure S5: CO<sub>2</sub> adsorption isotherms ( $T = 23 \pm 1 \text{ }^\circ\text{C}$ ) of CaCO<sub>3</sub>@C particles at different TEOS concentrations. RF ratio = 0.5 and etching time = 3 hours.

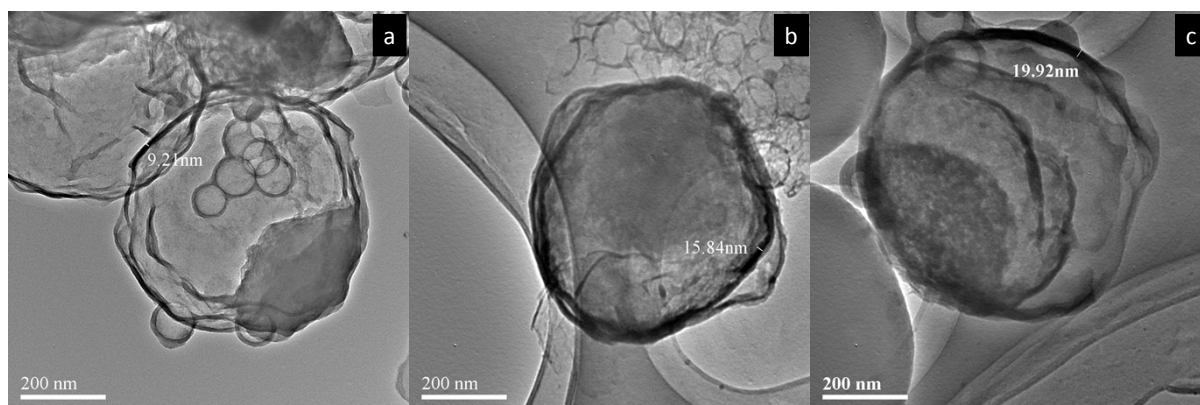
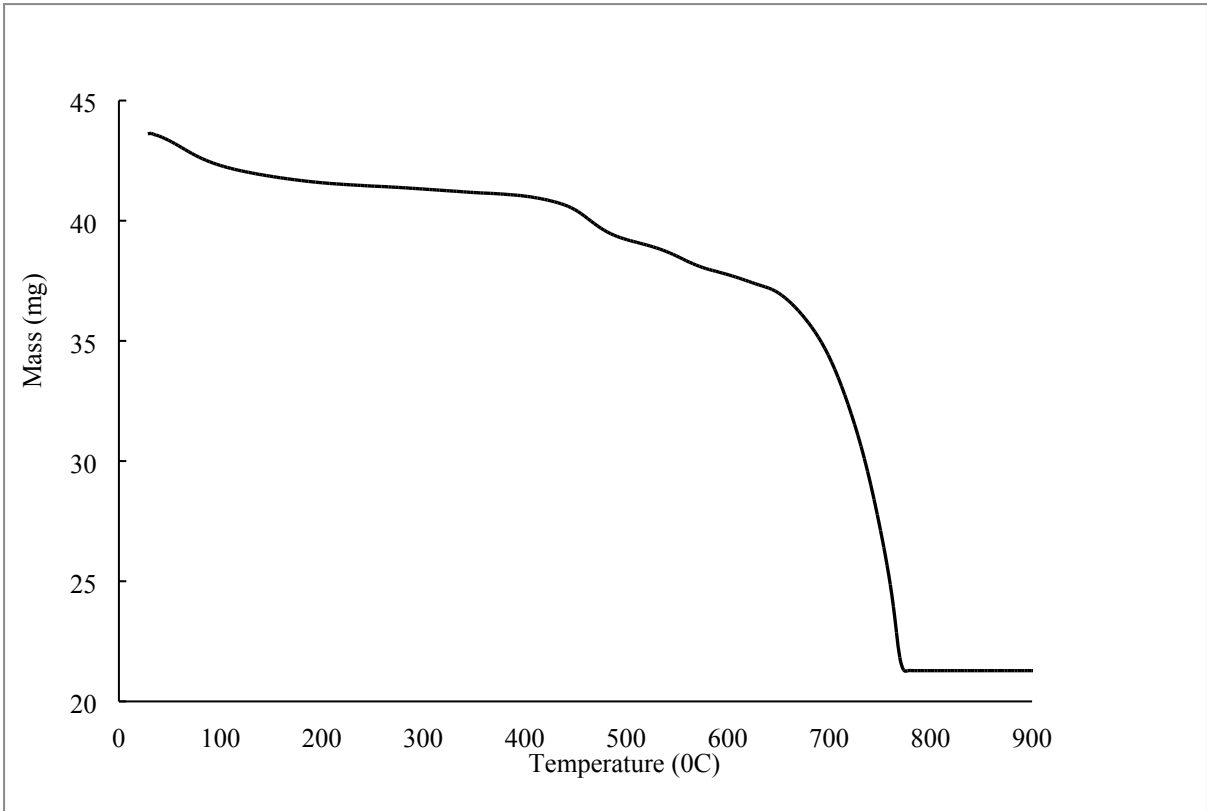
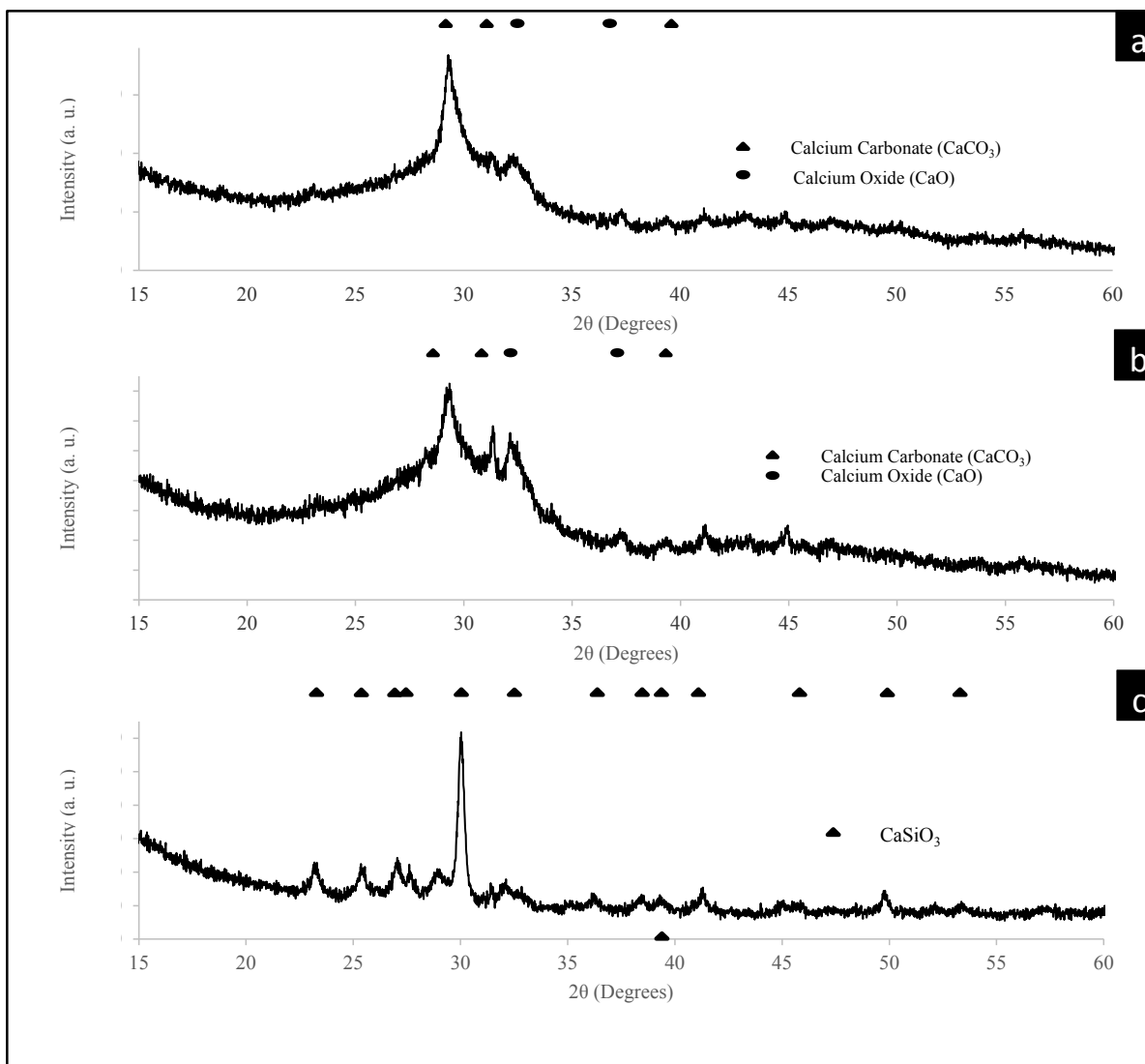


