Janus silica film with hydrophobic and hydrophilic surfaces grown at an oil–water interface†

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We report a new methyltrimethoxysilane (MTMS) based route to growing a Janus silica film at the oil–water interface, which upon drying shows anisotropic wetting by water on its two surfaces. The contact angle of water on the surface grown in contact with the oil-side is found to be ∼150°, but it is much smaller, ∼65°, on the side which grew in contact with the aqueous phase. This large difference in the contact angle is found to be primarily because of two reasons: (i) orientation of hydrophobic methyl groups towards the oil-side of the film as confirmed by micro-Raman spectroscopy, and (ii) microstructural differences in the oil and water-side surfaces of the film. The inherently hydrophobic silica cluster network on the oil-side surface also exhibits larger pores that provide an air cushion for the water droplet and engenders a large contact angle. Effects of oil–water interfacial tension on the film growth and on its wetting and microstructural properties are also investigated by addition of cationic and anionic surfactants in the aqueous subphase. Static and dynamic wetting properties of the oil-side surface indicate that these do not change significantly due to variations in either the microstructure or chemical nature of the surface alone, but is a combined effect of both. Interestingly, the Janus films showing asymmetric surface properties can also be grown directly and thus integrated with a variety of porous surfaces like cotton, paper, hydrogel and ceramic substrates by having these surfaces straddle an oil–water interface.

Introduction

Synthesis of superhydrophobic surfaces (contact angle $\theta > 150°$) is both of technological[1–2] and scientific interest.[3–5] A frequent aim in the synthesis of superhydrophobic materials is to produce environment-independent, robust, large surface areas with relative ease of fabrication. It is a further challenge to transfer or integrate it to other materials like cloths, glass/mirror panes, walls, *etc.* without affecting the native properties of these surfaces. It is known that such surfaces need to be chemically inert to water and rough (patterned or fractal) to be superhydrophobic.[6–9] Further, in many applications,[10–12] a surface or coating with markedly asymmetric wetting properties is desirable. We will refer to such a surface as a Janus film in analogy to the Janus particles and cylinders that have found several applications.[13–16] Although there are many reports on the synthesis and

applications of the Janus particles and cylinders, synthesis of Janus films is an unexplored area. These Janus films may be useful for oil–water separation[17] and microfludic applications.

We report here a new and very simple method for the synthesis of a Janus silica film that exhibits a unique asymmetry of its two surfaces towards wetting by water. We show that the methyltrimethoxysilane (MTMS) based silica films grown at an oil–water interface under suitable conditions and then dried indeed exhibit Janus characteristics. The oil-side surface of the dried silica films is nearly superhydrophobic whereas the water-side film surface is hydrophilic. This method of assembling the film at an oil–aqueous interface is also very useful for controlling the film thickness and porosity, for ease of film transfer or even for growing a Janus film directly on flexible and porous inorganic or polymeric substrates as demonstrated in the present work.

It was shown by Rao *et al.*[18] that hydrolysis and polycondensation of trifunctional MTMS forms a random 3-D silica backbone network and the inert Si–CH$_3$ groups make this network superhydrophobic. In the study of Rao *et al.*,[18] bulk aerogels were prepared by high temperature supercritical drying. Transfer of a film to a new substrate for its eventual use is of frequent interest in various applications. Bandyopadhyaya *et al.*[19] developed a new method to prepare transferable thin films of mesoporous silica by a modified sol–gel processing.

Synthesis and growth of materials at oil–water interfaces is of recent origin. Use of a liquid–liquid interface has been exploited for the synthesis of metal nano-crystals by Rao *et al.*[20–21] and synthesis of mesoporous silica by Faget *et al.*[22] The objective of our study is to grow Janus porous silica films at an oil–water interface with asymmetric wetting properties at the two surfaces

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of the film. A unique advantage of the method developed is that the interfacial film can be easily transferred to another substrate or can even be grown directly at another porous surface straddling an oil–water interface.
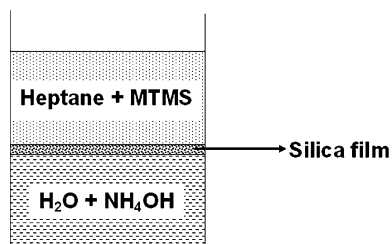
Experimental

Film preparation

A method was developed to grow nearly superhydrophobic/hydrophilic (Janus) silica films at a heptane–water interface. Methyltrimethoxysilane (MTMS) was used as the precursor for silica. Superhydrophobic aerogels have been prepared earlier by both single step and two-step sol–gel processing using MTMS as a precursor.[18,23] In the present work, typically 1 ml MTMS was diluted in 5 ml heptane (oil) (HPLC grade, Qualigens Chemicals) and this mixture was poured slowly on 10 ml of aqueous ammonia solution in a beaker such that the oil–water interface is free of any bubbles and drops. NH_4OH acts as a catalyst for the hydrolysis and condensation reactions between MTMS and water at the oil–water interface to form a silica network. Fig. 1 shows the schematic of this system. To study the effect of the reactant concentrations on the silica film properties, the NH_4OH molarity was varied from 0.05 M to 5 M, keeping the MTMS/heptane molar ratio (H) constant at 0.4. Further, the H value was varied from 0.04 to 0.4 at a constant NH_4OH concentration of 0.1 M. In addition to this, the effect of oil–water interfacial tension on the film growth was studied by dissolving either cationic cetyl trimethyl ammonium bromide (CTAB) [critical micelle concentration (CMC) = 0.9 mM] or anionic sodium dodecyl sulfate (SDS) (CMC = 8 mM) surfactants separately, in the aqueous ammonia solution (*i.e.* subphase). A tensiometer (Fisher Surface Tensiomat, USA, Model 21) using a Pt-ring probe was used to measure the oil–water interfacial tension with and without the surfactants. The surface tensions of water with surfactant and MTMS–heptane mixture were also measured.

