Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.
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Supporting Information

A simple and green synthesis method for Ca-adamantanecarboxylate: A novel precursor for high temperature CO_2 capture sorbent materials

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Material synthesis and characterization

All the chemicals, $Ca(OH)_2$ and 1-adamantanecarboxylic acid, were purchased from Sigma Aldrich and used as received. Deionised water (18. MΩ.cm resistivity, Millipore water purification system) was used throughout the experiment. Calcium adamantanecarboxylate (Ca-ada) was synthesized by employing a hydrothermal method. In a typical experiment, $Ca(OH)_2$ and 1-adamantanecarboxylic acid (Ca/adamantanecarboxylate =0.5) were taken in 100 mL water. The reaction mixture was stirred at RT for an hour to get homogeneous mixture. The resultant reaction mixture was transferred to a Teflon lined autoclave and hydrothermally treated at 150 °C for 24 h. The resultant product was recovered by filtration followed by drying at 65 °C overnight. The carbon supported CaO material was synthesized by decomposition of Ca-ada under inert atmosphere using N_2. In a typical experiment, 1g of Ca-ada was loaded into a quartz tube and subjected to decomposition at 700 °C under N_2 atmosphere (N_2 flow rate of 100 mL/min, ramp rate 5 °C/min, residence time 2 h).

Powder X-ray Diffraction (PXRD) patterns were recorded on a Bruker D8 Advance power diffractometer, using Ge-monochromated Cu-Kα1 radiation ($\lambda = 1.5406$ Å) from a sealed tube, operating at 40kV and 40mA with a LynxEye linear detector in reflectance mode. Data was collected over angular range of 2-75 °2θ with a step size of 0.009˚ over one hour span. The Fourier Transform Infrared spectra (FTIR) of samples were measured using Perkin Elmer spectrometer in ATR mode (4000 to 400cm^{-1}). The C, H and N analysis on the Ca-ada was carried out by placing approximately 3 mg of sample in a tin capsule and combusted in a high oxygen environment at 950 °C using an Exeter Analytical CE-440 elemental analyser calibrated with acetanilide. Elemental analysis of Ca^{2+} (ICP-OES) was carried out by atomic emission technique using Perkin Elmer Optima 5300DV. The sample for ICP analysis was prepared by decomposing Ca-ada at 900 °C under air and dissolving the resultant oxide in dilute nitric acid. The solution was diluted 20 times prior to analysis. Surface area analysis of the sample was carried out by gas adsorption technique (N_2, 77 K) using Micromeritics ASAP 2020 instrument. Prior to the gas adsorption measurement, the sample was degassed for 3 h at 150 °C. Transmission electron microscopy (TEM), high resolution TEM (HRTEM) images are acquired using a JEOL 2100F FEG TEM.

The surface morphology of the sample is characterized by scanning electron microscopy (SEM) using FEI Quanta FEG SEM. Solid state nuclear magnetic resonance (NMR) studies (^{1}H and ^{13}C) were carried out using a Varian VNMRS spectrometer. Raman spectra were recorded usinga Jobin Yvon Horiba LabRAM spectrometer using Nd:YAG (532 nm) laser excitation.

CO_2 capture studies

Thermal analysis and CO_2 capture studies were performed using a thermogravimetric analyser (TA Instruments TA 500). For CO_2 capture studies, pristine Ca-ada was used instead of preformed CaO to avoid the CO_2 contamination. Freshly prepared Ca-ada was loaded into a TGA pan and decomposed under inert atmosphere (using 100 mL/min N_2, 2 h, 700 °C, 10 °C/min). Once the decomposition is over [the temperature was brought back (10 °C/min) to desired temperature], CO_2 gas was switched on (for 2 h) to test the uptake capacity of the resultant carbon supported CaO. Cycling performance of the resultant materials was studied by carrying out 10 consecutive carbonation-regeneration cycles. The carbonation step was performed at 600 °C for 30 min under CO_2 atmosphere and regeneration was conducted at 700 °C for 30 min under N_2. $Ca(OH)_2$ based CaO was derived by loading around 10 mg of sample into TGA pan and decomposed under inert atmosphere (using 100 mL/min N_2, 2 h, 700 °C, 10 °C/min). Once the decomposition is over [the temperature was brought back (10 °C/min) to desired temperature] CO_2 gas was switched on (for 2 h) to test the uptake capacity of the resultant CaO. The cycling performance was done similar to above except having different carbonation and regeneration temperatures (650/750 °C).

Carbonation and regeneration cycles were also carried out under different CO_2 concentrations. The carbonation was carried out under 14 % CO_2 (86 % N_2) for 30 min as described above and the regeneration was carried out under 80 % CO_2 (20 % N_2) for 30 min at different temperatures

(700, 850 and 920 °C). The sample was ramped at 10 °C/min from carbonation step to regeneration step. Once the regeneration step is complete, the sample was cooled under N_2 from the regeneration to the carbonation temperature to avoid any premature carbonation of the sample before reaching 600 °C (carbonation temperature). The carbonation and regeneration of the sample was also carried out under constant CO_2 concentration (50 %) at 850 °C while keeping all other experimental conditions constant.

