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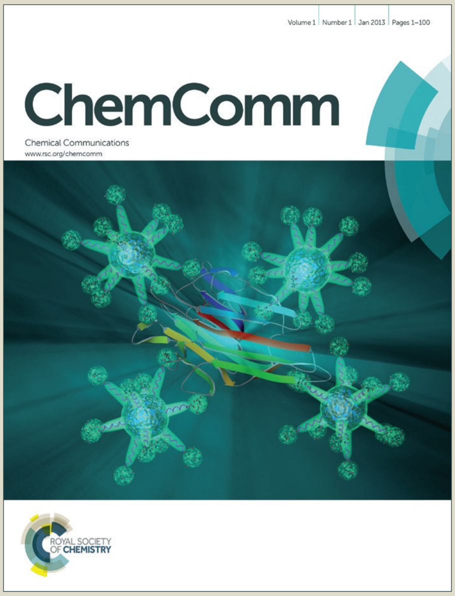

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CaO nanocrystals grown over SiO_2 microtubes for efficient CO_2 capture: Organogel sets the platform

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Materials that can capture and store CO_2 are important. Though CaO is a cheap sorbent, it is inefficient for practical purposes due to sintering and poor diffusion of CO_2 through the surface-$CaCO_3$ layer. We have developed a high performance, sintering-resistant CaO-based sorbent by uniformly nanofabricating the CaO nanocrystals on SiO_2 microtubes made by organogel templated polymerization.

There is serious concern about excessive levels of the greenhouse gas, CO_2, being spewed out to the atmosphere everyday as it contributes to global warming and the subsequent climate change.[1] At the same time, CO_2 is an important and cheap precursor for the production of several useful chemicals (*e.g.* methanol, dimethyl ether *etc.*).[2] Also, an efficient method for power production using CO_2 gas has been recently proposed.[3] Importantly, Lithium/CO_2 rechargeable battery is an emerging system for efficient energy storage.[4] Hence CO_2 capture and storage (CCS) is important and materials that can adsorb/absorb CO_2 are of great interest.[5] The reversibility of the carbonation of CaO to $CaCO_3$ has prompted researchers to explore quick lime (CaO) as a cheap and recyclable sorbent for CCS.[6] However, the carbonation reaction is not very efficient due to 'sintering'[6b,7] (aggregation of CaO crystals/particles upon carbonation resulting in the reduction of the surface area) and the consequent inaccessibility of CaO in the inner part of aggregates for carbonation owing to the poor diffusion of CO_2 through the $CaCO_3$ layer formed on the surface. It is essential to increase the surface area-to-volume ratio of the active CaO sorbent to minimize the effect of sintering.[6c] As powdered CaO aggregate upon several cycles of carbonation and calcination, they are also not suitable for practical purpose.[8] This has led researchers to use CaO adsorbed on inert matrices such as silica.[9] Though physical blend of CaO and silica has been used, the efficiency is not satisfactory after a few cycles presumably due to the phase separation into individual phases.[10] Exploiting the use of structured silica as the matrix for the first time, we herein report an efficient sintering-resistant and economically viable sorbent that can be used for the multiple carbonation-calcination cycles.

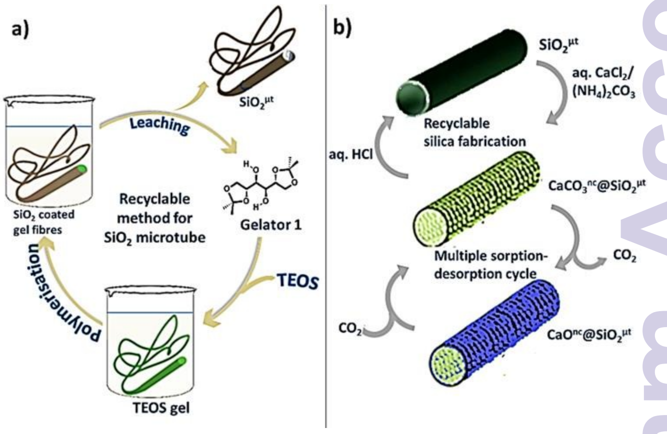

Fig. 1 Schematic proposal for (a) large-scale preparation of hollow silica microtubes using recyclable organogel-template; (b) use of silica microtubes as platform for growing CaO nanocrystals and their use as sintering-free sorbent for multi-cycle calcium looping.

