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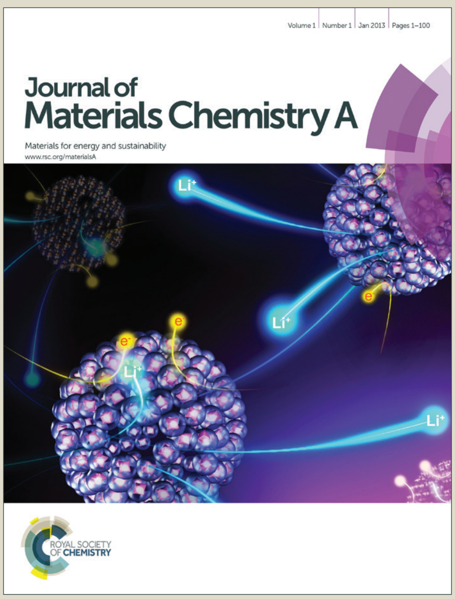

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FULL PAPER

Graphical Abstract

Bulk Superhydrophobic Materials; a Facile and Efficient Approach to Access Superhydrophobicity by Silane and Urethane Chemistries

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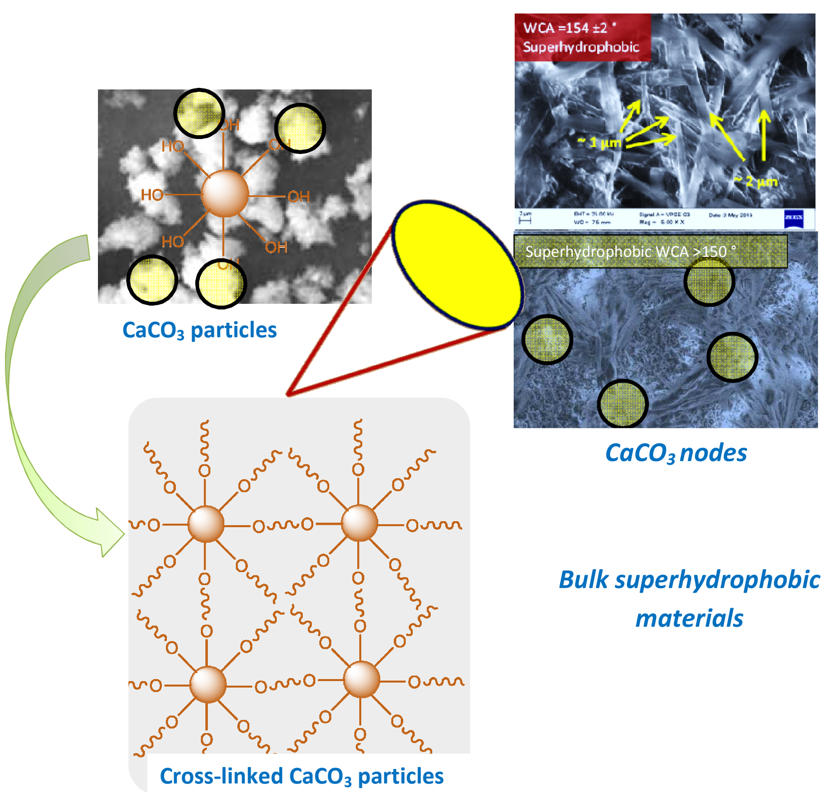
$CaCO_3$ based bulk superhydrophobic material are synthesised by capping the surface OH grups with siloxane segments which were crosslinked by urethane chemistry. The crosslinked material displays static contact angle ~ 155° and water-roll-off angle ~ 5-8° through the thickness. The bulk level SH behaviour is achieved through both inter and intra particle hydrogen bonding and cross-linked rod-shaped morphology of the material.



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PAPER

Bulk Superhydrophobic Materials; a Facile and Efficient Approach to Access Superhydrophobicity by Silane and Urethane Chemistries

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The present contribution addresses a promising method for constructing 'bulk' level superhydrophobicity on $CaCO_3$ microparticles by employing silane and urethane chemistries in sequence. The silanol terminated short chain polydimethyl siloxane (PDMS) segments were grafted on to the $CaCO_3$ surface. The particles were characterised by FTIR, Raman spectroscopy and GPC analyses. By the reaction of silanol groups on the surface of $CaCO_3$ particles with isocyanate functionalities, the crosslinking of particles was accomplished. The resultant coating exhibited water contact angle >150 ° with sliding angle ~5-8 ° on entire material. The bulk level SH behaviour is attributed to both inter and intra particle hydrogen bonding which are substantiated by FTIR. The rod-shaped morphology of bulk material is evidenced in SEM images which is due to the encasing of well-connected microparticles by PDMS chains.