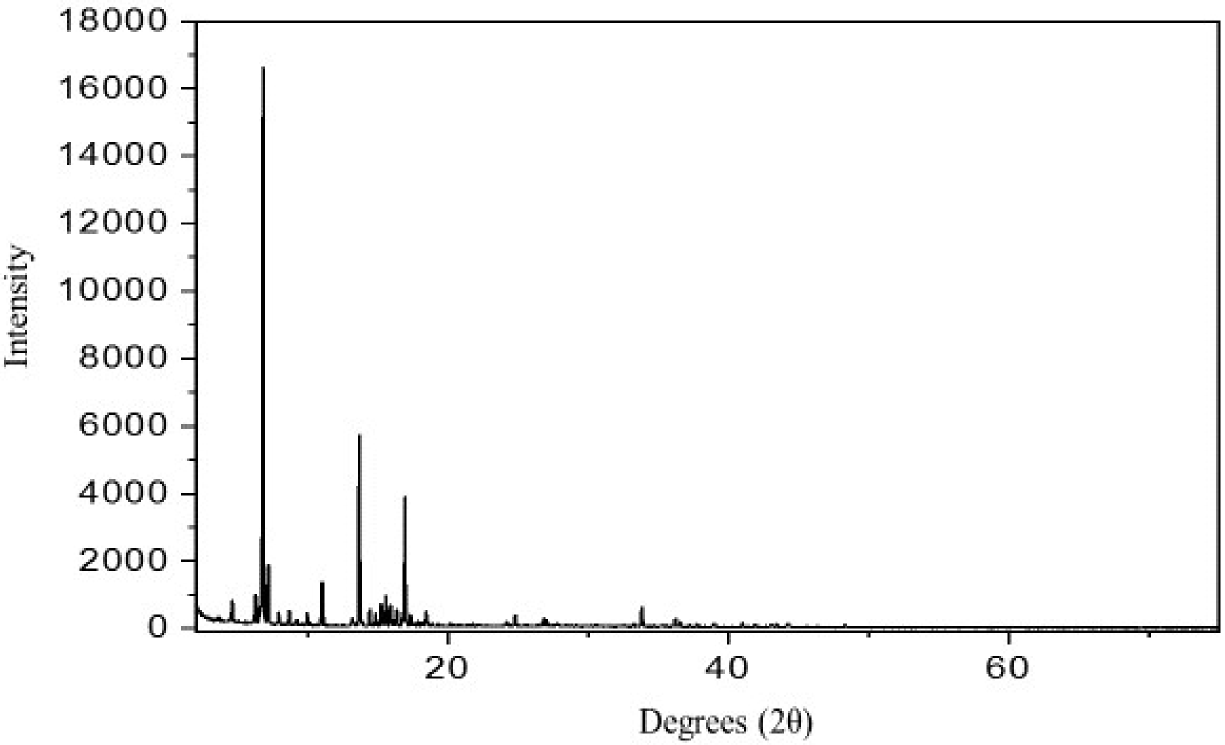

Fig. S1 PXRD pattern of Ca-ada synthesized by hydrothermal synthesis method at 150 °C.

Table S1. List of reflections and their *d*-spacing appeared in Ca-ada synthesized by hydrothermal method at 150 °C.

Degrees (°2θ)	*d*-spacing (Å)
3.66	24.12
4.61	19.15
6.27	14.08
6.58	13.42
6.82	12.95
7.92	11.15
8.67	10.19
9.95	8.88
11.02	8.02
13.17	6.71
14.43	6.13
14.83	5.96
15.91	5.56
16.35	5.41
16.91	5.23
17.33	5.11
17.87	4.95
24.21	3.67
26.81	3.32
33.25	2.69
33.82	2.64
36.21	2.47
36.57	2.45
37.25	2.411
37.76	2.38
39.15	2.29

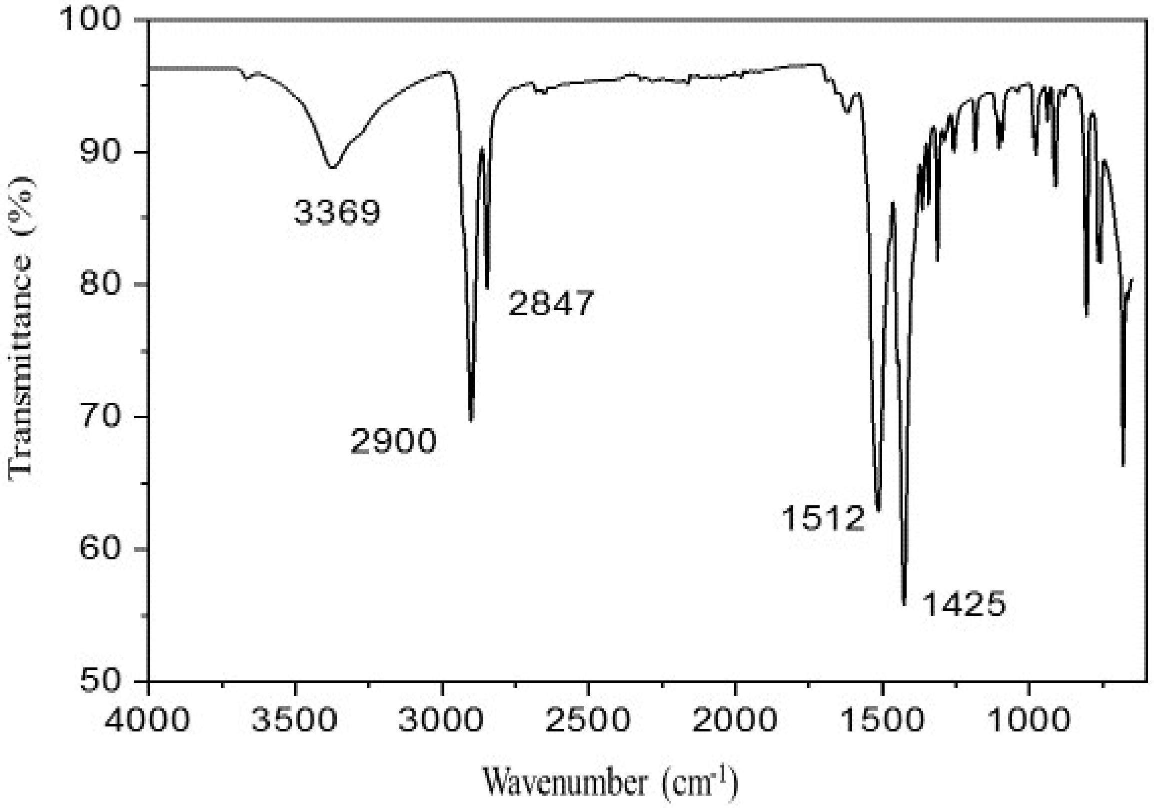

Fig. S2 IR spectrum of Ca-ada synthesized by hydrothermal synthesis method at 150 °C.