Film drying and contact angle measurements

The silica film at the oil–water interface was allowed to grow for different time periods. However, in most cases, a growth period of 2 h was kept constant, which was found sufficient for the formation of self-supporting (thickness ∼500 μm) silica films that were hard enough to be lifted with tweezers without warping. Thinner films, which were not self-supporting, had to be more carefully transferred on a solid substrate by dipping a rigid substrate like a cleaned glass piece underneath the film and slowly raising it. The thinner films could also be thus used for

their further characterization. To study the growth of this film on various substrates like cotton, ceramic and other porous membranes, these substrates were suspended in the beaker in such a way so that the bottom of the substrate got barely wet by aqueous ammonia. The MTMS–heptane mixture was then slowly poured on top of it. The aqueous–oil interface thus formed within the porous substrate. The growth of silica film was initiated at this embedded interface from where it gradually also grew out of the porous medium.

All the films (self-supporting as well as films transferred/grown on substrates) were dried by increasing the temperature in successive steps every 2 h from the room temperature to 60 °C and finally up to 100 °C in an air oven to avoid cracking of the film due to rapid solvent evaporation.

Static and dynamic contact angle measurements were performed using a contact angle goniometer (Rame-hart Inc.). In most cases, we used 5 μl (∼3 mm spherical drop diameter) water droplets. Contact angle measurements with smaller droplets (∼0.5 μl) could also be performed on the films deposited on a rigid substrate. The contact angle measurements with smaller droplets were more difficult on the self-supporting silica films because small scale wrinkles sometime make it difficult to precisely locate the base of smaller droplets. The microstructure of the Janus silica film surfaces was studied using a scanning electron microscope (SEM) (Model: FEI Quanta 200) after sputter coating with an ultra thin layer of gold.

Results and discussion

The unique anisotropic wetting behavior of the oil and water-side surfaces of a typical silica film grown at an oil–water interface is shown in Fig. 2. The oil-side surface is nearly superhydrophobic with a contact angle θ (0.5 μl drop) $\cong 150°$ while the water-side surface is hydrophilic ($\theta \cong 60°$). Advancing contact angle measurements on a horizontal surface give information about the static wetting properties of the substrate. In addition, contact angle hysteresis further determines the true hydrophobic character of a surface.[24] A smaller contact angle hysteresis facilitates the easy removal of water droplets by sliding or rolling (see ESI†). Hence, we also studied the effect of various film synthesis parameters on the static as well as dynamic wetting properties of the silica films by measuring the advancing and
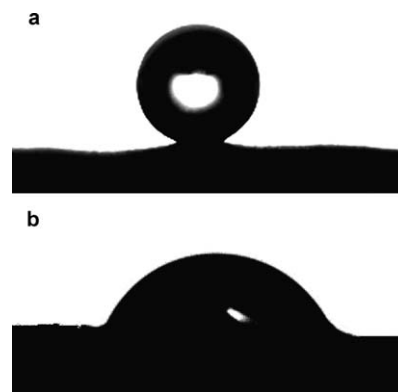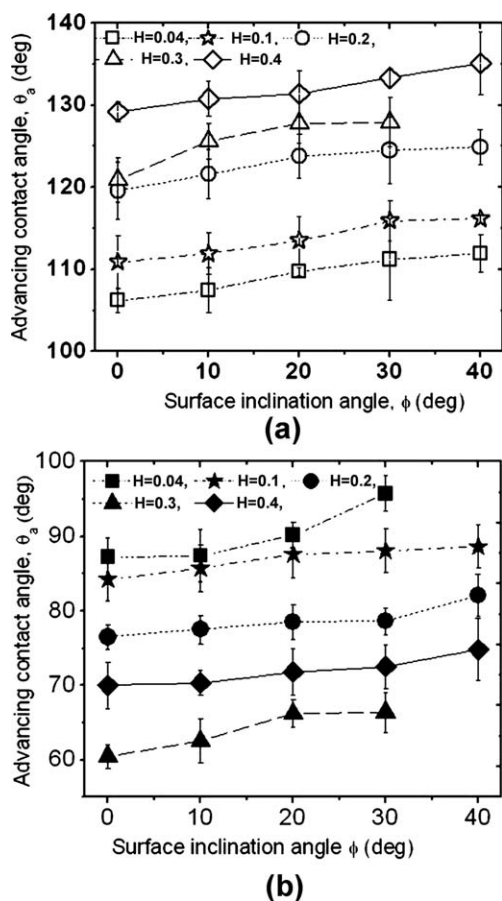

Fig. 2 Janus wetting properties of a typical dried silica film grown at an oil–water interface: (a) oil-side surface, contact angle $\theta \approx 150°$ and (b) water-side surface, $\theta \approx 60°$. Drop volume is 0.5 μl.

Fig. 1 Schematic diagram of the experimental setup used to grow silica film at the oil–water interface.

receding contact angles of water droplets. This was achieved by slowly tilting the goniometer stage containing the silica surface and recording the front (advancing) and the rear (receding) angles until the droplet started to slide or until the maximum tilt angle for the stage was reached.