1. Introduction

Superhydrophobic (SH) surfaces have been inspired since the observation and understanding of water rolling/self-cleaning properties of lotus leaves and the exotic SH features of insects like water strider. [1-5] The extreme non-wetting property of superhydrophobic materials offers anti-reflectivity, anti-fouling and microfluidic valve applications. Generally, achieving both low surface energy and micro/nano level surface roughness on material surfaces breed the situation of superhydrophobicity. Sophisticated and expensive routes such as electro spinning, plasma etching, costly fluorine containing molecules and complex process control are normally essential for realising SH surfaces. [6-8] In most cases, surface functionalization is performed on micro/nanoparticle surface and utilizing fluorine based molecules. The protruding groups on the surface of these materials prevent water molecules from entering inside to bring surface superhydrophobicity. [9,10] The resultant superhydrophobic surfaces are susceptible to damage and are not durable because superhydrophobicity primarily exists only on the surface of the materials. Once the surface is removed, SH properties will vanish. Bulk level SH enables total protection to materials/coatings from moisture ingress.

Bulk superhydrophobicity is a peculiar approach to extend surface topographies (responsible for SH) into the bulk by creating both roughness and low surface energy in the bulk. [11] Previously, Grinstaff et al reported 3D (bulk SH) coatings *via* eletcrospraying process. [11a] Bulk SH from porous polyelectrolyte multilayers were demonstrated by controlled release of small organic molecules for biomedical applications. [11b] Though this material exhibits bulk SH, water ingress on immersion in water is the basis of controlled release. Another porous bulk SH material is prepared from polycaprolactone and hydrophobic polymer dopant poly (glycerol monostearate-cocaprolactone) by electrospinning method.[11c] Both these cases, physics of entrapped air play the vital role in delivering bulk level SH. Bulk SH (to certain extent) is also revealed by a coating made of polymerized organosilane/attapulgite (POS/APT) nanocomposites.[11d] Self-healable SH materials are also a kind of bulk SH systems, but the success of these materials rely fully on the self-healing capability which generally underperform on multiple cycling.[12]

Despite several efforts to develop micro/nanoparticle based durable superhydrophobic surfaces, no meaningful work has been conducted on inexpensive $CaCO_3$ particles (in fact we have never come across any work on bulk SH coatings from calcium carbonate particles). This may be due to the highly unreactive hydroxyl groups on surface of $CaCO_3$ which are very difficult to functionalise (unfunctionalised calcium carbonate particles are superhdyrophilic). However, nano $CaCO_3$ and polyvinylidene fluoride in the presence of tridecafluorooctyl triethoxysilane resulted in water contact angle (WCA) of 153°.[13]

Superhydrophobic coating with WCA of 155° was also prepared from heptadecafluorodecyl trimethoxysilane modified CaCO3 and polyacrylate. [14] Low surface energy monolayer of stearicacid modified micro and nano sized $CaCO_3$ suspensions also resulted in superhydrophobicity.[15] Takahara et al prepared superhydrophobic lamellar vaterite ($CaCO_3$) in the presence of oleic acid and heptadecafluorodecyl trimethoxysilane which exhibited SH property with contact angle 152°. [16]

In contrast to the reported works, the novelty of present work is that it explores the feasibility of surface functionalisation of calcium carbonate particles through the surface OH groups which are otherwise known for their poor amenability for chemical transformation and bulk superhydrophobic materials are realised. In other words, this article presents the preparation of a bulk superhydrophobic material from calcium carbonate microparticles. The surface grafting by polydimethylsilxane and subsequent crosslinking of the microparticles are successfully carried out. Highly reactive aromatic isocyanate is employed for polymer end-capping and further crosslinking. Superhydrophobicity of the material in the surface and bulk is demonstrated. The inter and intraparticle hydrogen bonding among cross-linked $CaCO_3$ particles are also investigated.

2. Experimental

2.1 Materials

$CaCO_3$ microparticles (Sisco Research Laboratory, India) were used after drying at 120 °C for 12 hours and kept in a sealed container. Dichlorodimethyl silane (99.5%, Aldrich, USA), triethylamine (99%, Fisher Scientific, India), methanol (99%, Sisco Research Laboratory, India), toluene (99%, Central Drug House, India) were used as received.

