

## Electronic Supplementary Information

# CaO nanocrystals grown over SiO<sub>2</sub> microtubes for efficient CO<sub>2</sub> capture: Organogel sets the platform

Annamalai Prathap<sup>a</sup>, M. M. Shaijumon<sup>b</sup> and Kana M. Sureshan<sup>a\*</sup>

<sup>a</sup> School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Kerala, 695016. India. Fax: (+) 0091-4712597427; Tel: +914712599412; E-mail: [kms@iisertvm.ac.in](mailto:kms@iisertvm.ac.in).  
Home page: <http://kms514.wix.com/kmsgroup>

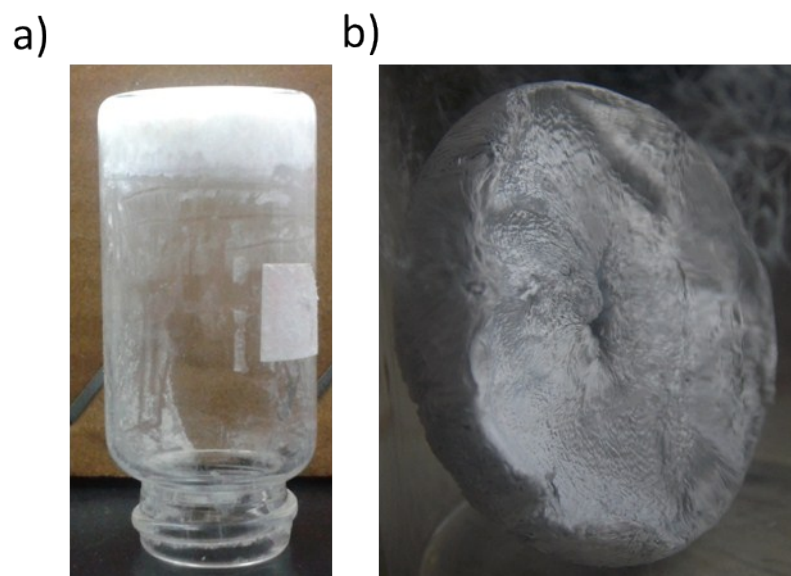
<sup>b</sup> School of Physics, Indian Institute of Science Education and Research Thiruvananthapuram, Kerala, 695016. India.

### 1. Materials and methods:

Chemicals and solvents were purchased from Sigma-Aldrich and were used without further purification. The gelator **1** was synthesized as reported.<sup>1</sup> TLC analyses were carried out using precoated TLC silica gel 60 F<sub>254</sub> purchased from Merck. Chromatograms were visualized by dipping the plates into either chromic acid staining solution or ceric ammonium sulphate staining solution followed by heating. The column chromatography was carried out using 200-400 mesh silica gel. NMR spectra were recorded on an Avance II-500 (Bruker) NMR spectrometer. IR spectra were recorded using IR Prestige-21 (Shimadzu) spectrometer. Powder X-ray diffraction spectra (PXRD) were recorded using an X'pert PRO (PANalytics) powder diffractometer. TGA analysis were done using Universal V4.7A TA instrument at a heating rate of 20 °C/min. SEM images were recorded using JEOL JSM-5600LV Scanning Electron Microscope. TEM images were recorded using JEOL, JEM-2100 Transmission

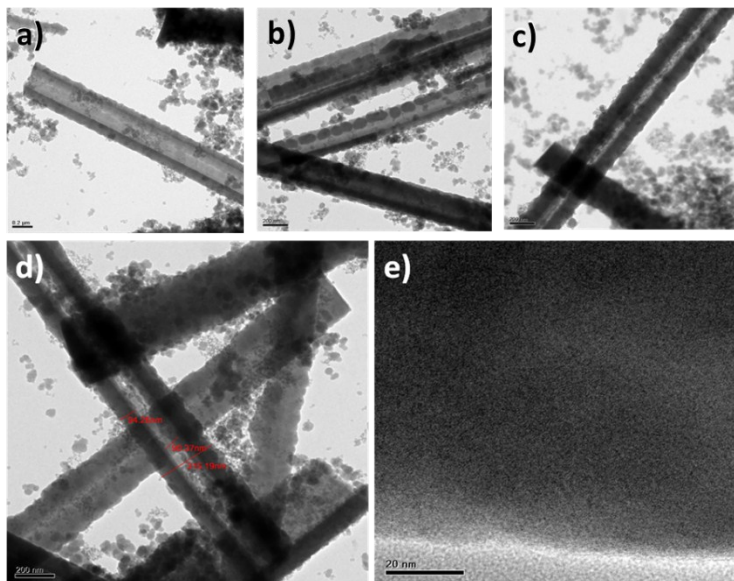
Electron Microscope. BET surface area measurement was carried out using Micromeritics 3-Flex surface characterization analyser at 77K.

**2. Preparation of silica tubes:** A 10 wt% gel of **1**<sup>1</sup> in TEOS (100 mg /1 mL) was made along with catalytic amount of benzylamine and water. This strong gel was left opened for 10 days at room temperature. The TEOS was allowed for natural evaporation under room temperature. The colloidal wet gel became white solid after 10 days without any reduction in volume (Fig. S1). This solidified gel was washed first with DCM (5mL x 3) and then by MeOH (5mL x 3). The silica obtained was dried in an oven at 110 °C for 2 hours. The yield of the silica fibres obtained was found to be in the range 80 – 110% by weight of the gelator (i.e, 80 – 110 mg silica for 100 mg gelator). Evaporation of these combined washings returned the gelator completely and this recovered gelator could be used again to make TEOS gel and silica.