We envisioned that, in order to prevent phase separation and thus the ensuing sintering, it is necessary to immobilize the nanosized CaO particles uniformly on a high-surface-area matrix. Also, it has been known $CaCO_3$ layer of thickness above 50 nm would limit the diffusion of CO_2 through it.[6b] In this context, we planned to decorate nanoparticles of CaO on micro-structured silica forms. As hollow tubes give maximum surface area due to the availability of inner and outer surfaces for nanofabrication, we planned to grow nanocrystals of CaO (CaO^{nc}) on silica microtubes ($SiO_2^{\mu t}$).

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Organogels, formed by the entrapment of solvent by the superstructures formed as a result of the self-assembly of low molecular mass organogelators (LMOG), are attractive materials and have been exploited for various applications.[11] Shinkai *et al*. demonstrated that the microstructures of organogels can be used as templates to synthesize micro-structured silica of different shapes[12] by polymerising TEOS on the gel fibres followed by removal of the gelator by calcination. Though elegant, this usual method is not suitable for the large scale preparation of silica tubes. For templating, the attraction between anionic silica species and the gel fibres is important[13] and hence the gelators exploited for the preparation of silica tubes are complex molecules with cationic moiety in them. Gelations of such special molecules often require a special mixture of solvents (*eg*. mixture of acetic acid and DMSO) and SiO_2 precursor (TEOS) needs to be introduced at a later stage. The usual method of destructive removal (calcination) of the template is not practical for large scale preparation of SiO_2 tubes. For large scale preparation of silica tubes, it is essential to (i) use a simple, cheap and easy-to-prepare gelator as the template, (ii) the gelator should be able to congeal the silica precursor TEOS, (iii) develop a method for recovering and recycling the gelator instead of calcining. Screening of various gelators we have developed in our lab,[14] revealed that 1,2;5,6-di-*O*-isopropylidene mannitol **1** (Fig. 1a) could congeal TEOS without a co-solvent, which makes the envisioned process easy. Also SEM analysis of the xerogel made from TEOS gel of **1** showed fibrillar morphology of the self-assembled gelator (Fig. 2a).

As the gelator **1** is known to interact with anions through hydrogen bonding,[15] we wondered whether the hydrogen bonded gel fibers of **1** can be used as template for the preparation of silica tubes. It is anticipated that the hydrogen bonding interaction between the gelator network and the silanol produced in situ upon hydrolysis of TEOS would bring the template effect.[16] In order to initiate the polymerization, catalytic amounts of benzylamine and water were added to 6 wt% TEOS gel of compound **1**. It was observed that after the templated polymerization, the volatile TEOS and the ethanol produced in the polymerization underwent evaporation to yield only SiO_2-coated gelator fibres. (†ESI Fig. S1). As the gelator **1** is a simple uncharged molecule, the gel template could be extracted with dichloromethane and methanol to obtain hollow silica tubes. The recovered gelator could be reused multiple times for the preparation of SiO_2 tubes. Thus, this method is advantageous over the traditional method of destroying the gelator/template by calcination.