2.2 *Functionalisation and surface polymerisation of $CaCO_3$ particles*

About 20 g of dried $CaCO_3$ powder was dispersed in about 150 ml triethylamine (TEA) and kept under ultrasonication for 30 minutes at 60 °C. The dispersed slurry was then poured in a three necked round bottom flask equipped with stirrer, dropping funnel, nitrogen inlet and placed in an oil bath maintained at 50 °C. To this, 10 ml of dichlorodimethylsilane (DCDMS) was added drop wise for half an hour with constant stirring and reaction continued for additional two hours under nitrogen. The liberated HCl was scavenged by TEA to form triethylamine hydrochloride salt. Subsequently, about 20 ml water was added slowly for about one hour to carry out hydrolysis and further polymerization reaction of DCDMS over microparticle surface. The functionalized $CaCO_3$ particles were recovered by filtration and by washing several times with methanol-water mixture (50-50 v/v).The washed powder was then dried at 80 °C under vacuum for 24 hours. The colour of $CaCO_3$ particles was changed from white to light orange due to grafting of siloxane over the $CaCO_3$ surface. The cross-linking of $CaCO_3$ particles through silanol-isocyanate reaction is accomplished by reacting the *f*$CaCO_3$ with tolylene diisocyanate.

2.3. Characterisation

The FT-IR spectra were recorded in a Perkin Elmer Spectrum GX-A FTIR spectrometer in the 4000 - 400 cm^{-1} wavenumber range. The Raman spectra were recorded in a WITec alpha 300R spectrometer using 532 nm laser source. The average molecular weight and molecular weight distribution were determined in Waters 515 Gel Permeation Chromatograph (GPC) equipped with Waters 414 differential refractometer using tetrahydrofuran (THF) solvent and at a flow rate of 1.0 mL/min. Polystyrene standards were used. The surface area analysis was carried out by the surface area analyser (Micromeritics TriStar II) by Brunauer-Emmett-Teller (BET) method. (Samples were degassed at 100 °C for 12 hours before analysis). The water contact angles of film surfaces were measured with the standard sessile drop (drop size 2 and 5μl) technique by using a Dataphysics contact angle meter OCA-20. The advancing (maximum contact angle observed on continuous addition of water droplets) and receding angle (minimum angle observed by continuous withdrawing of water droplets) were carried out in contact angle unit. Morphology of microparticles and SH material were investigated using Carl Zeiss scanning electron microscope (SEM).

3. Results and Discussion

Firstly, the surface hydroxyl groups of $CaCO_3$ microparticles (1-7μm, *SI1*) were reacted with highly reactive dichlorodimethylsilane in triethylamine solvent under inert atmosphere. Subsequently, hydrolysis and polymerization of the attached silane moiety on the surface of microparticles were accomplished.

Figure 1 FTIR and Raman spectra of unfunctionalised $CaCO_3$ and siloxane functionalized $CaCO_3$ microparticles (*f*$CaCO_3$)

The bands at 2925 cm^{-1} (C-H stretching), 1260 cm^{-1} (CH_3 bending) and 803 cm^{-1} (CH_3 rocking) in FTIR imply the successful functionalization. The characteristic peaks of calcite form of $CaCO_3$ were seen at 714, 877 and 1485 cm^{-1} whereas Si-O-Si stretching was observed at 1020 cm^{-1} and 1100 cm^{-1} respectively. The raman shifts at 2908 cm^{-1} and 2967 cm^{-1} (antisymmetric stretching vibrations of CH_3), prove the grafting of siloxane chain over microparticle surface (Figure 1).

The average molecular weight of attached siloxane segments was assessed by size exclusion chromatography (the $fCaCO_3$ were digested in tetrahydrofuran in order to dissolve out the organic part). The siloxane segments have M_n of 11400 g/mol *(SI2)* and polydispersity index of 1.2 which tags that the polymerization occurred nearly in a controlled fashion on the $CaCO_3$ surface. These results imply that an average of 150 silane units (Si $(CH_3)_2$-O-) constitute one chain of the siloxane segment on the surface of microparticle. The surface areas of $CaCO_3$ and $fCaCO_3$ obtained by BET method are 5.28 and 1.94 m^2/g respectively. The lower surface area of $fCaCO_3$ is attributed to the high coverage of polymer chains over microparticle surface. The number of silane segments grafted onto the microparticle surface is 1.69 molecules/m² and actual coverage density is 1.02 µmol/m² as calculated from Berendson equation [16b].

$$\text{Grafting density} = \left[\frac{10^6\,P_c}{(1200n_c - P_cM_1)}\,x\,\frac{1}{S_{BET}}\right]x\,\frac{N_A}{10^{24}} \qquad (1)$$

where P_c is percent (%) of carbon on the surface of $CaCO_3$ particles, n_c is the number of carbon atoms per anchored siloxane chain, M_1 is the molecular weight of the siloxane chain, S_{BET} is the specific surface area of the silica, N_A is Avogadro's constant. Here, P_c =1.5% (from CHN analysis), $n_c \sim 300$ $S_{BET} = 5.28$ m^2/g and M_1 =11400 g/mol (from GPC analysis).