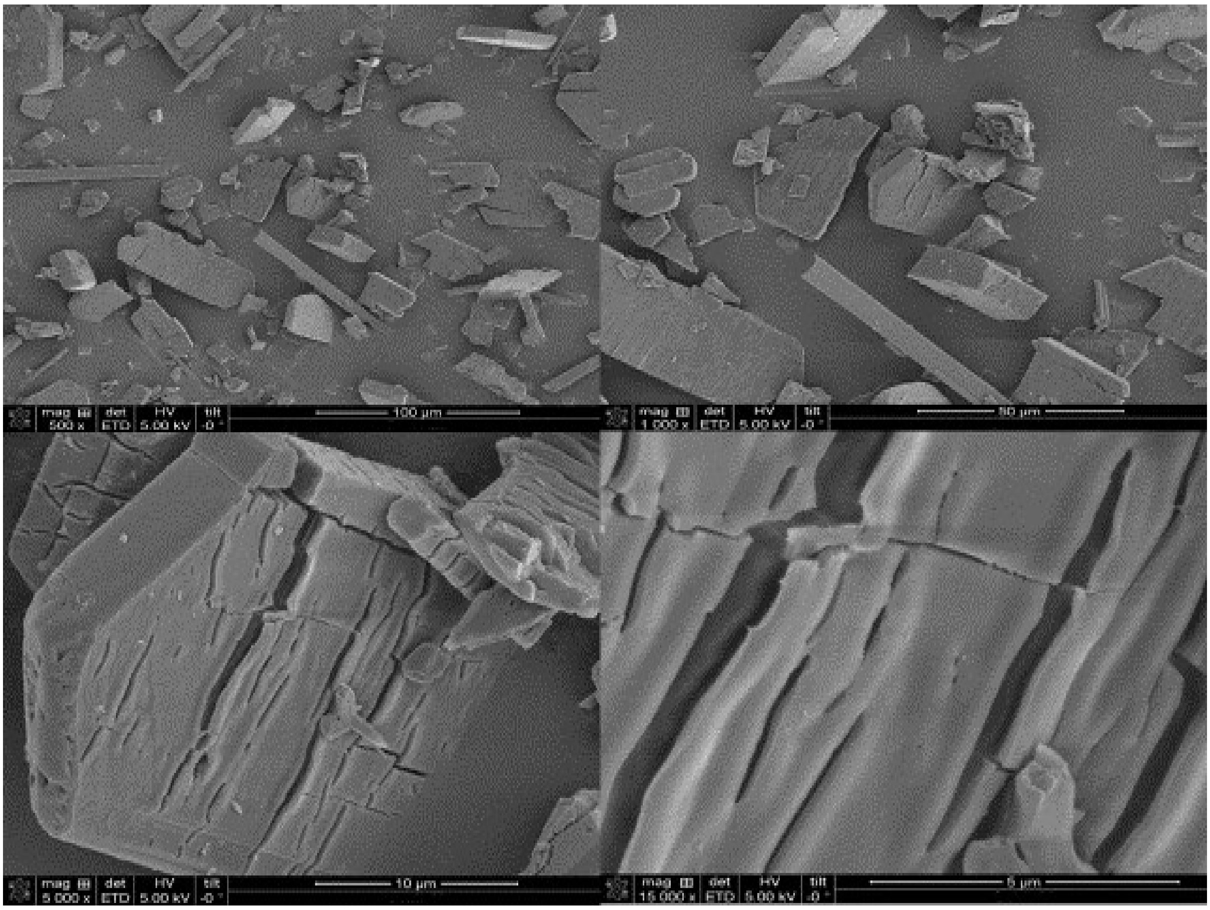

Fig. S3 SEM images of Ca-ada synthesized by hydrothermal synthesis method at 150 °C.