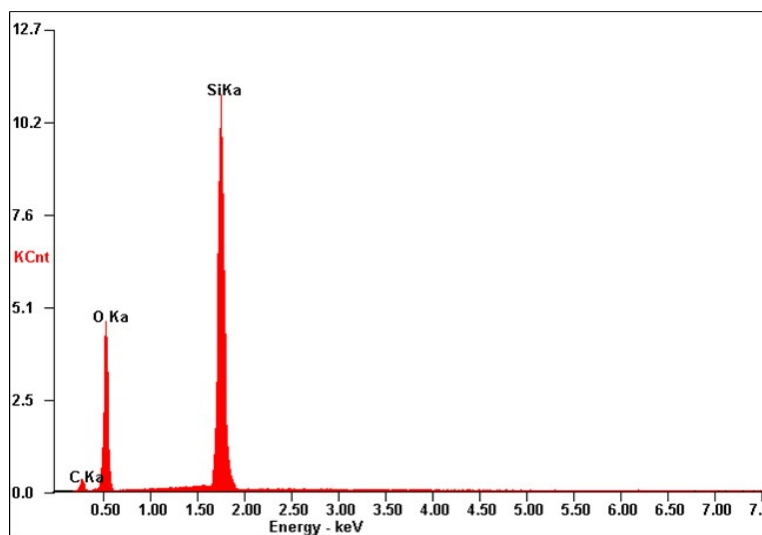
**Fig. S1** a) 5 days aged TEOS gel of **1** (10 wt%) and b) the polymerised silica after washing off the gelators after 10 days.

**3. TEM sampling procedure:** A pinch of silica microtubes was immersed in MeOH solvent and sonicated well for 10 minutes. Then the turbid MeOH solution was drop-casted in the TEM grid and the sample in the TEM grid was dried well in a vacuum desiccator for overnight. In the case of CaCO<sub>3</sub> coated silica tubes, deionized water was used as the solvent for drop-casting purpose.



**Fig. S2** a), b) and c) show the TEM images of various portions of silica tubes. d) showing the diameter and the cross section and e) shows the surface of the tube at higher resolution.

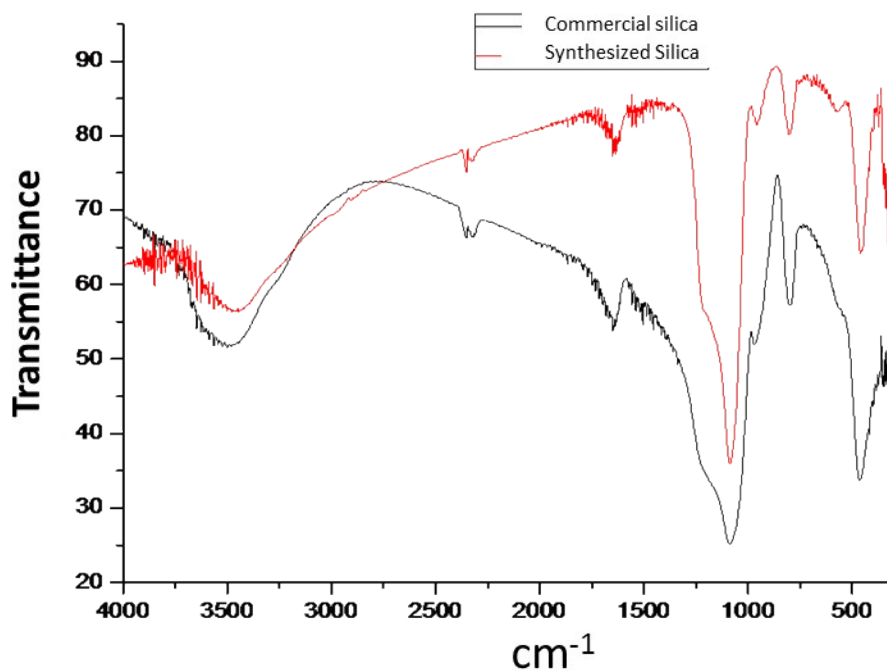
**4. SEM Analysis:** A pinch of silica microtubes was immersed in MeOH solvent and sonicated well for 10 minutes. Then the turbid MeOH solution was drop-casted over silicon wafer or carbon tape. The silicon wafer was then dried in a vacuum desiccator and was analysed in a scanning electron microscope.



**Fig. S3** SEM-EDAX spectrum showing the elemental composition of silica tubes alone. The trace of carbon peak is due to the carbon tape used in the analysis.