Wetting properties and contact angle hysteresis studies

The MTMS based Janus silica films prepared at the oil–water interface are extremely stable in the presence of water even after drying. The cracking and flaking observed in the ordinary gels and membranes is due to the capillary adsorption of water into the hydrophilic pores of the dry gel. The adsorption of water generates differential stresses on the wet and dry parts of the films because of the capillary pressure and tears it away. However, as the films prepared in the present studies are intrinsically nearly superhydrophobic because of the –CH$_3$ groups, there is very little penetration of water in the pores. Even on the water-side surface, which is hydrophilic and water spreads and sticks to it, no structural changes were observed. It suggests that the hydrophilicity of the film is limited to a thin surface layer on the water-side of the film.
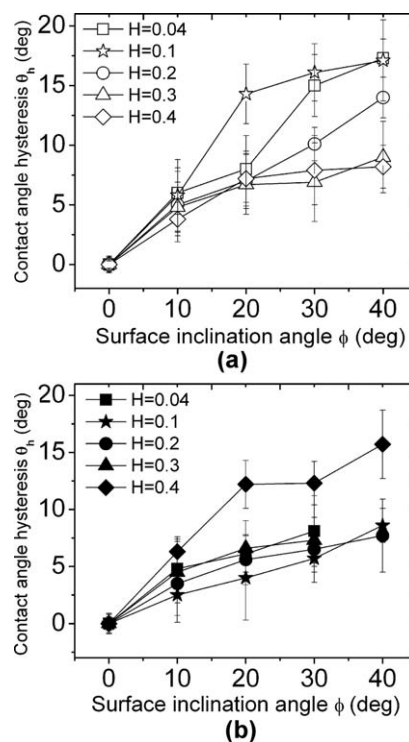
Fig. 3 shows the advancing contact angle of a 5 µl water drop on a tilted (inclination angle ϕ = 0 to 40°) surface of the silica film prepared using different MTMS/heptane molar ratios (H). As H increases from 0.04 to 0.4, the static contact angle increases from 106° to 130° on the oil-side surface, whereas it decreased from 90° to ~65° on the water-side surface. An increased concentration of MTMS leads to a better organic group coverage of the surface, which increases the contact angle. Also, for higher MTMS concentrations, crosslinking of silica particles increases and the film grows more rapidly. This results in thicker silica films of higher roughness as evidenced by the scanning electron micrographs shown later. For H = 0.04 (lower MTMS concentration), the film surface is relatively smooth as compared to that of H = 0.4. This increase in the roughness of the film leads to an increase in the contact angle on the hydrophobic oil-side surface of the film and decreases the contact angle on the water-side hydrophilic surface of the film. These observations are consistent with the earlier reports where it was shown that roughness and porosity of a solid substrate greatly enhance the intrinsic hydrophilicity or hydrophobicity of the surface.[8,25] For still higher H values (>0.4), the self-supporting films become macroscopically rough with wrinkles and it was thus not possible to quantify their wetting properties by contact angle measurements with small droplets.

To study the dynamic wetting properties of these films, contact angle hysteresis (i.e. the difference between advancing and receding contact angles) was measured and is plotted as a function of angle of inclination for oil and water-side surfaces in Fig. 4. It is seen that for higher H (>0.3), the hysteresis on the oil-side surface is lower than 8° even at a surface inclination of 40°. On the other hand, the hysteresis was higher (~15°) on the water-side surface for H = 0.4. These results indicate that

Fig. 3 Advancing contact angle of a 5 µl water droplet on the (a) oil (hydrophobic, hollow symbols) and (b) water-side (hydrophilic, filled symbols) surface of the silica film as a function of MTMS/heptane molar ratio and surface inclination angle.

Fig. 4 Contact angle hysteresis for 5 µl water droplets on the (a) oil and (b) water-side surface of the silica film prepared using different MTMS/heptane molar ratios (H).

some optimal wetting properties of the film are obtained at $H = 0.4$. These include: (a) maximum static contact angle on the oil-side, (b) maximum asymmetry of the contact angle (static as well as dynamic) on the two sides as discussed later, (c) minimum hysteresis of the contact angle on the oil-side which facilitates easy removal of water droplets from this surface, and (d) maximum hysteresis of the contact angle on the water-side which further helps retention of water on this side.

Effect of subphase NH_4OH concentration on the growth and physico-chemical properties of the silica film was studied by varying the NH_4OH concentration from 0.05 to 5 M. With increase in the aqueous subphase NH_4OH concentration, the silica film grows more rapidly. It was found that for NH_4OH concentrations >0.1 M, the overall microstructural and wetting properties of the oil and water-side surfaces of the films do not change significantly. However, there is considerable variation in the wetting properties of the films prepared at still lower NH_4OH concentrations, for example, at 0.05 M NH_4OH. Table 1 summarizes the contact angle values for silica films prepared using different NH_4OH concentrations.

At very low concentrations of NH_4OH (<0.1 M), the growth rate is very slow and very thin films grow at the interface. In addition, small thicknesses may also promote greater homogeneity of various concentrations across the film. Indeed, the difference in the wetting properties of the oil and water-side surfaces is not found to be prominent in the case of thinner films grown with less than 0.1 M NH_4OH. At higher NH_4OH concentrations, the films are thicker and acquire marked asymmetry of the two surfaces. In all cases, the water-side surface of the film is less porous, while the oil-side surface is more porous and is made up of large silica clusters and air pockets that increase its roughness (as described in the microstructural observations below). These observations show that a favourable chemistry at the surface alone is not sufficient for the surface to be superhydrophobic. Roughness and porosity of the oil-side surface, in addition, are equally important in significantly enhancing its hydrophobic nature.