From scanning electron microscopy, it is obvious that $fCaCO_3$ possessed good surface coverage of siloxane in view of bigger size of $fCaCO_3$ as compared to bare microparticles (*SI3a,b)*. The EDX (Electron dispersive X-ray) also shows additional silicon peak in elemental analysis (*SI3c,d*). However, the $fCaCO_3$ particles are superhydrophilic and no hydrophobicity was observed (*via* contact angle experiments) in spite of possessing a good coverage of siloxane segments. In the next step, the siloxane segments were end capped by bifunctional aromatic isocyanate molecule *viz*: tolylene diisocyante (TDI). TDI is chosen because i) it is a strong moisture scavenger and ii) strong electrophile to attract very weak nucleophiles. The TDI treated microparticle mixture was coated over glass slide and reaction was initiated at ambient temperature under vacuum (vacuum is used to avoid reaction of NCO with atmospheric moisture and to facilitate the reaction exclusively with -OH of siloxane chains). The viscosity of mixture increased with time due to urethane bond formation and further crosslinking (urethane bond formation between microparticles). The reaction was continued at 80 °C under vacuum for 24 hours, then the coating was kept at ambient temperature for 7-10 days. The FT-IR absorption spectrum of resultant coating shows urethane linkage with absorption at 1703 cm^{-1} (C=O) and at 3331 cm^{-1} (N-H) respectively. The lower absorption peak at 1671 cm^{-1} implies the hydrogen bonded C=O groups (however, urea bond (NH-CO-NH) formation cannot be avoided as NCO-mositure reaction can progress to some extent, in which case the -CO peak in urea bond can appear at below 1700 cm^{-1}). Absence of isocyanate peak at 2273 cm^{-1} ensures complete reaction of TDI molecule.

Scheme 1 Preparation of cross-linked $CaCO_3$ microparticles by silane modification and urethane crosslinking.

The raman spectrum of coating exhibits absorption bands at 1298 cm^{-1} (-C-N stretching), 1700 cm^{-1} (hydrogen bonded C=O stretching) and 1615 cm^{-1} (N-H bending) confirming urethane linkage in the coating (*SI4*). The synthetic scheme for the preparation of SH coating is shown in Scheme 1.

The coating exhibited excellent water repulsion features with water contact angle 154±2° and a surface energy of 19.5 mJ/m^2 (calculated from Harmonic mean method using three liquids *viz:* water, diiodomethane and ethylene glycol). The water droplets rolled-off with a roll-off angle between 5-8 °. Figure 2 shows the resting of water droplets on the SH surface and their roll-off sequence.

Figure 2 Pictures showing the superhydrophobic features of cross-linked $CaCO_3$ micro particle coating over glass slide a) Water droplet viewed through modern camera (inset: water droplet observed through contact angle meter) b) Roll-off of water droplets at a sliding angle <8 °.

Undoubtedly, the superhydrophobic properties with water-rolling properties (Cassie state) of the coatings are attributed to some unusual self-assembled morphology patterns. The SEM image (Figure 3b, right side) shows the self-assembled cross-linked structures of SH surfaces that are responsible for the excellent surface properties. The brighter portions of SEM images imply the cross-connected rod or twig like structure. The images show also the distinct surface morphology and no phenomenon of agglomeration of microparticles in SH coatings.

Viewed further, we noticed that these coatings are not showing the characteristic 'petal effect' associated with microparticle based SH coating.[17] The 'petal effect' (wet Wenzel state) is a phenomenon observed in red roses such that WCA will be >150 ° but no roll-off behaviour will be observed (even the petal is turned upside down) due to strong adhesion of water molecules to the surface. The petal effect is associated with close array of micropapillae (typically 15 to 75 µm) on the surface of flowers.[16]

The coating prepared in this work principally consists of large number of urethane bonds and in general, the -O-CO-NH groups have strong tendency to form H-bond with water molecules and further stable adhesion to water may lead to 'petal effect'.[18] The expected 'petal effect' is not observed here because all the -O–CO-NH groups are in the loop of strong inter and intra particle hydrogen bonding (Figure 4).

Figure 3 a) SEM images of a) polydimethylsiloxane grafted $CaCO_3$ microparticles and b) morphology of surface in which the diameters of cross-connected rods /bristles are 1-3 µm in size.

The intense hydrogen bonding of -CO with NH moieties on the siloxane units of the same microparticle and the siloxane chains of other microparticles is evidenced in the lowering of -C=O frequency which is observed at 1647 cm^{-1} (free CO generally appears at or above 1700 cm^{-1}, Figure 5) and at 1620 cm^{-1} respectively. The -NH peaks were appeared at 3317 cm^{-1}. The absence of 'petal effect' in this coating even with the densely packed microrods (like micron level papillae in roses) is ascribed also to the 3-dimensional hydrogen bonding of siloxane chains in which micro $CaCO_3$ particles are encased (hence rod shape in a cross-linked fashion). The diameter of rods is about 1-3 µm (marked in figure 3) and they are cross-connected. In addition, the stability of inter and intra particle hydrogen bonding is tested by thermal cycling tests from 30 to 100 °C for 5 times wherein no change in contact angle and in superhydrophobic properties were noted which imply the strength of hydrogen bonding exist in the SH coating. This irreversible hydrogen bonded network protects the coating from interaction with water molecules and renders it highly water repellent.