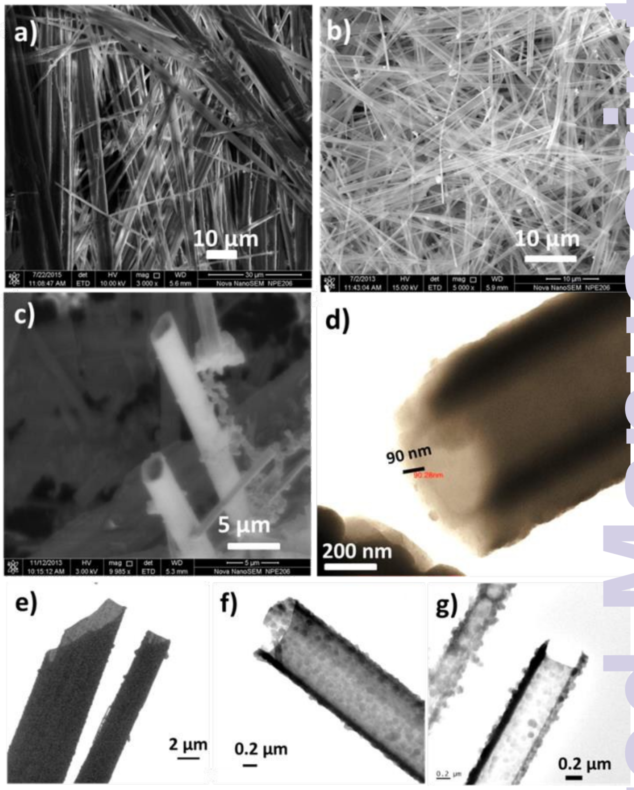

Fig. 2 a) SEM image of xerogel of **1** made from its TEOS gel. (b) SEM image of th silica microtubes made from 6 wt% gel of **1** in TEOS. c) SEM image showing t e hollow tubes. d) TEM image of the cross section of a silica tube showing a w thickness of ~90 nm. e-g) TEM images of silica tubes made from 13 wt%, 10 wt% and 6 wt% gel of **1** in TEOS respectively showing different diameters.

Analysis of the polymerized silica by SEM revealed that th fibrillar morphology as in the organogel is preserved even after transcription to silica and tubes of several micrometres leng could be seen (Fig. 2b). Both SEM and TEM analyses indicated that the silica fibres have hollow tubular structure (Fig. 2c- , †ESI Fig. S2).). These tubes have a wall thickness of around nm as evidenced from TEM analysis (Fig. 2d). SEM-EDAX (Energy dispersive X-ray spectroscopy) analysis has shown peaks due to SiO_2 only suggesting that the gelator 1 has bee completely removed during washing (†ESI Fig. S3). The R spectrum of the silica microtubes matched with that of the commercial silica (200-400 mesh) sample (†ESI Fig. S4). Th PXRD data of these silica tubes suggested that they a amorphous in nature (†ESI Fig. S5). BET surface area analysis revealed that these silica tubes have large surface area a anticipated. (†ESI Fig. S6). Interestingly, the average diamete of the tubes could be tuned from nanometers to micromet rs by changing the concentration of the gelator as suggeste by SEM (†ESI Fig. S7) and TEM (Fig. 2e-2g) analyses. Upon increasing the gelator concentration, the gel fibres of larg diameters are formed. Templated TEOS polymerization ov these fibres leads to the formation of silica tubes of large diameters. For instance, the use of TEOS gels having gelato concentrations of 13 wt%, 10 wt% and 6 wt% as templat yielded silica tubes of average diameters of 2 µm (Fig. 2e), 70 nm (Fig. 2f) and 500 nm (Fig. 2g) respectively as eviden from TEM analyses. Though inconsequential, the length of the tubes is not amenable to tuning by this method. To the best of our knowledge, this is the first report on the synthesis of size controllable SiO_2 tubes using organogels as the template.

Having achieved a scalable method for large-scale preparation of silica microtubes, without losing the template, we next attempted for growing nanocrystals of CaO on the surfaces of these hollow tubes. Initially, $CaCO_3$ nanocrystals were grown by keeping a suspension of silica microtubes in calcium chloride solution in a closed desiccator containing solid ammonium carbonate. The *in situ* generated CO_2 gas slowly diffuse into the aqueous solution and the carbonic acid thus generated reacts with $CaCl_2$ to give $CaCO_3$.[17] This slow diffusion is important for slow growth and uniform distribution of $CaCO_3$ over the silica tube surface.