The effect of oil–water interfacial tension was studied by addition of surfactants to the aqueous subphase. In particular, it is of interest to determine if the film growth rate and, consequently, its thickness, microstructure and wetting properties, could be controlled by the addition of surfactants. The surface and interfacial tension values of various liquids used in the present study were measured experimentally and are listed in Table 2.

Table 1 Static contact angle (surface inclination, $\phi = 0°$) of water droplets (5 µl) on the oil and water-sides of the silica films prepared at various NH_4OH concentrations by keeping the MTMS/heptane molar ratio $H = 0.4$

NH_4OH concentration/M	Static contact angle (θ)	
	Oil-side surface[a]/deg	Water-side surface[a]/deg
0.05	107.0 ($\pm$2.5)	91 ($\pm$2.6)
0.1	132.0 ($\pm$2.8)	75 ($\pm$2.3)
0.5	130.8 ($\pm$3.5)	82 ($\pm$2.1)
1	132.0 ($\pm$2)	82 ($\pm$3.2)
5	122.7 ($\pm$3)	62 ($\pm$3.1)

[a] Figures in brackets indicate error estimated from three independent measurements.

Table 2 Surface and interfacial tension of liquids used to prepare silica films

Aqueous subphase liquid	Liquid surface tension/mN⁻¹ m [a]	Subphase–heptane interface tension/mN m⁻¹ [a]
Water	69 ($\pm$1)	49 ($\pm$2)
Heptane	21 ($\pm$2)	—
Below CMC CTAB	53 ($\pm$1)	25 ($\pm$1)
Above CMC CTAB	34 ($\pm$1)	2 ($\pm$1)
Below CMC SDS	47 ($\pm$1)	30 ($\pm$1)
Above CMC SDS	34 ($\pm$1)	5 ($\pm$2)

[a] Figures in brackets indicate error estimated from three independent measurements.

Interestingly, for both CTAB and SDS surfactants, a maximum static contact angle ($\theta \approx 140°$) at the oil-side surface of the silica film was obtained using a subphase solution with the surfactant concentration a little higher than the critical micelle concentration (CMC), even though the two surfactants seem to affect the film formation in different ways. It was observed that the films grew faster in the case of CTAB subphase, possibly because ammonia molecules in the CTAB may act as a catalyst to increase the hydrolysis and condensation rates of MTMS and water. As the CTAB concentration was increased further, the subphase became turbid due to the dispersion of silica particles in the subphase. It should be noted that there is a possibility of oil in water microemulsion formation stabilized by the micelles near the oil–water interface in the presence of higher surfactant concentrations, as reported by Schacht et al.[26] in the case of tetraethoxysilane (TEOS) based mesoprous materials. It is then possible that hydrophobic –CH$_3$ groups of some MTMS molecules may orient themselves interior of the micelles. However, MTMS will continue to condense on the outer walls of micelle as shown by Schacht et al., which may again make the surface hydrophobic. It was observed that for the silica films prepared using CTAB concentrations much above the CMC, the contact angle on the water-side surface also increased to about 100°. The fast crosslinking of the MTMS molecules in the presence of CTAB also may not allow the organic groups to orient towards oil-side. In contrast to the growth characteristics in the presence of CTAB, when SDS was dissolved in the subphase, the subphase always remained clear and the film thickness decreased with increase in SDS concentration. Both of these observations indicate that SDS does not allow MTMS to react with water. Although, the exact reaction mechanism of SDS and MTMS is still unknown, these observations are consistent with the report of Suzumura et al.,[27] where it was observed that addition of SDS to a mixture of polar solvent and MTMS decreases the rate of siloxane phase separation.

From these observations, we selected the following synthesis parameters for preparation of the Janus silica films with optimal oil-side surface hydrophobicity: $H = 0.4$ with 0.1 M NH_4OH subphase. Different cases of the subphase investigated were: (i) without any surfactant, (ii) with CTAB subphase concentration > CMC, and (iii) with SDS concentration > CMC. The static contact angles measured using a 0.5 µl water droplet on oil and water-side surfaces of these selected silica films are given in Table 3.

Table 3 Static contact angle (surface inclination, $\phi = 0°$) of 0.5 μl ($\cong$ 1 mm diameter) water droplets on the oil and water-sides of the silica film prepared using different aqueous subphases but keeping constant the MTMS/heptane molar ratio, $H = 0.4$ and NH_4OH catalyst concentration, 0.1 M.

| Nature of aqueous subphase | Static contact angle ($\theta_{0.5\mu l}$) | |
	Oil-side surface[a]/deg	Water-side surface[a]/deg
CTAB conc. > CMC	153 (±2.4)	75 (±4.5)
SDS conc. > CMC	154 (±2)	68 (±3.4)
No surfactant	152 (±3.2)	65 (±4)

[a] Figures in brackets indicate error estimated from three independent measurements.

Fig. 6 Raman spectra of oil (a and b) and water-side (c and d) surfaces of two dry silica films prepared at the oil–water interface using different MTMS/heptane (H) values. Surfaces (a and c) correspond to oil and water-side surfaces of the silica film prepared using $H = 0.4$, respectively. The curves b and d correspond to oil and water-side surfaces of the film prepared using $H = 0.04$.

