Transparent Hydrophobic Hybrid Silica Films by Green and Chemical Surfactants

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ABSTRACT: Monodispersed and transparent hybrid silica wires were synthesized by the sol−gel method using the chemical surfactant trimethoxysilyl (C₉TMOS or C₁₁H₂₆O₃Si) and, for the first time, by green surfactants (Nelumbo nucifera/lotus leaf extract). The purpose was to introduce a less toxic, cost-effective, and one-step easy approach to get superhydrophobic silica films. Each of the surfactants was used at two different concentrations to investigate hydrophobicity of the films. Assembly of silica wires was obtained by dip-coating and vacuum filtration methods on glass and cellulose acetate filter paper as substrates, respectively. The water contact angle (CA) up to 154° was measured for hybrid silica films on filter paper, which revealed their superhydrophobicity as compared to hydrophobic behavior of those films coated on a glass substrate with CA up to 135°. Chemical, optical, and structural properties of prepared films were characterized by Fourier transform infrared spectroscopy, UV−vis spectroscopy, scanning electron microscopy, thermogravimetry, and differential scanning calorimetry. The hybrid silica wires prepared displayed good transparency, low surface energy, and superhydrophobicity. These silica assemblies can create outstanding and multifunctional structures with superhydrophobic coatings for waterproof electronic devices, military uniforms, self-cleaning surfaces, etc.

INTRODUCTION

The green chemistry approach has become very popular in recent years because it is environmentally friendly and less toxic in contrast to conventional chemical methods. In green synthesis, plant extracts are used for the bioreduction of materials to form nanoparticles. Green synthesis has numerous applications in nanotechnology such as in medicine, water cleaning, green solar cells, and energy applications. It has been demonstrated that plant metabolites such as terpenoids, sugars, polyphenols, alkaloids, proteins, and phenolic acids play a significant role in the reduction of material ions into nanoparticles.1,2

Primarily, most of hydrophobic coatings and films were used as edible protective films/coatings.3−5 It has been well established that the use of nanofillers such as titanium dioxide,6 zinc oxide,7 silica,8 etc. can generate transparent superhydrophobic coatings for large-scale industrial applications in various fields. Multifunctional transparent silica films/coatings are becoming very popular these days due to their variety of applications from anti-icing9 to antifogging,10 anti fouling,11 anticoronation,12 and anticorrosion.13

To the best of our knowledge, no work has been reported yet on transparent hybrid silica hydrophobic coatings prepared by green synthesis. In the present research work, the hybrid silica films/coatings have been synthesized using a green surfactant (Nelumbo nucifera leaf extract), for the first time, as well as by a chemical surfactant (trimethoxycysilane (C₉TMOS)). The synthesis was inspired by the work of Deliang et al.14 with some modifications that produced excellent water-repellent films on glass slides and cellulose acetate filter paper using the dip-coating method and vacuum filtration, respectively. The effect of the concentration of surfactants on the hydrophobicity of the films was also studied.15 At the industrial level, these hybrid hydrophobic silica films may be used from microfluidic16 and optical devices17 to sensors,18 battery technology,19 ballistic uniforms,20 surgical tools,21 self-cleaning,22 anticorrosion surfaces, etc.23

Wettability by Measuring the Contact Angle (CA). The water contact angles (CAs) of the silica films were measured by a 3D digital camera to study the wettability of the films. First, the silica films grown on cellulose filter paper, prepared by 40 μL of green surfactant (N. nucifera/lotus leaf extract), resulted into the CA of 149° (Figure 1a), showing hydrophobicity, which improved to CA of 150° by doubling the amount of green surfactant, as shown in Figure 1b. The hydrophobic behavior of the films is due to the fact that the N. nucifera leaf extract has long-chain secondary alcohol nonacosan-10-ol and secondary alkanediols as its main chemical constituents. The long-chain secondary alcohols especially secondary alkanediols with a chain length of 29 carbon atoms had already been reported in the composition of tubular wax of N. nucifera.24 These long-chain alkyl groups appear on the surface of the silica film, making it water-repellent.24 Increasing the amount of surfactant adds more alkyl groups to the surface of the film, hence making it more hydrophobic.
Figure 1. Digital photographs of the contact angle formed between the water drop and transparent hybrid silica films on cellulose acetate filter paper using (a) 40 μL of N. nucifera/lotus leaf extract (CA = 149°), (b) 80 μL of N. nucifera/lotus leaf extract (CA = 150°), (c) 40 μL of C8TMOS (CA = 152°), and (d) 80 μL of C8TMOS (CA = 154°).