The morphology of the hollow tubes remained unchanged even after the "carbonation" as evidenced from SEM (Fig. 3a) and TEM (Fig. 3b) analyses. Depending on the concentration of $CaCl_2$ solution and the exposure time, the amount of $CaCO_3$ formed over the silica tubes could be tuned as evidenced from the weight of the composites made under different conditions (†ESI) and from SEM-EDAX analyses of these materials after calcination to CaO (†ESI Fig. S8). For instance, the more the concentration of $CaCl_2$ or the more is the exposure time, the more is the $CaCO_3$ loading. TEM analysis revealed the granular morphology and the distribution of CaO nanocrystals over silica tubes. (†ESI Fig. S10). PXRD analysis of the $CaCO_3$-coated silica tubes showed the presence of fcc nanocrystals of $CaCO_3$ (Fig. 3c).[18]] SEM-EDAX mapping revealed the uniform distribution of CaO nanocrystals on silica tubes (†ESI Fig. S11). The carbonated tubes were calcined at 800 °C to convert the nanocrystals of $CaCO_3$ to nanocrystals of CaO on silica tubes. Even after calcination, the tubular morphology is maintained as evidenced from SEM analysis (†ESI Fig. S12). PXRD analysis of the tubes after calcination proved the crystalline nature of CaO (Fig. 3d) on the amorphous silica.

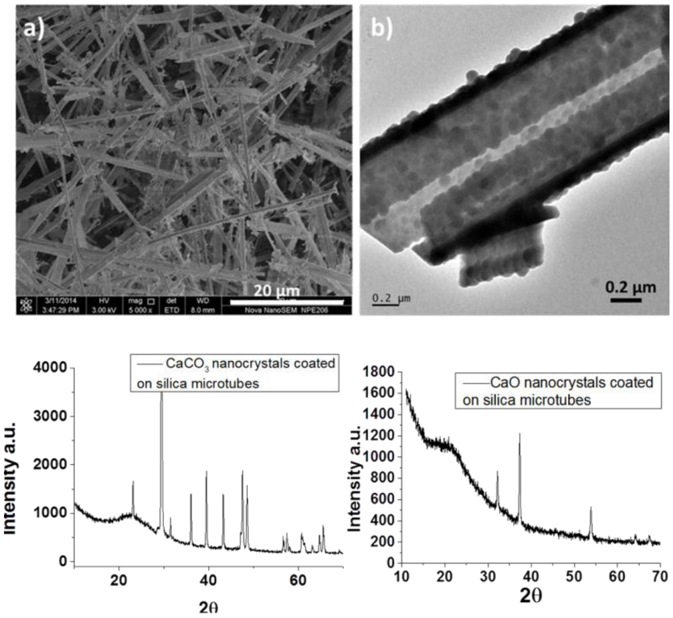

Fig. 3 a) SEM image of silica microtubes after growing $CaCO_3$ nanocrystals over their surface. b) TEM image of the $CaCO_3^{nc}$-grown-SiO_2 microtubes, showing the growth of $CaCO_3$ nanocrystals on either surface of the SiO_2 tubes. c) PXRD spectrum of $CaCO_3$-grown on SiO_2 microtubes showing crystalline $CaCO_3$ over amorphous SiO_2 d) PXRD spectrum of CaO-SiO_2 microtubes showing crystalline CaO over amorphous SiO_2.

The CO_2 sorption and desorption studies were done in a TGA instrument using a $CaO^{nc}@SiO_2^{\mu t}$ sample having 33%, by weight, of CaO. The carbonation was done at 760 °C and the calcination at 800 °C. The CO_2 uptake was found to be 22 wt% in the first cycle and 10 wt% at the 30th cycle with respect to the whole composite (Fig. 4a). This corresponds to 30 wt% absorption with respect to the active CaO sorbent even at the 30th cycle. The average CO_2 uptake for 30 cycles is 0.37 g per gram of active sorbent (CaO), which is the best among the SiO_2-based CaO sorbents reported so far.[6b]