## 5. IR Spectroscopy

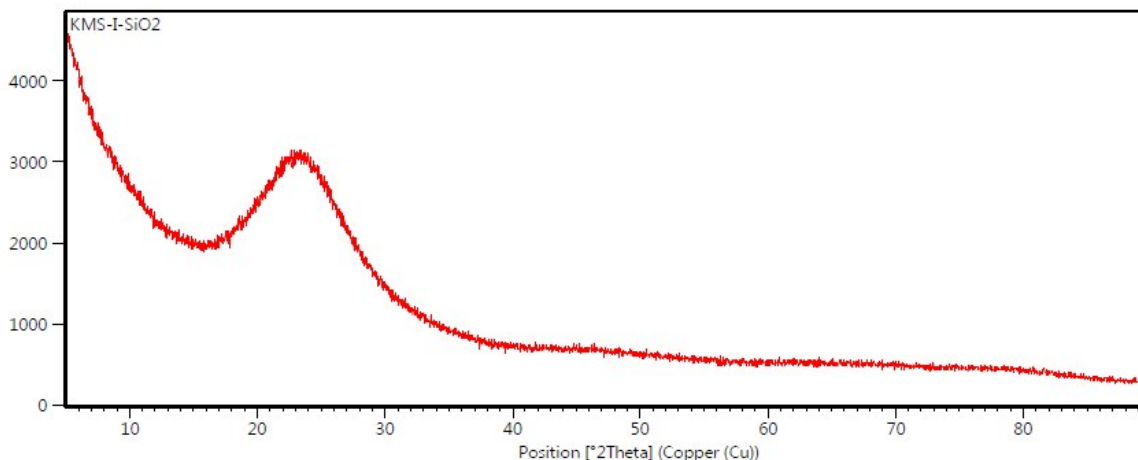
The silica obtained was dried and powdered by a pestle and mortar. The powdered sample was then analysed by IR spectroscopy using KBr pellet sampling method. The IR spectrum of a commercial sample of silica gel was also recorded under the same conditions. Both the spectra were identical (Fig. S4).



**Fig. S4** Overlay of the IR spectra of the synthesized silica and the commercial silica

## 6. PXRD Analysis

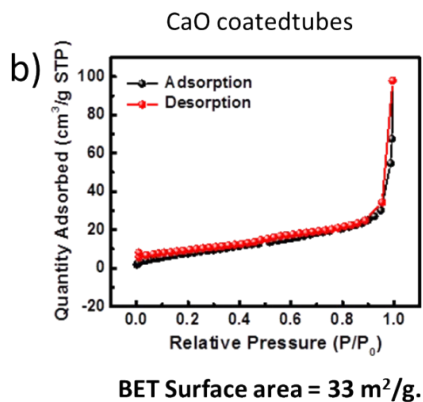
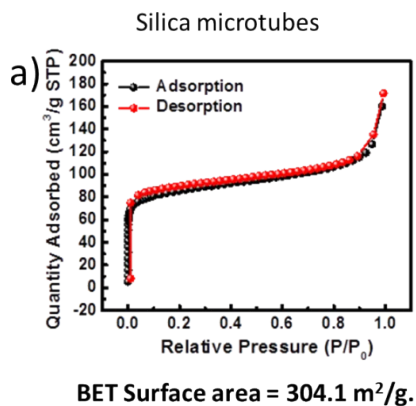
The well dried fluffy powdered silica was placed as such in the PXRD instrument and was analyzed at a scan rate 2.9°/min. at room temperature. This revealed that the templated silica is amorphous in nature.



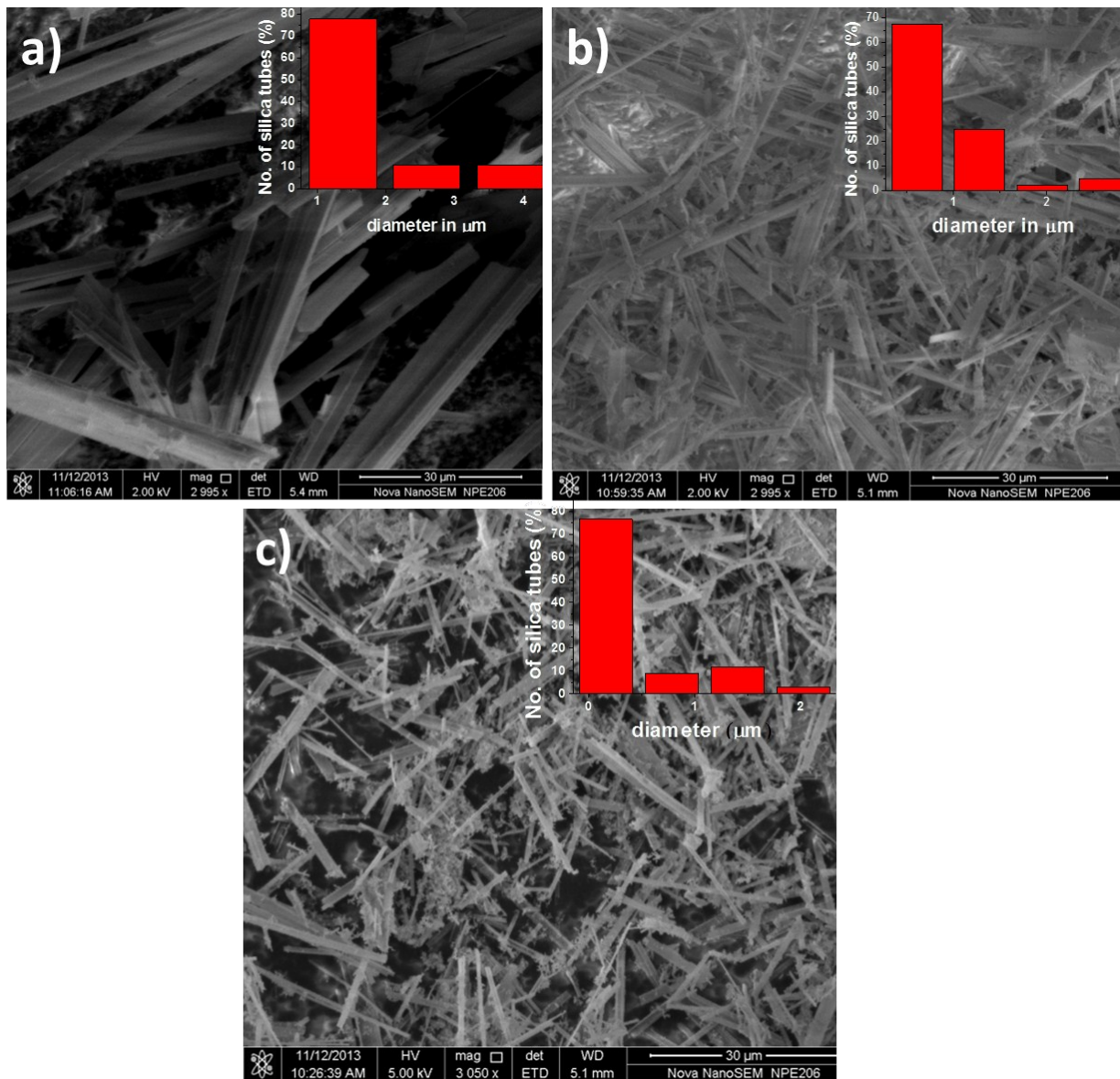
**Fig. S5** XRD spectrum of silica tubes prepared by using organogel as template. The pattern showing the amorphous nature matches exactly with the commercial silica