Figure 2. Digital photographs of contact angles between the drop and transparent hybrid silica films on the glass substrate using (a) 40 μL of lotus leaf extract (CA = 111°), (b) 80 μL of lotus leaf extract (CA = 118°), (c) 40 μL of C8TMOS (CA = 125°), and (d) 80 μL of C8TMOS (CA = 135°).

On the other hand, silica films grown on cellulose filter paper prepared by 40 μL of chemical surfactant (trimethoxyoctylsilane (C8TMOS) or C11H23O3Si) have shown a CA of 152°, which indicates that prepared films are superhydrophobic, as shown in Figure 1c. This superhydrophobicity is attributed to the long-chain C8 alkyl group, which covers the building blocks of Si films. Increasing the surfactant up to 80 μL resulted in a larger CA of 154°, as shown in Figure 1d showing improved superhydrophobicity of the films, which is ascribed to more octadecyl C8 groups grown on silica films.

Second, the silica films coated on glass slides prepared by 40 and 80 μL of green surfactant resulted in CAs of 111° and 118°, respectively, whereas in the case of chemical surfactant (C8TMOS), CAs were found to be 125 and 135°, respectively, for the same concentrations as shown in Figure 2a–d. The CAs showed that these bottom-up-constructed hybrid silica films are hydrophobic in nature. Overall, the contact angles (CAs) for the filter paper films were larger than those on the glass substrate because the roughness of the filter paper surface results into less surface free energy and larger contact angles. This increase in water repellency on doubling the amount of surfactant was much higher in the case of films deposited on the glass substrate (111–135°) as compared to films coated on filter paper (149–154°).

This is because the rough surface of filter paper already provided enough air pockets (Figure 3) and hence the decreased surface area of silica films resulted in superhydrophobicity. An increase in the amount of surfactant (both green and chemical) revealed close networking of the silica as well as more long carbon tails attached to silica wires (Figure 3b,d). The close networking of silica somewhat fills the air pockets (increasing the surface area), but increased number of long carbon tails on the silica coatings give it a hierarchical structure, increasing the water repellency of the films. Hence, the overall effect on the improvement of superhydrophobicity was observed within contact angles of 149° (showing a trend toward superhydrophobicity) to 154°. As materials having contact angle greater than 150° due to the presence of air pockets under liquid drops are superhydrophobic surfaces. However, in the case of the flat glass substrate, no air pockets are present on silica films (Figure 3e,d). The only roughness to the films comes from the silica network itself, providing water repellency in the hydrophobic range (111°), which increases drastically up to 24° (i.e. 154°) on doubling the amount of the surfactant. This considerable jump in water repellency is because the larger amount of surfactant results into much closer networking of silica, producing more air pockets (Figure 3d) on silica films and decreasing the surface area.

FTIR Analysis. Fourier transform infrared (FTIR) spectroscopy was performed by an IRTracer-100 FTIR spectrometer in the 4000–400 cm−1 range. The spectrum formed by molecular adsorption of IR radiation by silica wires forms molecular imprints of the sample, which are ascribed to different vibrations (Table 1).

Most of the plant waxes are hydrophobic, soluble in organic solvents, solid at room temperature, but soft and malleable. These waxes are made up of a mixture of aliphatic hydrocarbons and their derivatives with carbon chain lengths between 20 and 40 atoms. The main constituents are usually primary and secondary alcohols, fatty acids, ketones, and aldehydes. The waxes of N. nucifera (lotus) leaves consist of secondary alcohol nonacosan-10-ol and nonacosanediols as their main constituents. The high content of nonacosanediols results into the growth of a dense layer of very small wax tubules with a permanently hydrophobic surface.
Table 1. Characteristic Vibrational Frequencies (cm\(^{-1}\)) in FTIR Spectra of \(N. nucifera\)/Lotus Leaf Extract and Hybrid Silica Wires (SiWs) Synthesized without and with Surfactants (Green: \(N. nucifera\)/Lotus Leaf Extract and Chemical: \(C_8\)TMOS)\(^{44}\)