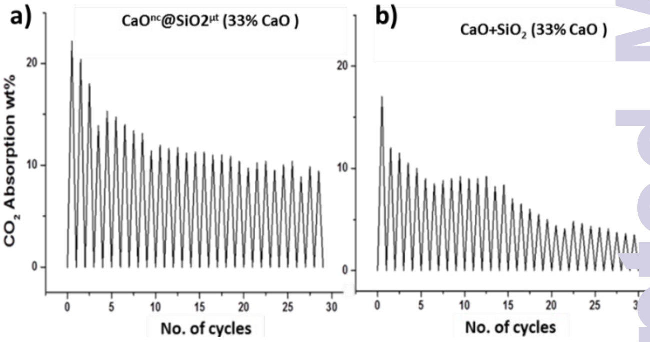

Fig. 4 TGA data showing the CO_2 absorption-desorption capacity over 30 cycles of a) $CaO^{nc}@SiO_2^{\mu t}$ b) Physically blended SiO_2 and CaO.

From the TGA data, it is clear that the CO_2 uptake capacity of $CaO^{nc}@SiO_2^{\mu t}$ decreases only gradually unlike a sudden drop in the case of only CaO.[19] In cases of pure CaO (†ESI Fig. S13), and a physical blend of SiO_2 and CaO (Fig. 4b), the CO_2 capture efficiencies were decreased by 34% and 27% respectively, in the second cycle, relative to the first cycle due to sintering. Remarkably, only a relative reduction of 7.6% (1.7 absolute %) was observed in the case of $CaO^{nc}@SiO_2^{\mu t}$. After the fifth cycle, the drop in efficiency is less than 1% between two successive cycles and after the 10th cycle the uptake capacity is almost stable. This remarkable 30 wt% absorption with respect to CaO even at the 30th cycle is possible only because of the negligible sintering due to the uniform distribution of CaO nanocrystals over the high surface area silica microtubes. On the other hand, a physical blend of silica and CaO in the same ratio as the tubes showed a sudden decrease to 7% (Fig. 4b) by the 7th cycle and the efficiency kept on decreasing. Usually, owing to the slow diffusion of CO_2 to the bulk of the CaO sorbent, each carbonation-calcination cycle is lengthy (100 min/cycle) and hence are not practically feasible when multi-cycle process is envisioned.[20] Remarkably, due to the nanofabrication in our case, the rate of absorption and release of CO_2 is very fast and hence each carbonation-calcination cycle can be done in 21 minutes. Also the absorption happens even at low CO_2 pressure (14 sccm and 5 Psi).

The SEM image of the silica tubes recorded even after 30 cycles clearly shows the robustness and structural integrity of the silica tubes (†ESI Fig. S14). This has motivated us to investigate the recyclability of these silica tubes. For this, the tubes were washed with dilute HCl solution, which dissolved the $CaCO_3$/CaO to regenerate the pure silica tubes. These regenerated tubes were also morphologically intact as evidenced from SEM analysis (†ESI Fig. S15). These regenerated microtubes could be reused for growing CaO nanocrystals again and for new rounds of carbonation calcination cycles.

In summary, capture and storage of CO_2 is an important issue of current emergency. Though CaO can stoichiometrically and reversibly react with CO_2, CaO-based sorbents are not efficient for practical purpose due to sintering. The most important criterion to prevent the sintering and to increase the capturing capacity is to increase the surface area by manipulating CaO at the nano level with uniform distribution. We have addressed this problem by decorating nanocrystals of CaO on SiO_2 microtubes. SiO_2 microtubes of tuneable thickness were easily prepared via sol-gel transcription method using a cheaply available organogelator as the template and through a method that allows the recovery and recycling of the gelator. We have fabricated nanocrystals of CaO on these silica microtubes and demonstrated its superior efficiency in CO_2 uptake and release. This robust composite could be used for multiple carbonation and calcinations cycles without compromising the efficiency. The robust nature of the silica tubes allows recycling of these microtubes for multiple rounds of nanofabrication with CaO. This is the first use of structured silica for such an application. This report of the development of a high-performance, sintering-free sorbent for calcium looping not only offers a method for possible adoption in practical applications but also demonstrates the importance of supramolecular chemistry in tackling such practical problems.

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