### 7. Synthesis of SiO<sub>2</sub> tubes of different diameters (Concentration dependent size controllable silica tubes)

Gelator **1** (100 mg) was dissolved in 1 mL of TEOS in a glass vial (to make 10 w% gel). To the hot solution, catalytic amount of benzylamine and deionized water was added. Gels of 6 wt% (100 mg/1.5 mL) and 13 wt% (100 mg/0.7 mL) were also made by similar procedure. The TEOS gels formed were kept opened for 8-10 days. After 8-10 days the silica microtubes were obtained by washing off the gelator followed by drying.



**Fig. S6** a) and b) showing the N<sub>2</sub> adsorption and desorption isotherms carried out at 77K. The BET surface area of silica microtubes and CaO coated silica microtubes are calculated to be 304.1 m<sup>2</sup>/g and 33 m<sup>2</sup>/g respectively.

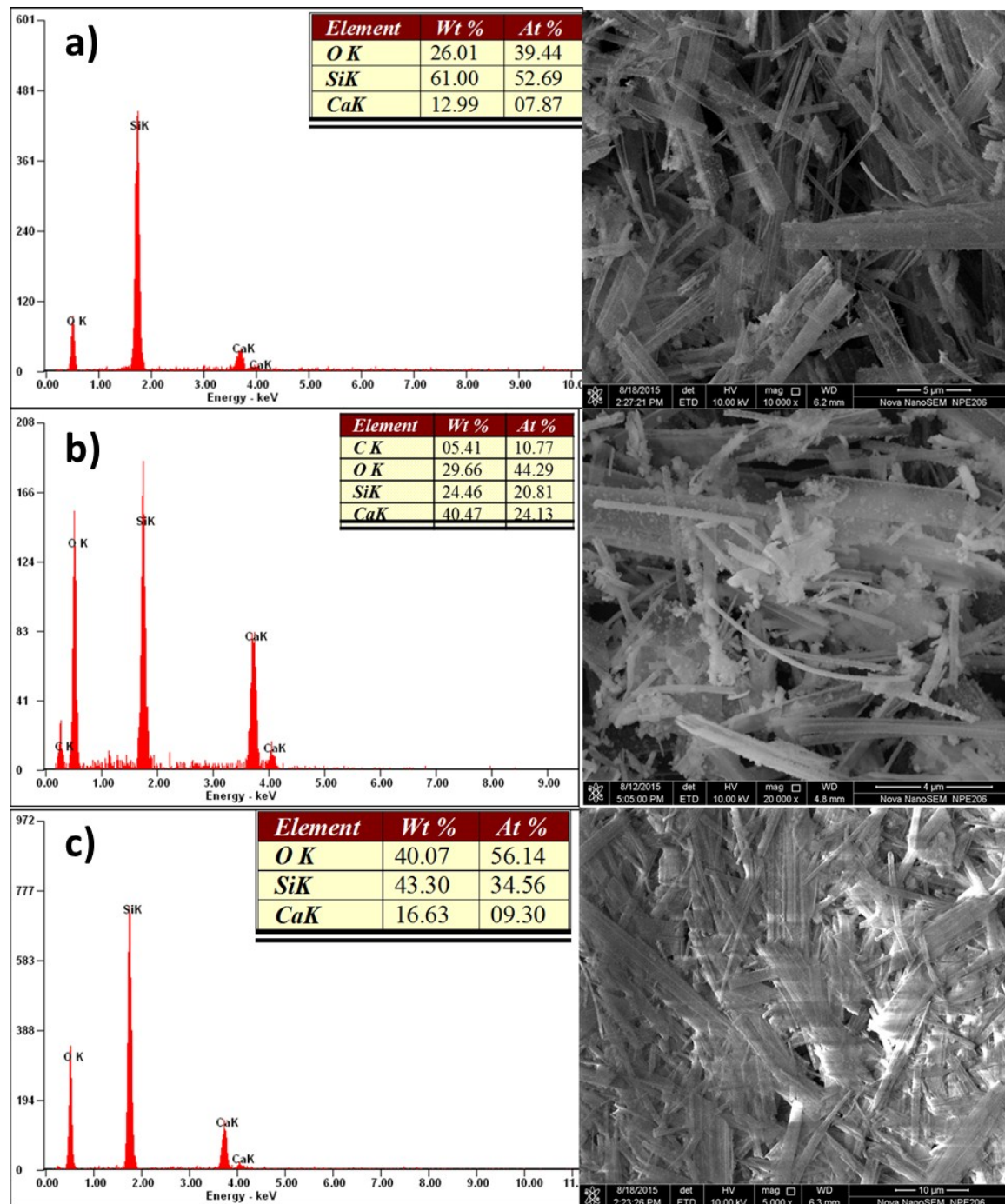


**Fig. S7** SEM images of silica tubes made from: (a) 13 wt% TEOS gel; (b) 10 wt% TEOS gel and (c) 6 wt% TEOS gel. The inserts show the size distribution of silica tubes.