| lotus extract | SiWs prepared without surfactant | types of vibrations | structural units | references |
|---------------|----------------------------------|--------------------|-----------------|------------|
|               | 40 μL  | 80 μL  | 40 μL  | 80 μL  | O–H and SiO–H | H–O–H–H\(_2\)O and SiO–H–H\(_2\)O | 30, 31 |
|               | 3387  | 3345  | 3352  | 3359  | \(\nu\) C–H | \(-CH_3\) | 34 |
| 3289          | 2958  | 2979  | 2979  | 2979  | \(\nu\) C–H | \(-CH\(_3\)\) | 34 |
| 2855          | 2854  | 2854  | 2854  | 2854  | \(\nu\) C–H | \(-CH\(_3\)\) | 34 |
| 2109          | 2100  | 2100  | 2100  | 2100  | O–H bending of water | H–O–H | 28 |
| 1635          | 1642  | 1646  | 1651  | 1651  | C=O stretching | C=O | 30–32 |
| 1410          | 1478  | 1478  | 1478  | 1478  | CH\(_2\) bending | \(-CH\(_2\)\) | 33 |
| 1294          | 1374  | 1375  | 1375  | 1375  | C=O stretching | glycosidic bond in cuticle | 29 |
| 1059          | 1039  | 1039  | 1037  | 1037  | C=O–C stretching | glycosidic bond in cuticle | 29 |
|               | 918   | 944   | 941   | 940   | \(\nu\)Si-O–Si | Si–O–Si–O | 34 |
|               | 825   | 825   | 827   | 827   | \(\nu\)Si-O | Si–OH | 31, 35 |
|               | 741   |       |       |       | \(\gamma\) CH\(_2\) | | 34 |

\(\nu\): symmetric stretching vibrations, \(\nu\)as: asymmetric stretching vibrations, \(\delta\): in-plane stretching vibrations, \(\gamma\): symmetric deformation vibrations (bending), \(\gamma\): rocking vibrations.

The FTIR spectrum of the silica wires prepared without any green surfactant (\(N. nucifera\)/lotus leaf extract) and chemical surfactant (trimethoxycysisilane (\(C_8\)TMOS)) is shown in Figure 4b. The peak at 3347 cm\(^{-1}\) is attributed to the strong O–H stretching vibration of H\(_2\)O in the sample,\(^{32–34}\) which is due to the fact that silica particles have a tendency to absorb water from atmospheric air.\(^{34}\) The peaks at 2958 and 2855 cm\(^{-1}\) are attributed to the symmetric and asymmetric stretching vibrations of the C–H group, respectively.\(^{34}\) The peak at 1659 cm\(^{-1}\) is ascribed to imide C=O stretching and that at 1462 cm\(^{-1}\) is due to bending of \(-CH\(_3\)\).\(^{35}\) The peak at 1387 cm\(^{-1}\) is assigned to the C–H symmetric deformation vibrations (bending) of CH\(_2\) groups and that at 1294 cm\(^{-1}\) is attributed to the silicon-bonded alkyl group C–H bending. The band at 1040 cm\(^{-1}\) corresponds to asymmetric stretching vibrations of O–Si–O.\(^{36}\) The peak at 928 cm\(^{-1}\) is assigned to the Si–OH bond,\(^{33,37}\) whereas the one appearing at 846 cm\(^{-1}\) corresponds to the symmetric stretching vibrations of O–Si–O for the prepared sample.\(^{32,36}\) A very feeble peak at 741 cm\(^{-1}\) is ascribed to CH\(_2\) rocking vibrations.\(^{36}\) These bands are very important and especially those at 1040, 928, and 846 cm\(^{-1}\) confirm the presence of silica even without surfactant.

The FTIR spectrum of wires prepared using 40 and 80 μL of green surfactant (\(N. nucifera\)/lotus leaf extract) is shown in Figure 4c. The absorption peaks at 3338 and 3345 cm\(^{-1}\), respectively, are ascribed to stretching vibrations of the O–H bond of water present in silica particles.\(^{33,37}\) Peaks at 2979 and 2854 cm\(^{-1}\) are attributed to the symmetric and asymmetric stretching vibrations of the C–H group, respectively, and are due to the existence of many methyl (CH\(_3\)) groups.\(^{36}\) These methyl groups are a part of the surface of \(N. nucifera\) wax tubules.\(^{38}\) A weak peak at around 2100 cm\(^{-1}\) is present in the spectra of silica wires prepared by 80 μL of green surfactant,
which is absent in the sample prepared by 40 μL of the same surfactant. This peak is due to a combination of hindered rotation and O–H bending of water. The absence of this peak in the second sample is because there are much smaller number of silica wires to absorb water as compared to those in the first sample. The bands at 1642 and 1646 cm\(^{-1}\) correspond to imide C\(\equiv\)O stretching, whereas the peaks at 1478 cm\(^{-1}\) appear due to bending of –CH\(_2\)– in both samples. Weak peaks appearing at 1374 and 1375 cm\(^{-1}\) are assigned to the C–H symmetric deformation vibrations (bending) of –CH\(_2\) groups in the samples prepared by 40 and 80 μL of green surfactant, respectively, whereas the peak at 825 cm\(^{-1}\) corresponds to symmetric stretching vibrations of O–Si–O.32,36 The peaks at 941 and 940 cm\(^{-1}\) are attributed to the Si–OH bond, whereas those at 818 and 827 cm\(^{-1}\) correspond to symmetric stretching vibrations of O–Si–O for the samples prepared by 40 and 80 μL of C\(_8\)TMOS, respectively.