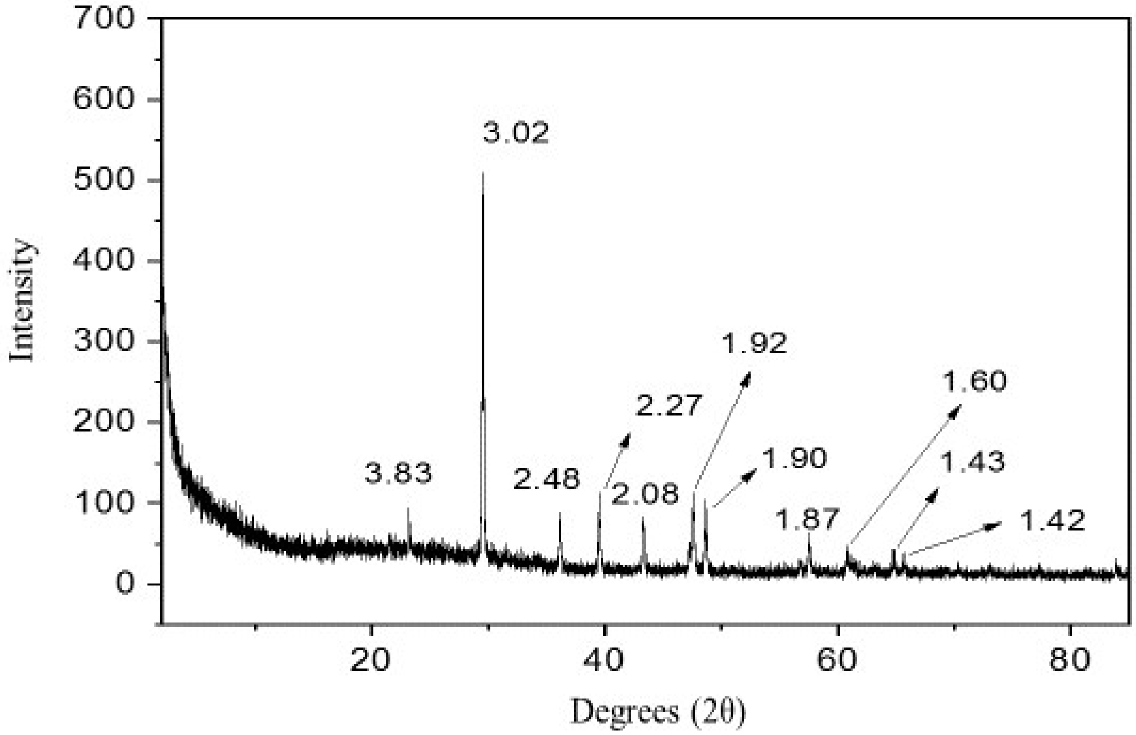

Fig. S4 PXRD pattern of hybrid organic-inorganic composite generated from Ca-ada.

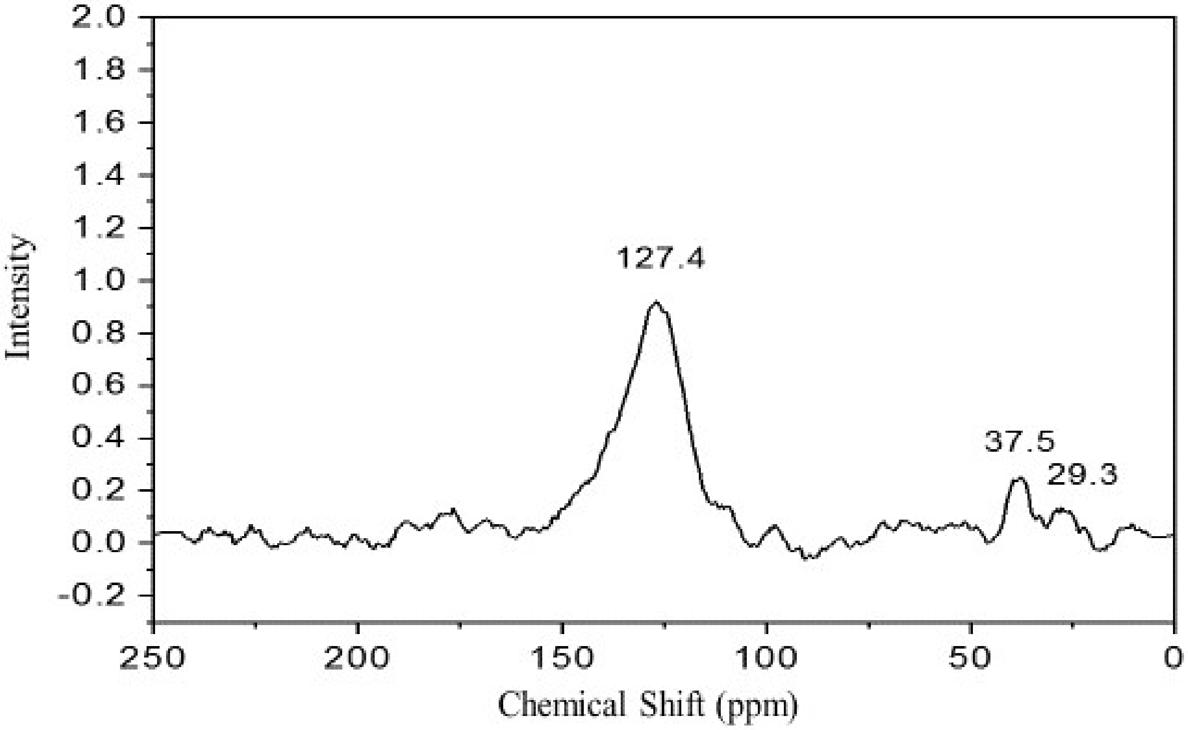

Fig. S5 ^{13}C spectrum of hybrid organic-inorganic composite generated from Ca-ada.