Figure 4 Inter and intra microparticle 3D hydrogen bonding in SH coating.

Figure 5 FTIR spectrum of SH coating indicates the hydrogen bonding of CO groups with NH groups-lower absorption of CO groups (at 1647 and 1620 cm^{-1}).

It is known that, most of the SH systems basically deal with the surface level SH properties. [6-10] The case of an entire coating (through thickness) exhibiting superhydrophobicity is rarely known.[11] To prove the bulk level SH feature of the present coating, a 1 mm thick coating was prepared (on glass slide) and contact angle experiments were conducted on the surface and bulk. The original surface (surface I) showed static water contact angle (SWCA) ~154 °, contact angle hysteresis (CAH) ~ 5.2 ° and roll-off angle ~ 7°. Then, the surface I was abraded (to a depth of *ca.* 0.2 mm using razor blade) to obtain surface II, it has SWCA ~156 °, CAH ~ 4.8 ° and roll-off angle ~ 6°. The surface III was obtained by again abrading the surface II. The surface III possessed SWCA ~158 °, CAH ~ 5.0 ° and roll-off angle ~ 6°. The slight increase in the SCA is due to the freshness of surface. Finally, by continuous removal of each surface, a very thin bottom layer is obtained which also displayed excellent SH measures with SWCA~166 °, CAH ~ 5.1 ° and roll-off angle ~ 6°. The SEM image of bottom surface is **(**Figure 6, *see SI5 also***)** varied slightly from the morphology of surface but similar rod/bristle patterns are vivid. The retention of roll-off angle, CAH and static WCA of bottom surface suggest that the top surface, middle portions and bottom (i.e. throughout the material) regions are very close in roughness and morphology features. We attempted to produce roughness of each layer through AFM (for a comparison), but due to the hard and crosslinked structure of material (due to improper contact of AFM probe), reliable results could not be generated.

Figure 6 Self-assembled morphology of bottom surface suggests that the cross-linked microparticles are encased in short PDMS chains.

We performed the surface removal experiments on aluminium surface also to ensure the bulk level SH and it also showed bulk level superhydrophobicity. Figure 7 shows the schematic of layer-by-layer cross-linked microparticles encased in PDMS chains (along with optical image of water droplets from contact angle instrument). This coating is durable in the sense that even if the surface is abraded during use in the long run; the next layer will support to sustain the superhydrophobic property of coating. In addition, this coating has relatively good adhesion to glass and stainless steel surfaces.

Figure 7 WCAs of surfaces from top to bottom (top) and schematic representation of layer-by-layer cross-linked $CaCO_3$microparticles encased in polydimethylsiloxane segments (bottom).

The mehcnical resistance of the coating was examined by exposing the coating to water droplets from a height of 15 cm for ~ 2 minutes (water drop-impact test) and no damage was noticed (WCA-153°). However, continous exposure to water shower from a running tap (15cm, 2 min.) damaged the top layer. But, the freshly exposed layer exhibited equally good or better hydrophobicity (WCA-159°). It validates again that the coating is superhydrophobic in the bulk. Here, the surface is not self-healed but, the underneath 3D surface facilitates the repelling of water droplets.

Conclusions

We have demonstrated a bulk superhydrophobic material by functionalising $CaCO_3$ microparticles and subsequent crosslinking by employing –OH-NCO reaction. The "NoN-REACTIVE" hydroxyl groups of calcium carbonate WERE successfully reacted with dichlorodimethyl silane to build up a PDMS graft. The cross-linking of siloxane segments on microparticle surface and in the bulk enable superhydrophobicity and water roll-off properties. The coating displays static contact angle ~ 155° and water-roll-off angle ~ 5-8° through the thickness of coating. The bulk level SH behaviour is attributed to both inter and intra particle hydrogen bonding and cross-linked rod-shaped morphology of material. This work evinces interest as no fluorine molecules is invoked for achieving such 3-D superhydrophobicity. This is the first ever report of using siloxane and urethane chemistries and that too based on inexpensive $CaCO_3$ microparticles for generating bulk superhydrophobic material and this approach can be extended to other micro/nanoparticles for developing more durable SH coatings.