**8. Growing of CaCO<sub>3</sub> nanocrystals on SiO<sub>2</sub> microtubes:** 50 mg of the dried silica tube was dispersed in the 0.3 M calcium chloride solution (3 mL) and sonicated for 10 min at room temperature. The uniformly dispersed solution was then placed in ammonium carbonate desiccator (desiccator containing solid ammonium carbonate) for 24 hours. The solution was

then centrifuged and the supernatant solution was discarded. The solid was washed with deionized water several times (10 mL x 5) and finally with acetone (10 mL) and then dried in a vacuum desiccator. The dried sample was weighed to calculate the weight of  $\text{CaCO}_3$  coated (94 mg of composite = 44 mg of  $\text{CaCO}_3$ ). It was calcined at 800 °C for 20 min to get  $\text{CaO@SiO}_2$  (74.2mg ~ 33% CaO).

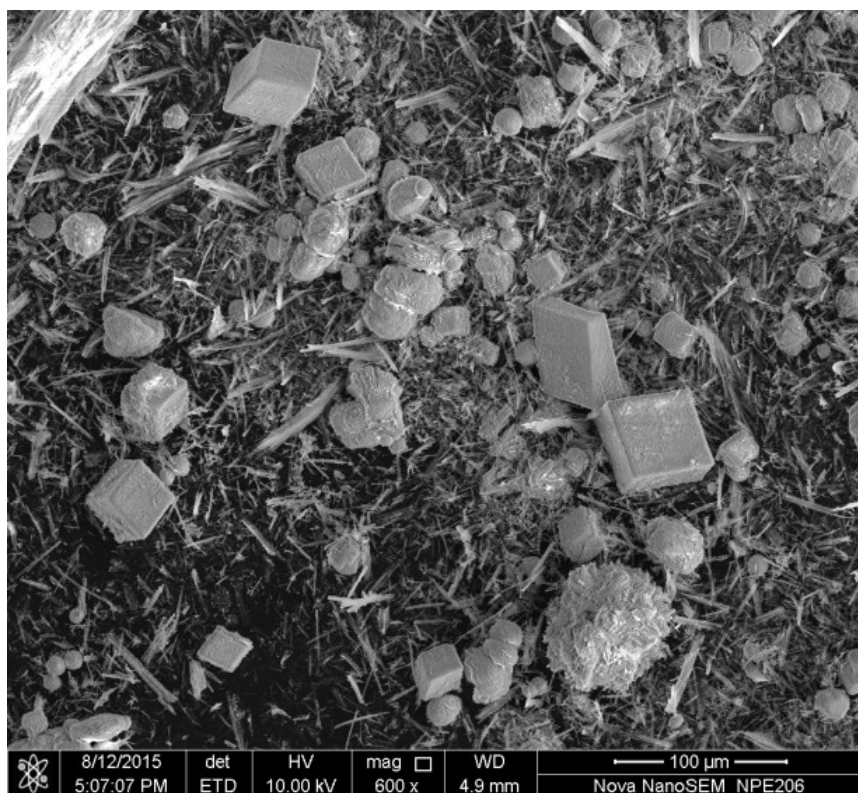
**9. Procedure for tuning the  $\text{CaCO}_3$  (CaO) content:** 50 mg each of dried silica tubes were taken in three conical flasks. To two of the flasks, 3 mL each of 0.5M  $\text{CaCl}_2$  solution were added and to the third flask, 3 mL of 0.3 M  $\text{CaCl}_2$  solution was added. All the three dispersions were sonicated for 10 min. at room temperature and then placed in an ammonium carbonate desiccator. One of the high-concentrated solutions (flask 1) and the less-concentrated solution (flask 3) were kept for 24 h and the other concentrated solution (flask 2) was kept for 50 h in the ammonium carbonate desiccator. These solutions were then centrifuged and the supernatant solutions were discarded. The solids left behind were washed with deionized water several times (10 mL x 5) and finally with acetone (10 mL) and then dried in vacuum desiccator. The dried samples were weighed to calculate the weight of  $\text{CaCO}_3$  coated in each of these cases. The amounts of  $\text{CaCO}_3$  deposited were found to be 39.7 mg, 92 mg and 27.1 mg respectively in the case of flasks 1-3 respectively. These  $\text{CaCO}_3@SiO_2$  were calcined to make  $\text{CaO@SiO}_2$  having different % of CaO.