It is seen that for all the silica films, the contact angle on the oil-side surface is around 153°, which is almost independent of the presence and type (cationic/anionic) of surfactant in the subphase. However one of the important aspects of the Janus films is their asymmetric wetting behavior on its two surfaces. Thus, the maximum difference in the wetting properties of the two surfaces, including both the static as well as the dynamic contact angles, was also evaluated. Fig. 5 shows this difference for films grown under different conditions. It was observed that the silica film prepared with SDS subphase conc. > CMC shows a large (∼60°) difference in the static contact angle. However, the asymmetry of the two surfaces decreases significantly for dynamic contact angles for this particular film. In contrast, the silica films prepared with an MTMS/heptane molar ratio (H) = 0.4 exhibit almost the same difference in contact angles (∼60°) under both static and dynamic wetting conditions.
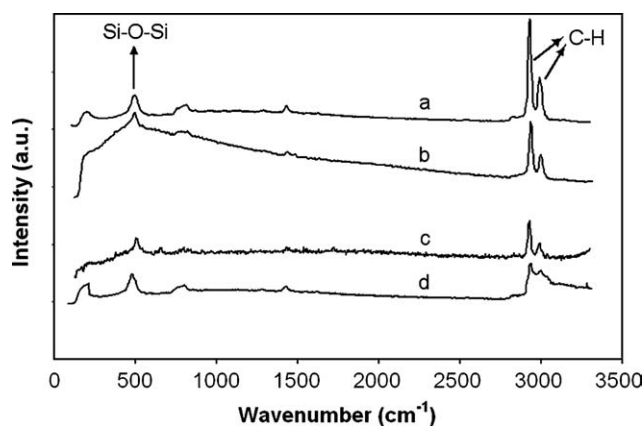
In what follows, we report on the surface characterization of the oil and water-side surfaces to ascertain the reasons for a marked difference in their wetting properties.

Surface chemical characteristics: Raman spectra

The surface chemical groups of the oil and water-side surfaces were studied using a confocal Raman microscope (CRM 200,
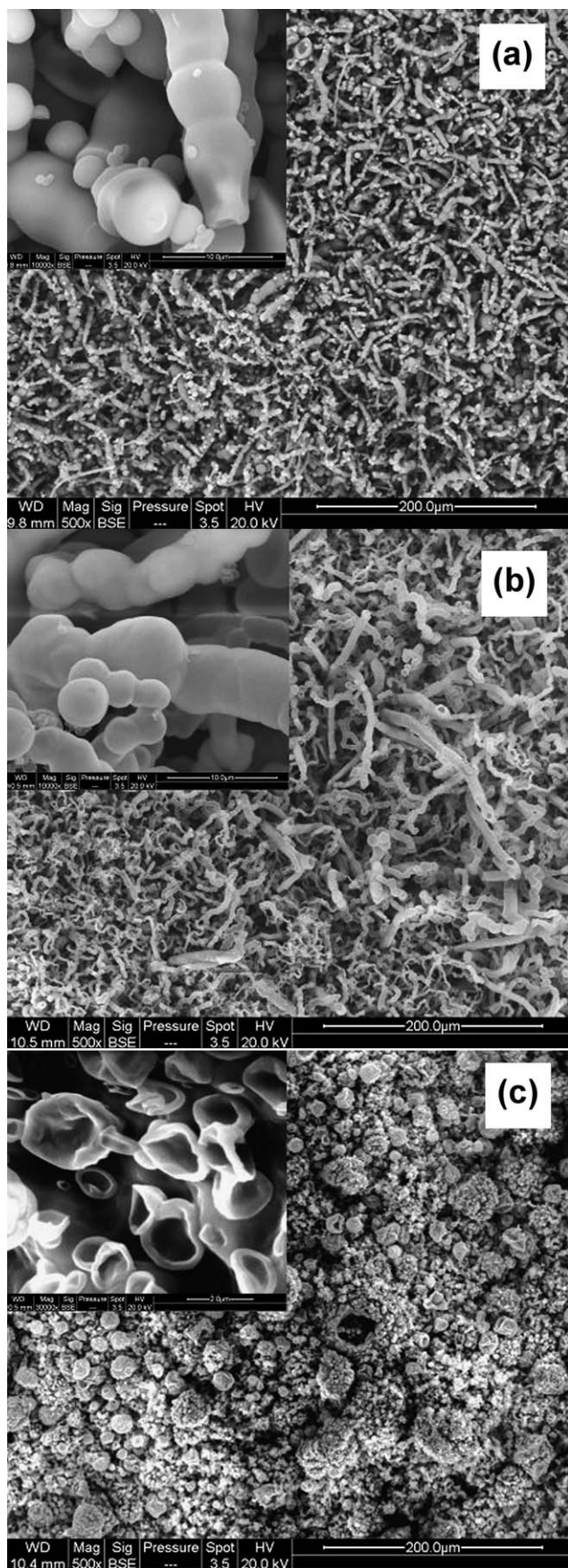

Fig. 5 Difference in the advancing contact angles for a 5 μl water droplet on the oil and water-side surfaces of silica films prepared using different aqueous subphases by keeping the MTMS/heptane molar ratio $H = 0.4$ and 0.1 M NH_4OH catalyst concentration. Square: CTAB subphase concentration > CMC; filled circle: SDS subphase conconcentration > CMC; diamond: $H = 0.4$, no surfactant.