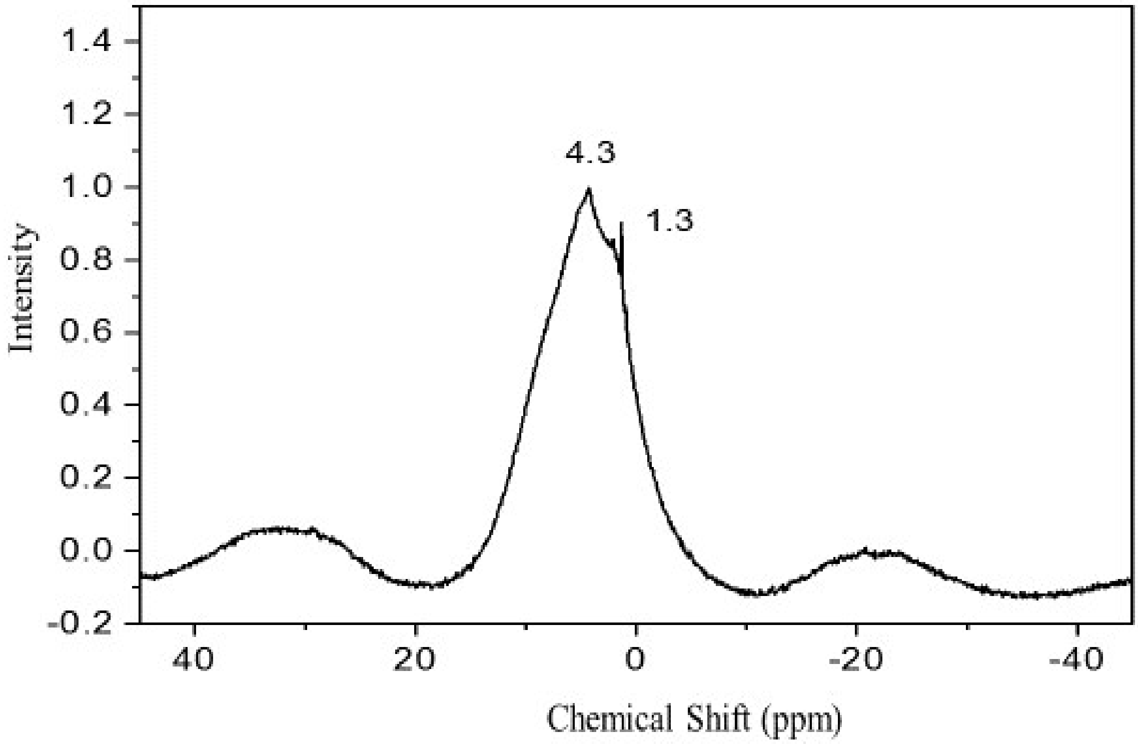

Fig. S6 ^{1}H spectrum of hybrid organic-inorganic composite generated from Ca-ada.

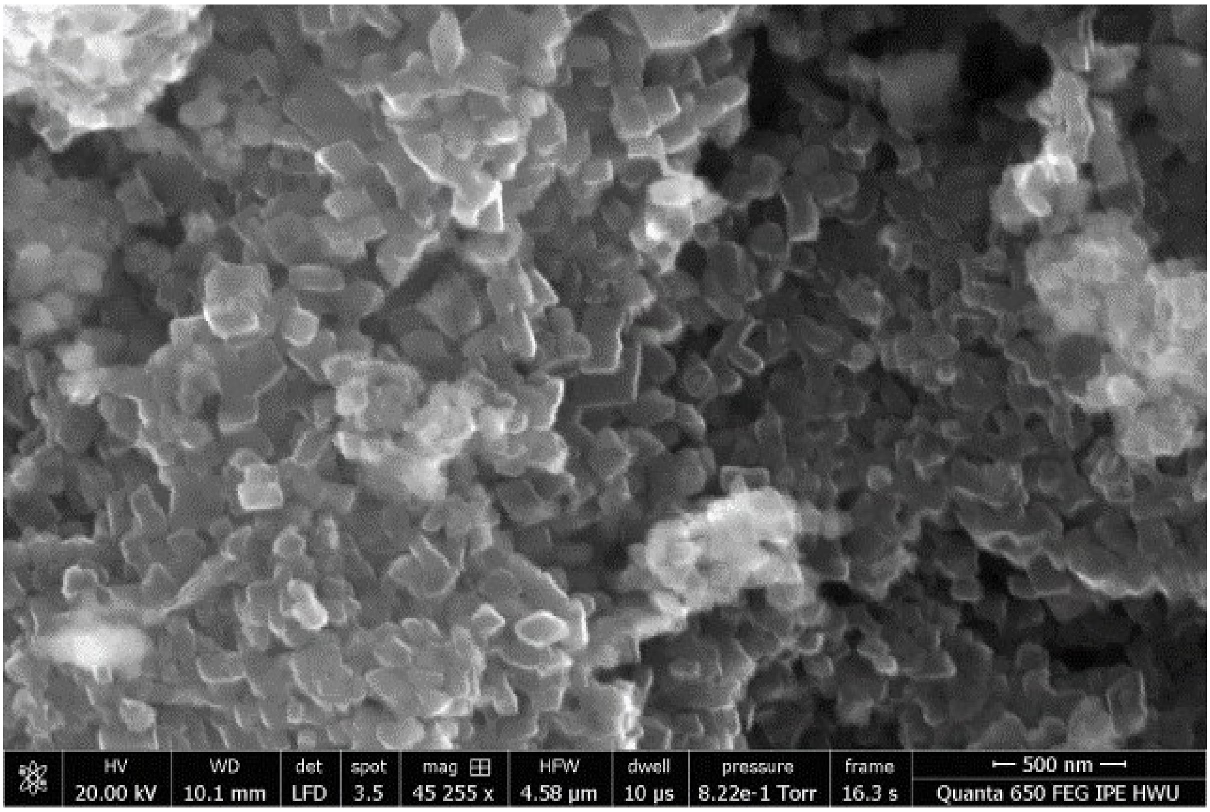

Fig. S7 SEM image of hybrid organic-inorganic composite generated from Ca-ada.