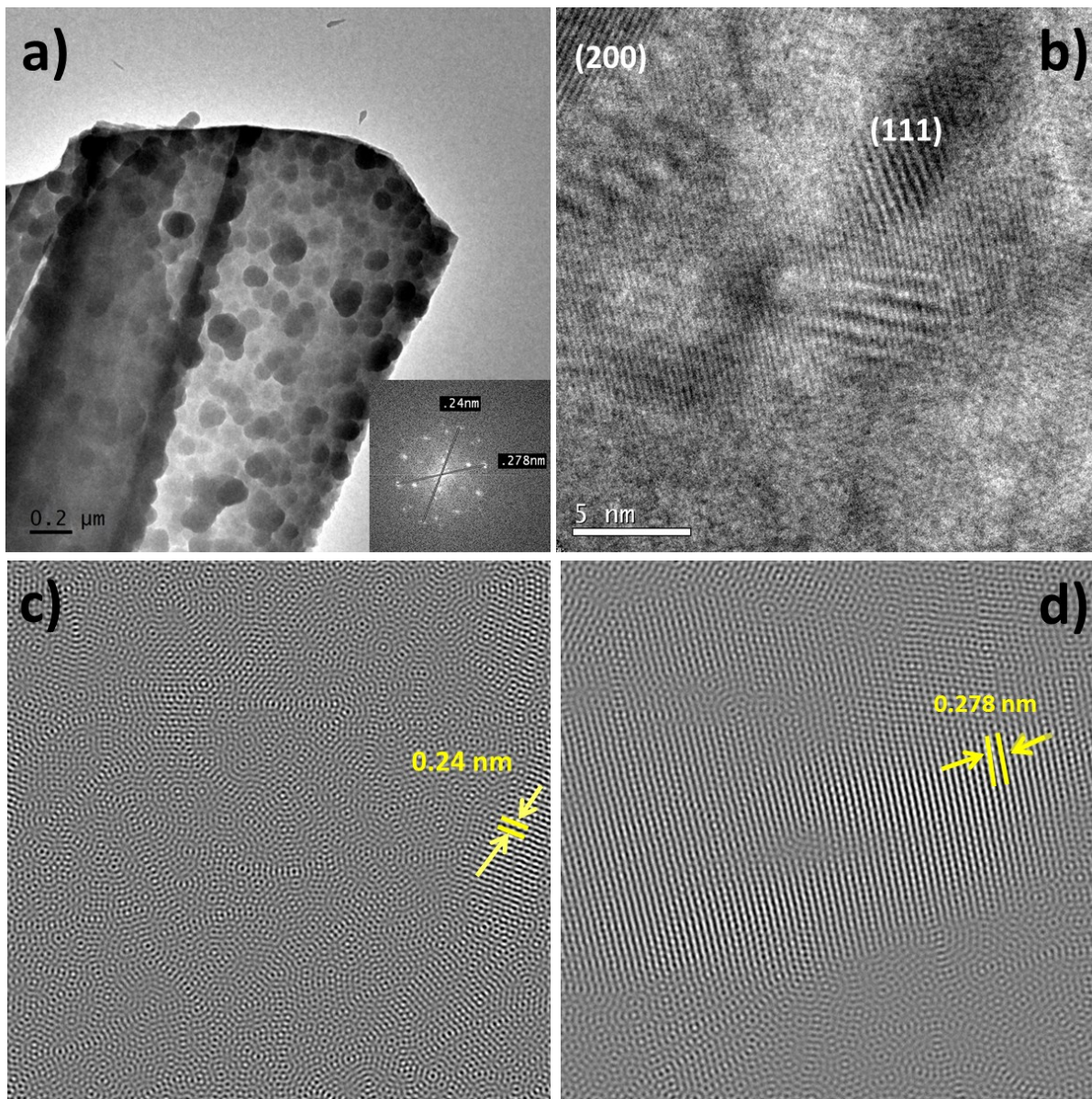
**Fig. S8** SEM-EDAX spectra of the sorbents  $\text{CaO}^{\text{nc}}@\text{SiO}_2^{\text{ut}}$  showing the variation of elemental composition with duration of crystallization and concentration of  $\text{CaCl}_2$  solution.  $\text{CaO}^{\text{nc}}@\text{SiO}_2^{\text{ut}}$  prepared by calcination of  $\text{CaCO}_3^{\text{nc}}@\text{SiO}_2^{\text{ut}}$  obtained from a) 50 mg silica tubes immersed in 3 mL of 0.5M  $\text{CaCl}_2$  solution for 24 hours b) 50 mg silica tubes immersed in 3