WiTec). A green ($\lambda = 532$nm) laser was used to excite (or annihilate) molecular vibrations and the corresponding energy shift (Stokes or anti-Stokes lines) in the inelastically scattered photon was measured, which is a fingerprint of the material under study. The advantage of confocal micro-Raman over other types of spectroscopic techniques like Raman or Fourier transform infrared spectra is that the area under investigation and signal depth can be controlled very precisely so that the chemistry of the surface groups at the two surfaces can be independently studied and clearly differentiated. The hardware (10) and software accumulations (10) and the integration time (3 s) were kept constant for all the measurements. Fig. 6 shows the Raman spectra of oil and water-side surfaces of the silica films prepared using two different H values. The curves a and c represent the spectra of the oil and water-side surfaces of a silica film prepared using $H = 0.4$, respectively. Whereas the curves b and d correspond to oil and water-side spectra for the film prepared using $H = 0.04$. Very strong absorption peaks around 2932 and 2999 cm^{-1} correspond to symmetric and asymmetric C–H vibrations.[28] Other prominent absorption peaks observed and their assigned bond vibrations for the oil-side surface are: 498 cm^{-1} –S–O–Si,[29] 790 cm^{-1} –Si–CH,[28,30] 1432 cm^{-1} deformation $\delta(CH_2)$ modes of methylene groups.[31,32] Comparing curves a and b, it is observed that the intensity of the C–H absorption band is less for films prepared using $H = 0.04$ to that of $H = 0.4$, which is expected due to the lower number of Si–CH$_3$ groups on the surface of the film prepared using $H = 0.04$.

It is also clearly seen that the C–H absorption peaks are far more pronounced for the oil-side surface as compared to the water-side surface of the silica film. This is because most of the organic groups (–CH$_3$) should indeed be oriented towards the oil-side. To confirm these results, Raman spectra of four different films were recorded and the area under the each of Si–O–Si and C–H peaks was calculated for all the surfaces. It was observed that the average total area under the C–H peaks (calculated in terms of CCD counts) on the oil-side surface was around 200 (±45) whereas it dropped to 60 (±25) for the water-side surface. However, the average area under the peak for Si–O–Si absorption

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band was observed to be about 50 ($\pm$15) for both the oil and water-side surfaces of these films. Therefore, as observed in the wetting behavior studies of the film, the contact angle of the water drop is much higher on the hydrophobic oil-side surface of the film than that of the native silica water-side surface.

Microstructural observations

Although the presence of organic groups (–CH_3) on the oil-side renders it hydrophobic, very large observed contact angles of water approaching superhydrophobicity clearly are also to do with the surface microstructure. Fig. 7 shows the SEM microstructure of the oil-side of the silica films prepared using different NH_4OH catalyst concentrations. The microstructures for 0.1 M and 1 M NH_4OH are shown in Fig. 7 (a) and (b), respectively. Both the surfaces show a porous network formed by chains of silica clusters (as seen in the inset of the figures), but addition of SDS surfactant to the subphase resulted in a flower like microstructure as seen in Fig. 7 (c), which, at a higher magnification, shows a secondary structure of deflated hollow silica spheres covering most of the surface [inset of Fig. 7(c)]. In both the cases, the resulting hierarchal surface is quite rough and presents opportunities for superhydrophobicity in the form of microscopic air pockets.

In contrast to the oil-side roughness, Fig. 8 shows the smoother microstructure of the water-side surface of the MTMS based silica films described above. As seen from Fig. 8 (a) and (b), the microstructure does not change greatly even though NH_4OH concentration increases from 0.1 M to 1 M. However, as compared to its oil-side counterpart, the water-side surface is devoid of micro-porosity. The solid phase of silica is now mostly continuous and there are no differentiable chains of silica clusters. Also, as seen from the insets in Fig. 8 (a) and (b), the surface is covered with secondary structures made up of smaller silica clusters. The microstructure of silica films prepared using a SDS subphase conc > 1 is shown in Fig. 8 (c). Though it has some resemblance to its oil-side counterpart, the water-side surface is smoother and much less porous. In addition, the secondary structures seen in the magnified view [see inset of Fig. 8 (c)] of the films are not made up of the hollow silica clusters as in the oil-side surface. It is precisely this lack of hierarchal roughness that engenders a moderately hydrophilic, rather than a superhydrophilic, water-side of the silica film.

In summary, it is observed that the oil-side surface of the silica films are highly porous and rough as compared to the water-side surface, irrespective of the synthesis parameters. This is because, in the vicinity of water, hydrolysis and condensation reactions of MTMS molecules are faster due to the presence of large numbers of water and ammonia molecules. Hence, the silica film starts to form in the vicinity of water and growth continues towards the oil-side. Initially, there is little time for the individual clusters to grow before they crosslink with each other due to the presence of abundant water molecules for hydrolysis of MTMS. Such a surface is observed in Fig. 8. But as the film becomes thicker,