Figure S6: Effect of RF ratio on shell thickness of CaCO<sub>3</sub>@C particles; a) RF = 0.5, b) RF = 1 and c) RF = 1.5. TEOS concentration = 4 mL g<sup>-1</sup> CaCO<sub>3</sub>, etching time = 4 hours.



**Figure S7: TGA data representing mass loss of CaCO<sub>3</sub> nanoparticles under a flow of Argon**



**Figure S8: XRD data for CaCO<sub>3</sub>@C particles recalcined at: a) 650 °C, b) 700 °C and c) 750 °C. Recalcination was performed under N<sub>2</sub> for 1 hour.**



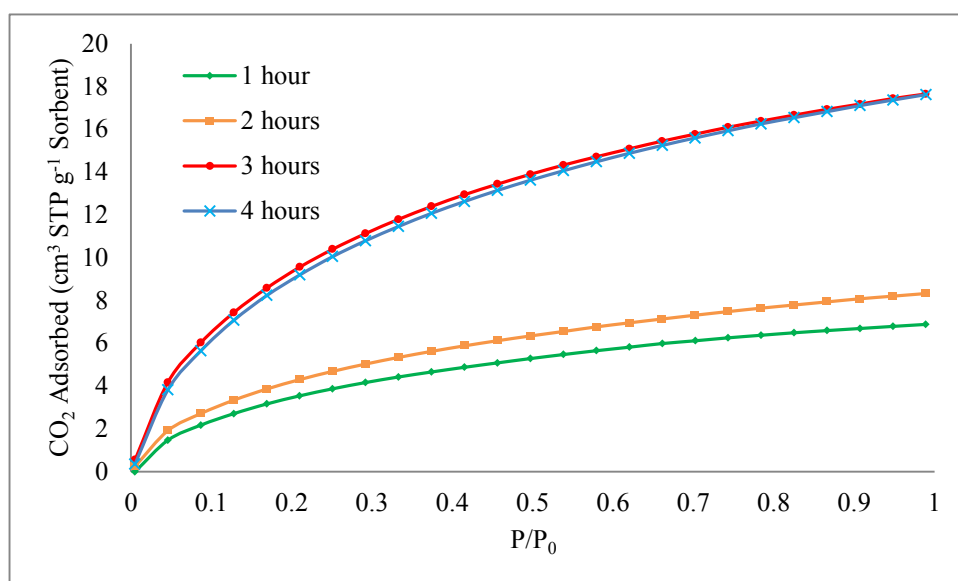


Figure S9: CO<sub>2</sub> adsorption isotherms ( $T = 23 \pm 1$  °C) of CaCO<sub>3</sub>@C particles at different etching times. TEOS concentration = 4 mL g<sup>-1</sup> CaCO<sub>3</sub>, RF ratio = 0.5.

## Notes and References

- 1 H. Chen, C. Deng and X. Zhang, *Angewandte Chemie International Edition*, 2010, 49, 607.