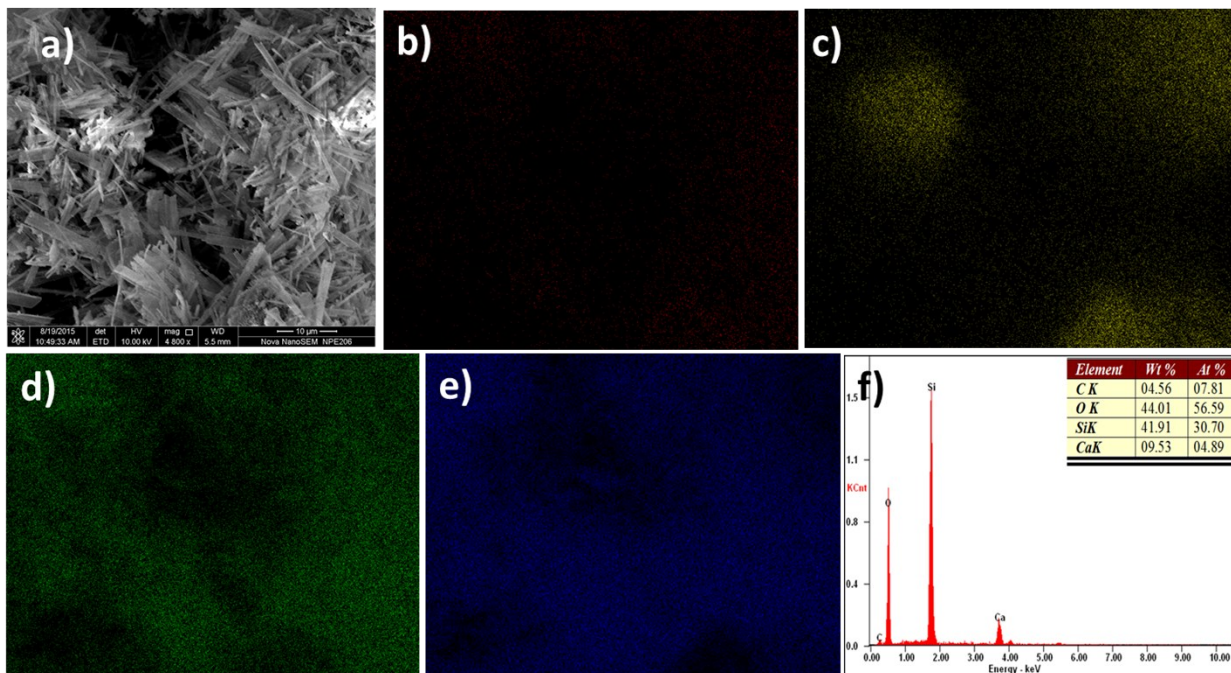
mL of 0.5M  $\text{CaCl}_2$  solution for 50 hours and c) 50 mg silica tubes immersed in 3 mL of 0.3M  $\text{CaCl}_2$  solution for 24 hours.



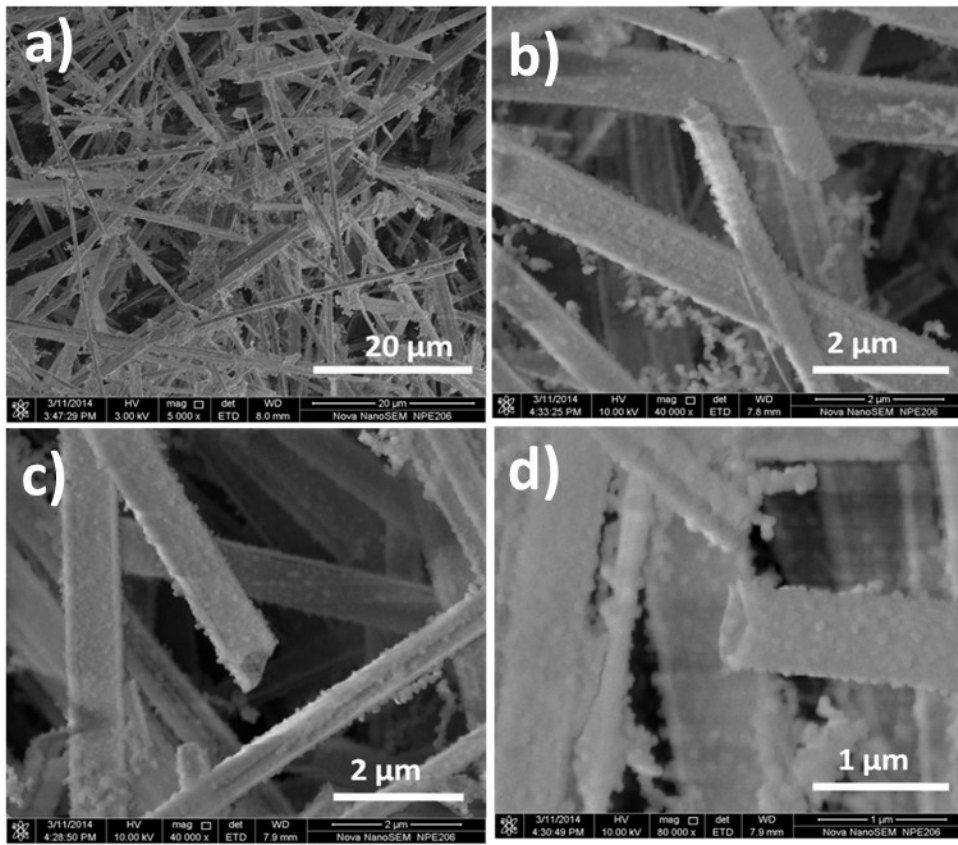
**Fig. S9** SEM image showing the phase separated  $\text{CaO}$  crystals at 40%  $\text{CaO}$  fabrication exceeds at 40% .