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Notes and References

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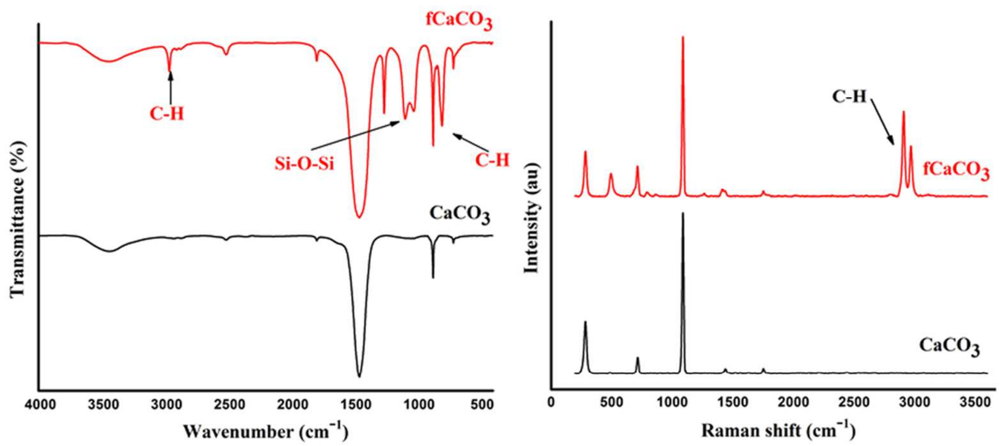

FTIR and Raman spectra of unfunctionalised CaCO3 and siloxane functionalized CaCO3 microparticles (fCaCO3)
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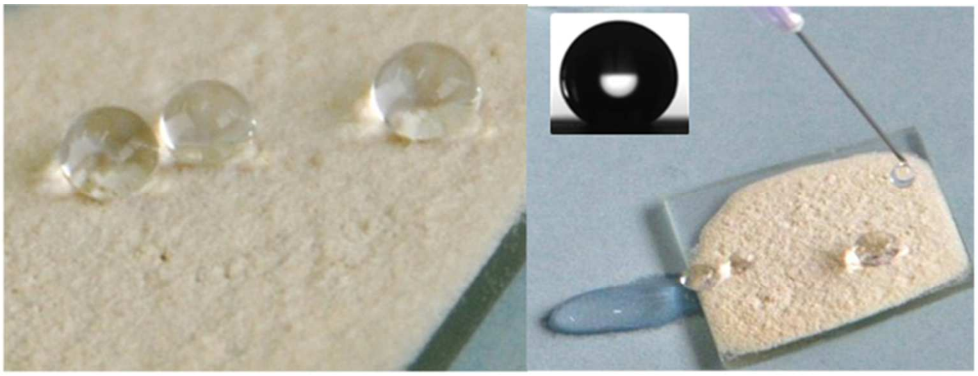
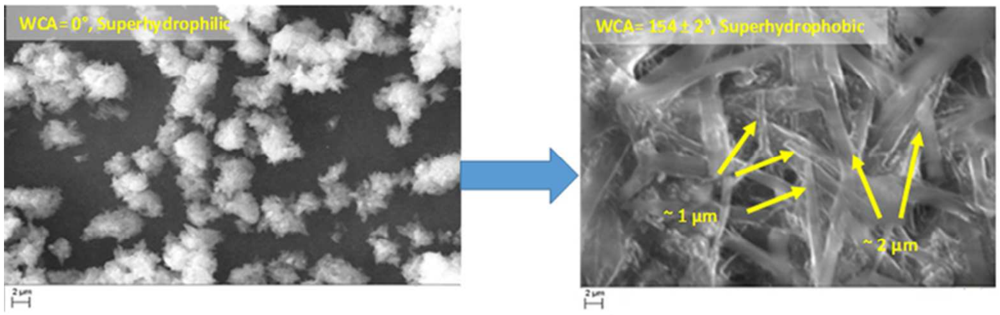
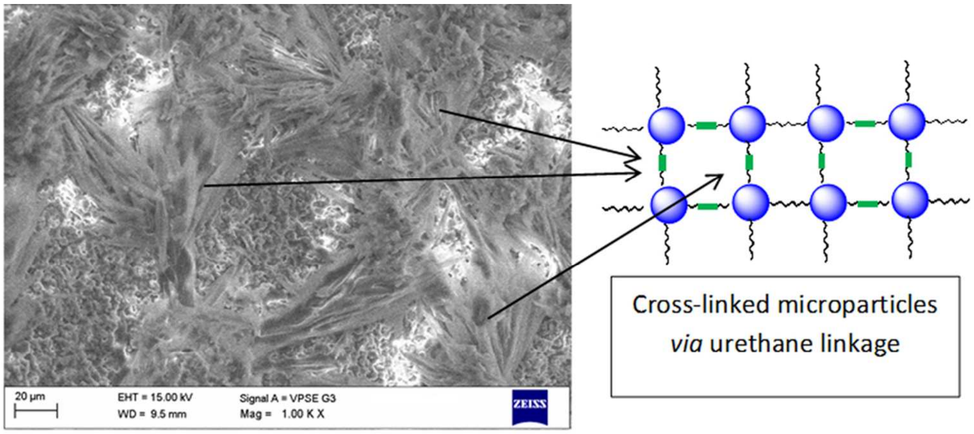