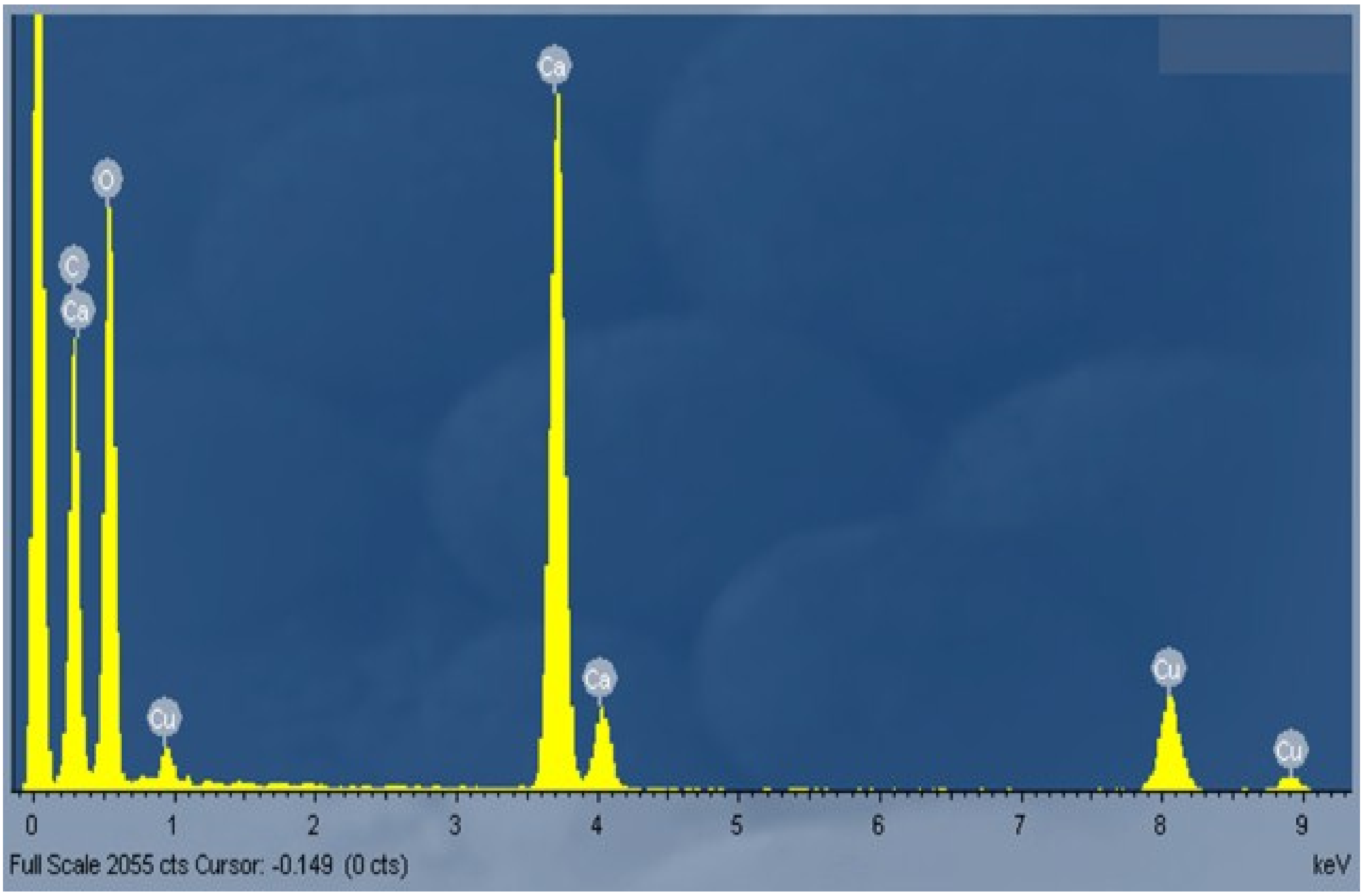

Fig. S8 **EDX spectrum of hybrid organic-inorganic composite generated from Ca-ada.**

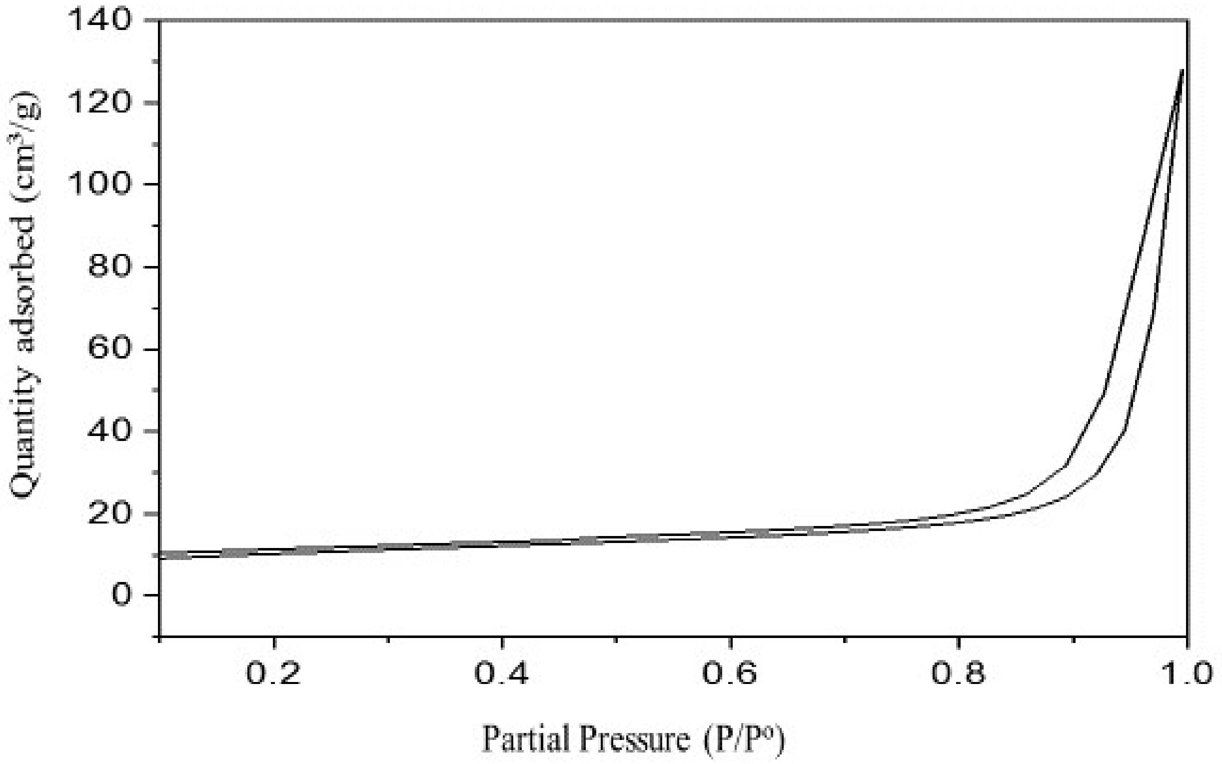

Fig. S9 N_2 adsorption/desorption isotherm (77 K) of hybrid organic-inorganic composite generated from Ca-ada.