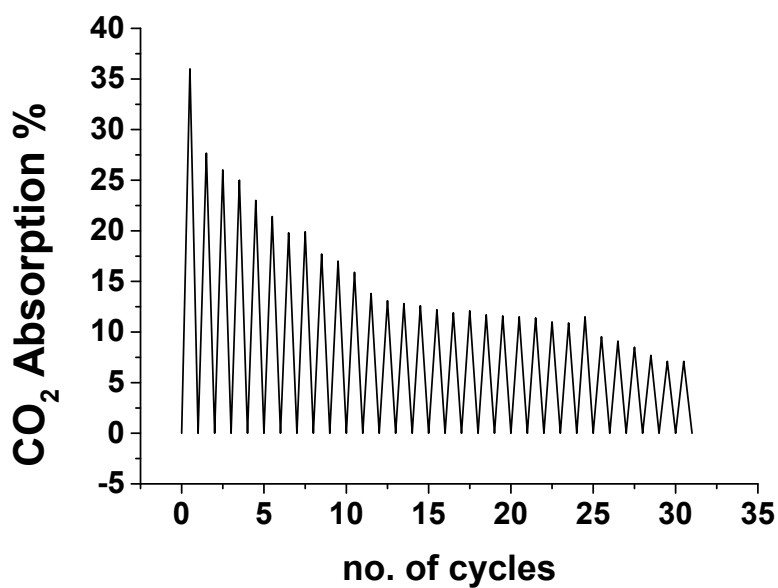
**Fig. S10** a) TEM image showing the silica tube coated with CaO nanoparticles (the intense black spots). The insert shows the corresponding FFT revealing the crystalline nature of CaO. The d-spacing calculated for CaO nanoparticles are matching with the literature data <sup>2</sup> b) HR-TEM image of CaO<sup>nc</sup>@SiO<sub>2</sub><sup>mt</sup> showing the lattice birefringence. The planes (200) and (111) are corresponding to the d-spacing 0.24 nm and 0.278 nm respectively. The c) and d) are inverted FFT images derived from the image b) showing the crystallinity of the CaO decorated silica tubes.



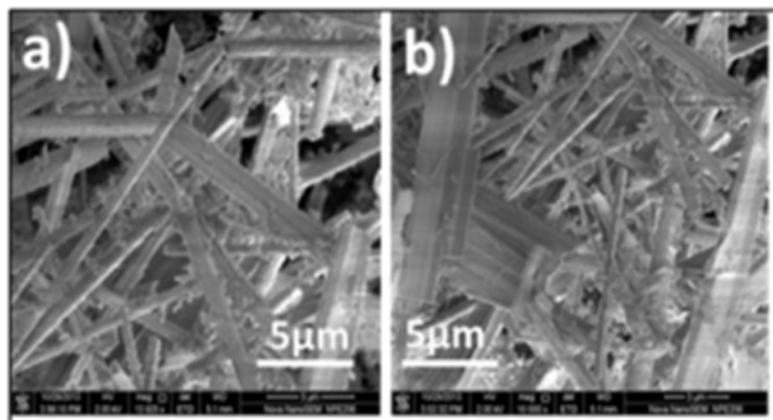
**Fig. S11** a) SEM image of silica tubes coated with CaO. Distribution of b) carbon (resulting from carbon tape) c) calcium d) oxygen e) silicon and f) EDAX data of the corresponding  $\text{CaO}^{\text{nc}}@\text{SiO}^{\text{ut}}$ .



**Fig. S12** SEM images of the silica tubes coated with  $\text{CaO}^{\text{nc}}@\text{SiO}_2^{\mu\text{T}}$  showing tubular morphology.

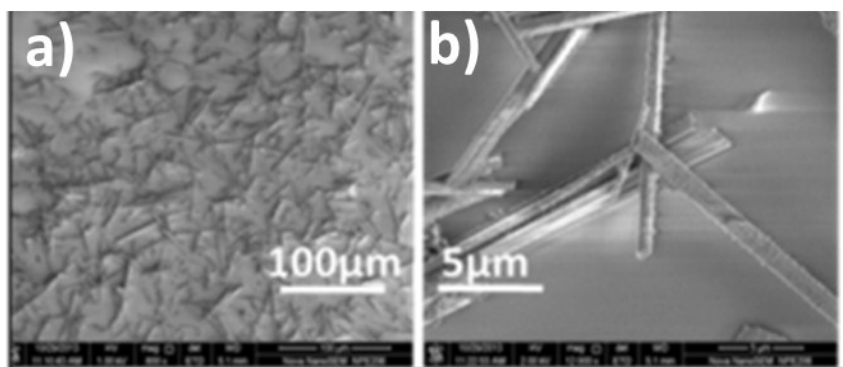


**Fig. S13** Sorption-desorption studies of commercial CaO powder (TGA data) showing drop in efficiency over several cycles.



**Fig. S14** a) and b) SEM images of the silica tubes coated with CaO nanocrystals showing the tubular structures after 30 cycles of sorption and desorption.

**10. Recycling of SiO<sub>2</sub> microtubes:** The CaO<sup>nc</sup>@SiO<sub>2</sub><sup>μt</sup> (10 mg) after 30 cycles of the CO<sub>2</sub> sorption and desorption was washed with 2 mL of 2N HCl. Then it was washed with deionized water (2 mL X 3), followed by acetone (5 mL). The solid thus obtained was dried in a vacuum oven. The dried sample was analyzed by SEM. It was found that no morphological change has happened to the silica tubes even after 30 cycles of carbonation and calcination (Fig. S12). This dried silica tubes were again carbonated using CaCl<sub>2</sub> solution & (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. The tubular morphology was seen in the SEM. The TGA data shows that the sorption and desorption performance of the CaO<sup>nc</sup> grown on recycled silica tubes were exactly the same as the fresh material.



**Fig. S15** a) and b) shows the SEM images of silica tubes after washing  $\text{CaO}^{\text{nc}}@\text{SiO}^{\text{ut}}$  with 2N HCl.

**References:**

1. A. Vidyasagar, K. Handore and K. M. Sureshan, *Angew. Chem. Int. Ed.* 2011, **50**, 8021
2. R. Kaminskas and R. Kubiliūtė, *Materials Science* 2010, **16**, 236