Fig. 7 SEM images of the oil-side surface of the MTMS based silica films prepared using $H = 0.4$ and various subphase solutions. (a) 0.1 M NH_4OH (b) 1 M NH_4OH (c) SDS subphase conc. > CMC, 0.1 M NH_4OH. Inset shows the magnified view of the surface of the silica clusters. The scale bar for the insets in (a) and (b) corresponds to 10 μm and in (c) to 2 μm.
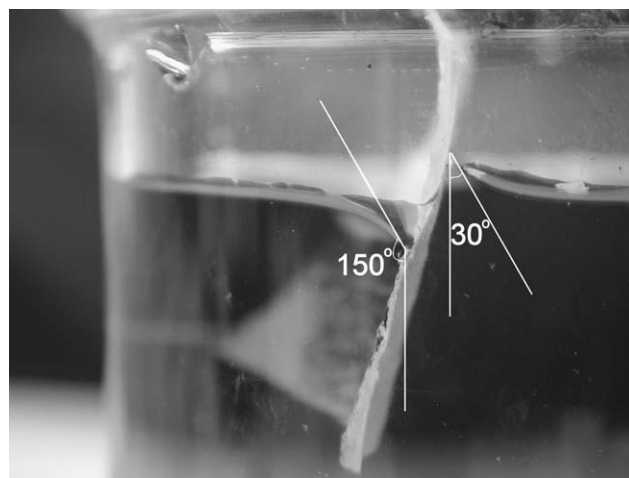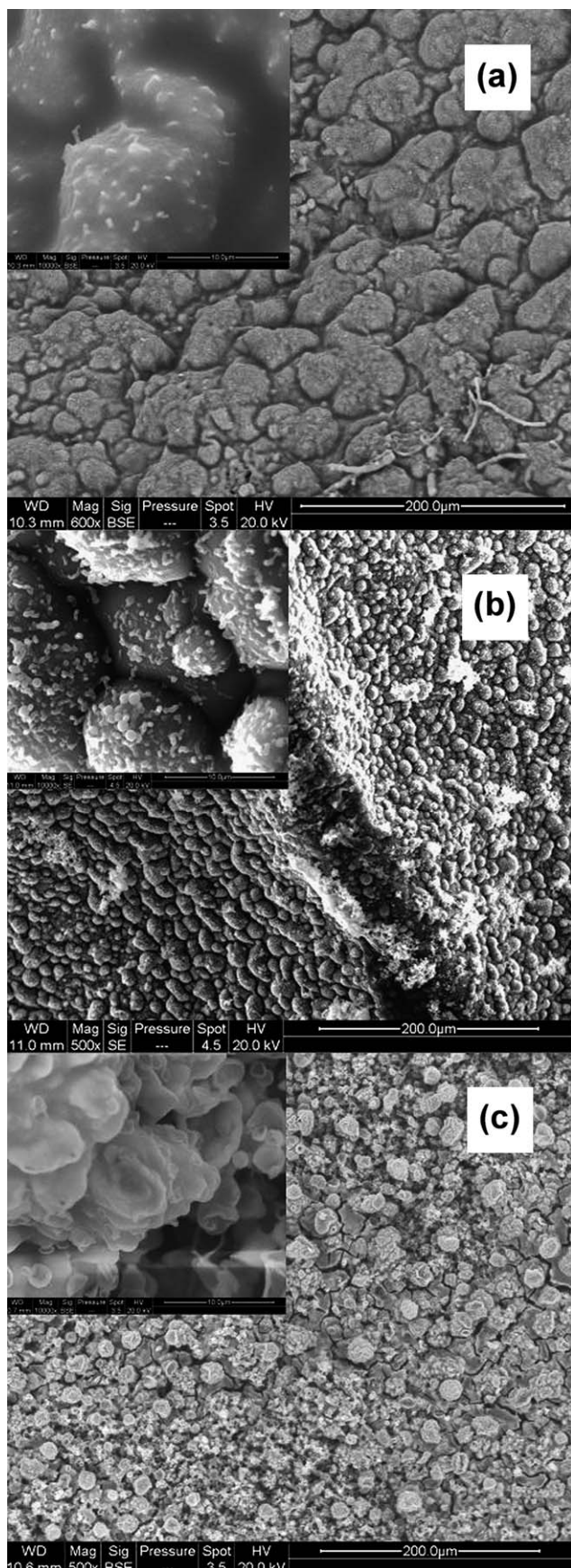
Fig. 9 A typical Janus silica film grown on a cotton cloth and then immersed vertically in a pool of water shows a contact angle of 150° on the oil-side and 30° on the water-side.

the silica network hinders the water supply to the rest of the unhydrolysed MTMS molecules. Silica nucleates slowly, so the individual clusters grow in size before crosslinking to each other. The silica network also becomes more porous because of smaller number of clusters, which are larger in size. This type of network is observed in the SEM images (Fig. 7) of the oil-side surface of the silica films.

The Janus silica films may have potential for applications that involve conflicting requirements of stain- and water-repellency and water compatibility on the twin surfaces of a porous material. We therefore explored the possibility of growing and integrating directly the Janus silica film on various porous supports like cloth, paper, membranes and ceramic materials by suspending these supports at an oil–water interface. The silica film thus grown indeed retained its asymmetric hydrophobic/hydrophilic properties on these supports. For example, the photograph in Fig. 9 shows a MTMS based silica film grown on a cotton cloth, which is then immersed in a pool of water. The oil-side surface of the film displays a contact angle of ~150° (note that the meniscus is positive on the left side of the film) and the other surface of the cotton remained hydrophilic (negative meniscus) with a contact angle of ~30°. This film could even be grown on a hydrogel surface imbibing the aqueous phase (results not shown) and covering the gel surface with a MTMS–heptane mixture. Such a thin composite shows pronounced Janus properties because the gel surface retains its native superhydrophilicity, but the silica surface displays hydrophobicity.

Conclusions

A new technique is reported for the preparation of Janus silica films showing anisotropic wetting properties on its two faces.

Fig. 8 The denser and smoother water-side surface of the MTMS based silica films prepared using various subphase solutions. (a) 0.1 M NH₄OH (b) 1 M NH₄OH (c) SDS subphase conc. > 1, 0.1 M NH₄OH. Insets show magnified view of the clusters revealing secondary structures on their surfaces. The scale bar in the inset figures corresponds to 10 μm.

The silica films were prepared at an oil–water interface and static and dynamic wetting properties of the dried film were studied. The effect of synthesis conditions like MTMS/heptane molar ratio (H) and NH$_4$OH concentration in the aqueous subphase on the dynamic wetting properties of the film was studied. Optimal films of pronounced asymmetry were prepared with $H = 0.4$, which produced superhydrophobicity ($\theta \approx 152°$) and a low contact angle hysteresis ($<8°$) on the oil-contacting face. This film also exhibited a large difference in the contact angle values for the oil and water-side surfaces that was higher than 60°. Higher MTMS concentration and roughness on the oil-side were responsible for these observed properties of the film.