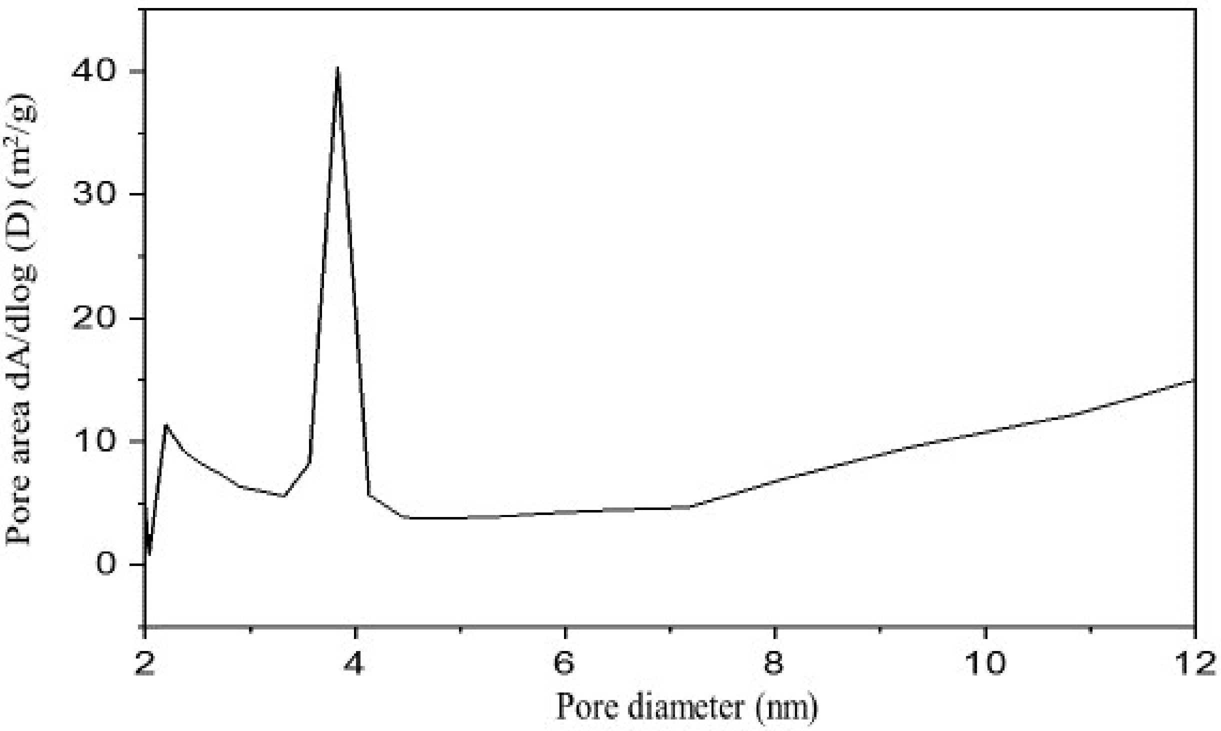

Fig. S10 Pore size distribution of hybrid organic-inorganic composite generated from Ca-ada.

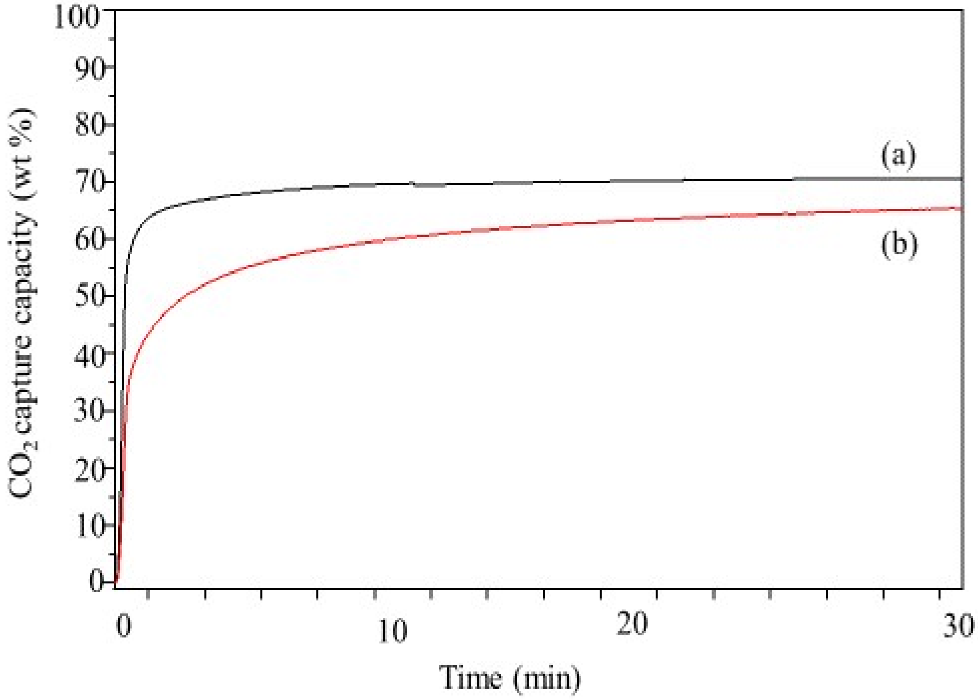

Fig. S11 **CO_2 capture capacity versus time for the hybrid organic-inorganic composite generated from Ca-ada under (a) 86 % and (b) 14 % CO_2 at 600 °C.**