Pictures showing the superhydrophobic features of cross-linked CaCO3 micro particle coating over glass slide a) Water droplet viewed through modern camera (inset: water droplet observed through contact angle meter) b) Roll-off of water droplets at a sliding angle <8 °.
74x28mm (300 x 300 DPI)

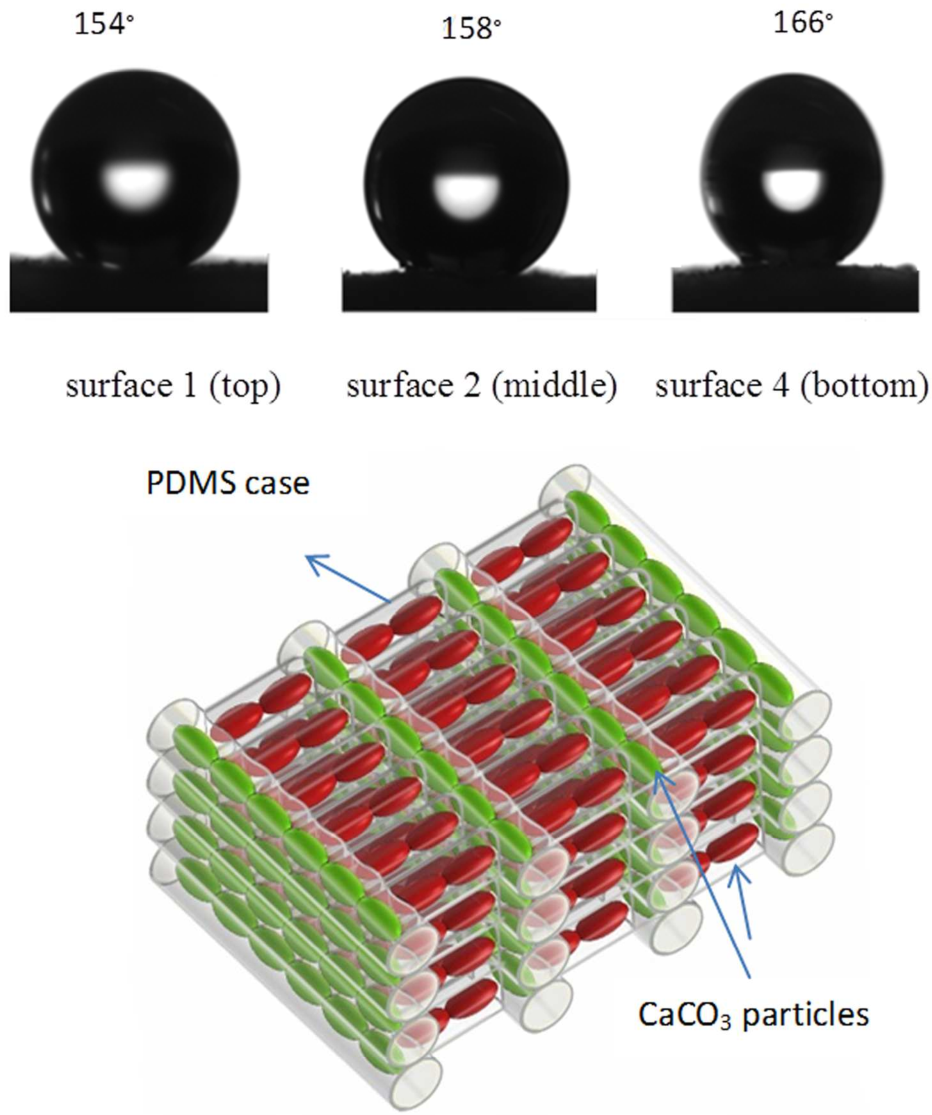


a) SEM images of a) polydimethylsiloxane grafted CaCO3 microparticles and b) morphology of surface in which the diameters of cross-connected rods /bristles are 1-3 µm in size.
67x22mm (300 x 300 DPI)