The oil–water interfacial tension was varied by addition of SDS and CTAB surfactants in the aqueous subphase. Films with large differences in the wetting properties (*i.e.* Janus effect) were obtained at subphase concentrations slightly above the CMC of both the surfactants. The highest static contact angle value of 154° was obtained for the oil-side surface of the silica film prepared using a SDS subphase concentration slightly above CMC.

The microstructural studies of these films reveal that the oil-side surface is highly porous and rough as compared to the water-side surface of the film. Micro-Raman studies of both sides of the film clearly show the presence of a large number of organic groups on the oil-side surface, indicating that the organic groups orient themselves towards the oil-side during film growth. These two contributing factors, namely, higher porosity and the presence of a large number of organic groups on the oil-side of the film surface lead to its nearly superhydrophobic nature, whereas the water-side of the silica film surface is relatively smooth and retains its moderate hydrophilicity.

Finally, it was possible to synthesize the Janus films at oil–water interfaces which are self-supporting, as well as grow them directly on various porous materials like cotton, paper and ceramics by straddling the oil–water interface by these porous supports.

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References

1 G. Zhiguang, F. Zhou, J. Hao and W. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 15670–15671.

2 F. Sun, G. Wang and L. Jiang, *J. Am. Chem. Soc.*, 2003, **125**, 14996–14997.
3 P. G. de Gennes, *Rev. Mod. Phys.*, 1985, **57**(3), 827.
4 L. Mahdevan and Y. Pomeau, *Phys. Fluids*, 1999, **11**(9), 2449.
5 A. Pascale and D. Quere, *Nature*, 2001, **411**, 924–927.
6 T. S. Shibuichi, T. Onda, N. Satoh and K. Tsuji, *J. Phys. Chem.*, 1996, **100**, 19512–19517.
7 Y. Chen, B. He, J. Lee and N. A. Patankar, *J. Colloid Interface Sci.*, 2005, **281**, 458–464.
8 A. Marmur, *Langmuir*, 2003, **19**, 8343–8348.
9 X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang and D. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 62–63.
10 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shumoghigoshi and T. Watanabe, *Nature*, 1997, **388**, 431–432.
11 A. Klaikherd, B. S. Sandanaraj, D. Vutukuri and S. Thayumanavan, *J. Am. Chem. Soc.*, 2006, **128**, 9231–9237.
12 Y. Lin, H. Skaff, A. Boker, A. D. Dinsmore, T. Emrick and T. Russell, *J. Am. Chem. Soc.*, 2003, **125**, 12690–12691.
13 V. N. Paunov and O. Cayre, *Adv. Mater.*, 2004, **16**, 788–791.
14 A. Perro, S. Reculusa, F. Pereira, M.-H. Delville, C. Mingotaud, E. Duguet, E. Bourgeat-Lamid and S. Ravaine, *Chem. Commun.*, 2005, 5542–5543.
15 Z. Li, D. Lee, M. F. Rubner and R. E. Cohen, *Macromolecules*, 2005, **38**, 7876–7879.
16 Y. Liu, V. Abetz and A. H. E. Muller, *Macromolecules*, 2003, **36**, 7894–7898.
17 A. V. Rao, N. D. Hegde and H. Hirashima, *J. Colloid Interface Sci.*, 2007, **305**, 124–132.
18 A. V. Rao, M. M. Kulkarni, D. P. Amalnerkar and T. Seth, *J. Non-Cryst. Solids*, 2003, **330**, 187–195.
19 R. Bandyopadhyaya, E. Nativ-Roth, R. Yerushalmi-Rozen and O. Regev, *Chem. Mater.*, 2003, **15**, 3619–3624.
20 C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, V. V. Agrawal and P. Saravanan, *J. Phys. Chem. B*, 2003, **107**, 7391–7395.
21 C. N. R. Rao, G. U. Kulkarni, V. V. Agrawal, U. K. Gautam, M. Ghosh and U. Tumkurkar, *J. Colloid Interface Sci.*, 2005, **289**, 305–318.
22 L. Faget, A. Berman and O. Regev, *Thin Solid Films*, 2001, **386**, 6–13.
23 A. V. Rao, S. D. Bhagat, H. Hirashima and G. M. Pajonk, *J. Colloid Interface Sci.*, 2006, **300**, 279–285.
24 D. Oner and T. J. McCarthy, *Langmuir*, 2000, **16**, 7777–7782.
25 T. Onda, S. Shibuichi, N. Satoh and K. Tsuji, *Langmuir*, 1996, **12**, 2125–2127.
26 S. Schacht, Q. Huo, I. G. Voigt-Martin, G. D. Stucky and F. Schuth, *Science*, 1996, **273**, 768–771.
27 Y. Suzumura, K. Kanamori, K. Nakanishi, K. Hirao and J. Yamamichi, *J. Chromatogr., A*, 2006, **1119**, 88–94.
28 V. Arjunan, S. Subramanian and S. Mohan, *Turk. J. Chem.*, 2003, **27**, 423–431.
29 S. Akyuz, *J. Inclusion Phenom.*, 1984, **3**, 403–407.
30 T. F. Tenisheva, *Russ. Chem. Bull.*, 1989, **38**(4), 767–772.
31 A. A. Morozov, L. V. Khristenko, A. Yu. Pentin, S. V. Krasnoshchekov, E. A. Chernyshev and T. L. Krasnova, *J. Appl. Spectrosc.*, 1984, **40**(6), 689–692.
32 J.-C. Panitz and A. Wokaun, *J. Sol-Gel Sci. Technol.*, 1997, **9**, 251–263.