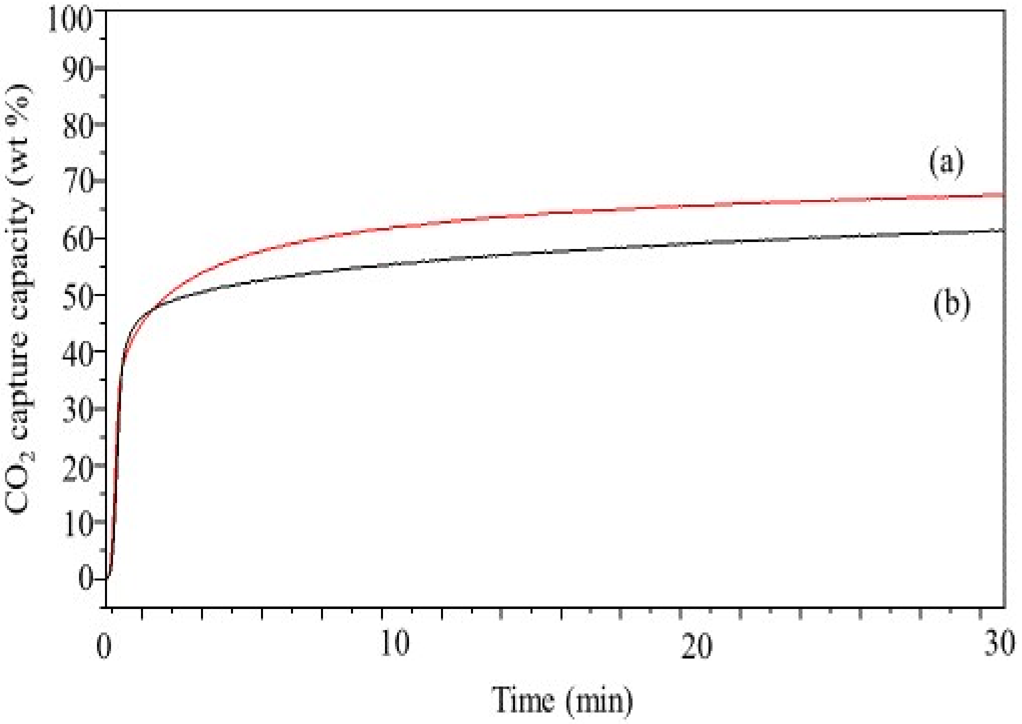

Fig. S12 CO$_2$ capture capacity versus time for the hybrid organic-inorganic composite generated from Ca-ada under 14 % CO$_2$ (a) first cycle and (b) tenth cycle.

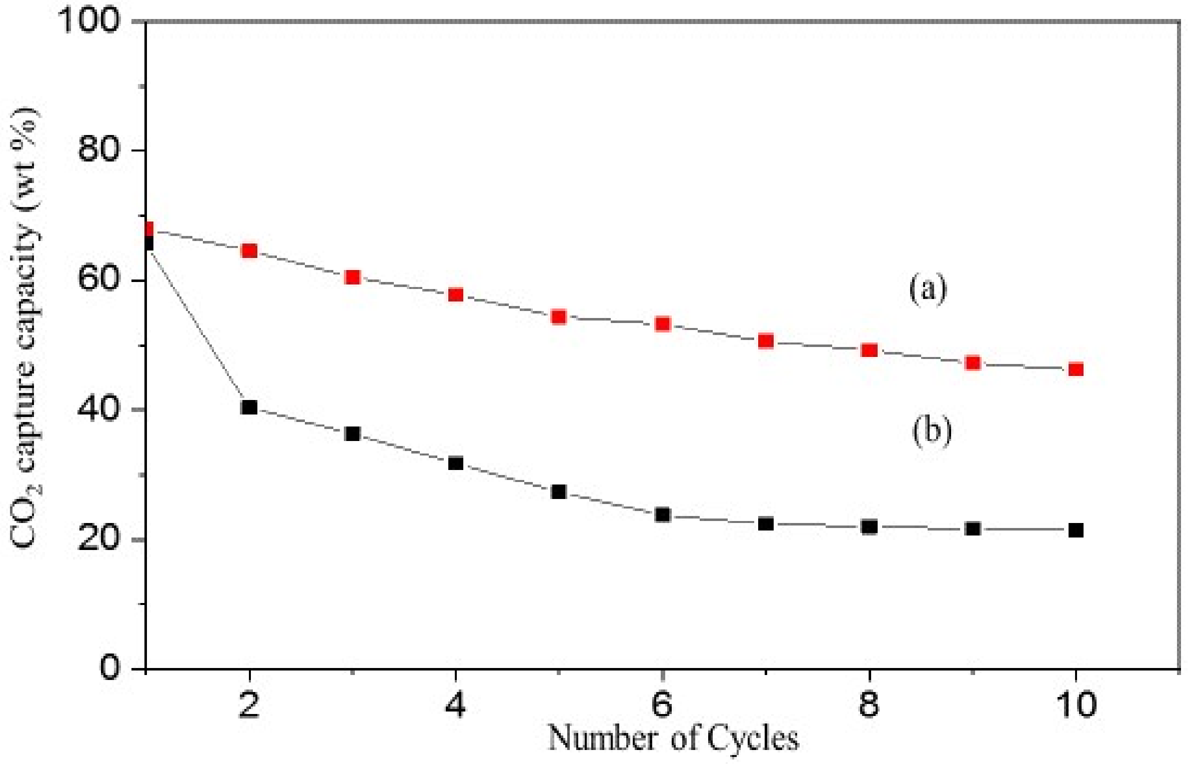

Fig. S13 CO$_2$ capture capacity versus cycle number for the hybrid organic-inorganic composite generated from Ca-ada: (a) regeneration at 850 °C under 50 % CO$_2$; (b) regeneration at 920 °C under 80 % CO$_2$.