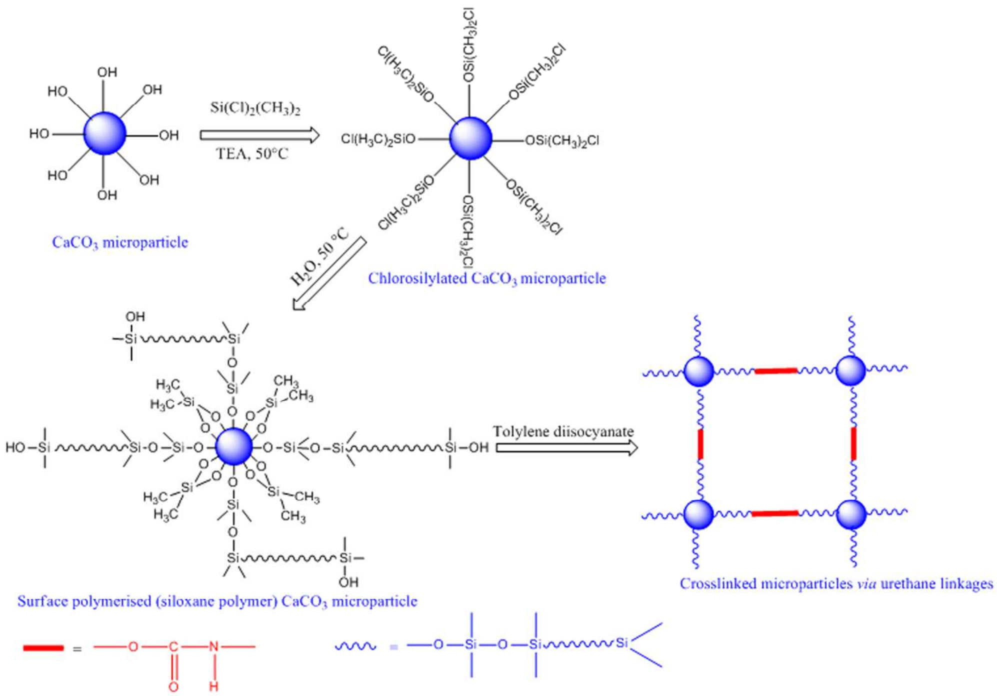
29x16mm (300 x 300 DPI)



Self-assembled morphology of bottom surface suggests that the cross-linked microparticles are encased in short PDMS chains.
91x39mm (300 x 300 DPI)

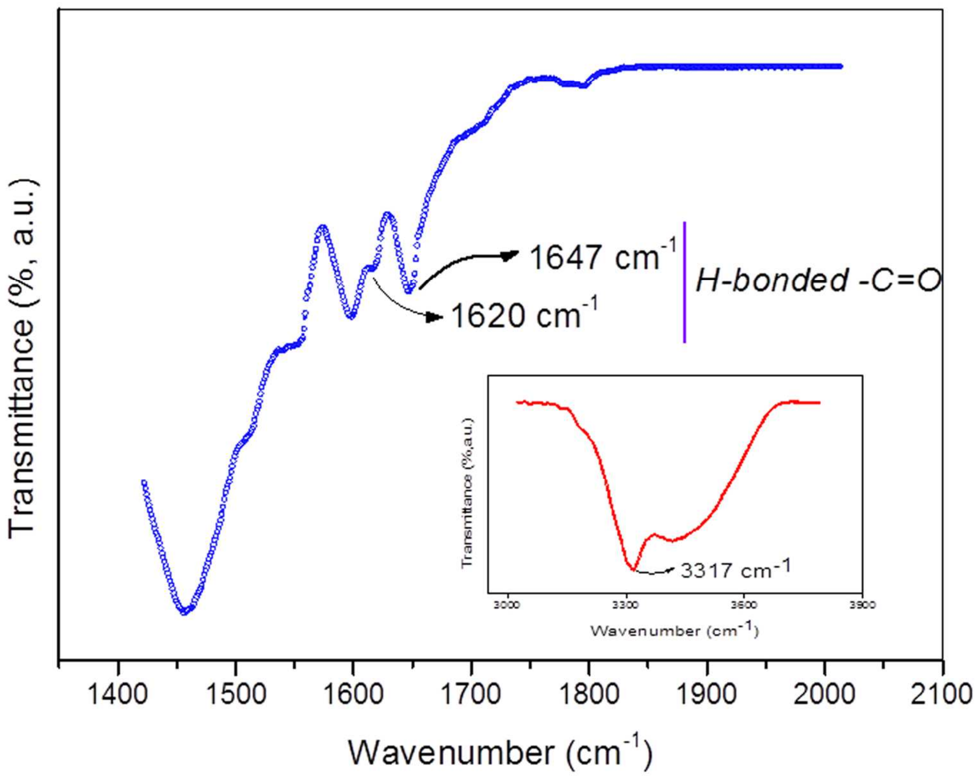


WCAs of surfaces from top to bottom (top) and schematic representation of layer-by-layer cross-linked CaCO3microparticles encased in polydimethylsiloxane segments (bottom).
205x255mm (300 x 300 DPI)



Preparation of cross-linked CaCO3 microparticles by silane modification and urethane crosslinking.

139x96mm (300 x 300 DPI)



147x116mm (300 x 300 DPI)