The spectra in Figure 4d revealed that both samples, prepared by 40 and 80 μL of C\(_8\)TMOS, give peaks due to symmetric (2979 cm\(^{-1}\)) and asymmetric stretching vibrations (2854 cm\(^{-1}\)) of the methyl group (CH\(_3\)) bending vibrations of –CH\(_2\)– (1478 cm\(^{-1}\)), and silicon-bonded alkyl group C–H bending (1268 cm\(^{-1}\)) around the same wavelengths as in the case of samples prepared by the green surfactant (N. nucifera leaf extract).

The bands associated with silica in the above discussion such as Si–O–Si and Si–O provide evidence of the presence of silica wires formed in the samples.

**Thermogravimetric Analysis of Samples.** Thermal analysis (TGA, DSC) of silica wires was carried out in an inert atmosphere under a flow of argon gas using Q 600 (TA Instruments) at a heating rate of 15 °C/min to trace the structural changes brought about by the thermal treatment.

The FTIR results of silica wires prepared by 40 and 80 μL of chemical surfactant (trimethoxyoctylsilane (C\(_8\)TMOS) or C\(_{11}\)H\(_{26}\)O\(_3\)Si) are shown in Figure 4d. The peaks at 3352 and 3339 cm\(^{-1}\) are ascribed to stretching vibrations of the O–H bond of water absorbed by silica wires from the atmosphere. A weak peak at around 2100 cm\(^{-1}\) is due to the combination of hindered rotation and O–H bending of water in the samples prepared by 40 and 80 μL of C\(_8\)TMOS. This peak intensity is low enough in the first sample as compared to the second sample, showing that there are smaller number of silica wires in it to absorb water content, as less amount of C\(_8\)TMOS supplies less Si and less silica mesh, which eventually absorbs less water. The band at 1651 cm\(^{-1}\) corresponds to the imide C\(\equiv\)O stretching. A weak peak appearing at around 1375 cm\(^{-1}\) is due to the C–H symmetric deformation vibrations (bending) of –CH\(_2\) groups in the samples. The band at 1037 cm\(^{-1}\) corresponds to asymmetric stretching vibrations of O–Si–O. Peaks at 941 and 940 cm\(^{-1}\) are attributed to the Si–OH bond, whereas those at 818 and 827 cm\(^{-1}\) correspond to symmetric stretching vibrations of O–Si–O for the samples prepared by 40 and 80 μL of C\(_8\)TMOS, respectively.

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The TGA and DSC curves of silica wires prepared without any surfactant are shown in Figure 5a. The results showed a drastic weight loss up to about 87.5% in the range 20–220 °C accompanied by an endothermic peak at 157 °C, indicating the desorption of water, which was absorbed by silica wires and is evident by stretching vibrational and bending peaks of the O–H bond observed in FTIR spectra (Figure 4). TGA and DSC curves of the sample shown in Figure 5a revealed the
sublimation effect in the sample, indicating that prepared silica wires are with good stability within the present temperature range.\textsuperscript{38}

The silica wires synthesized using 80 μL of green surfactant (\textit{N. nucifera}/lotus leaf extract) also show a sudden weight loss up to 33\% till the temperature exceeds 170 °C, which is also evident by an endothermic peak in the TGA curve at 134 °C showing the evaporation of physisorbed water,\textsuperscript{39,40} as shown in Figure 5b. Then, it maintains a plateau till 290 °C, after which there is again significant fall in the weight accompanied by an exothermic effect, which is due to decomposition of C\textsubscript{8} alkyl groups capped on silica films.\textsuperscript{14,40} The sample showed sublimation effect, showing no phase change.

The silica film prepared using 80 μL of chemical surfactant (C\textsubscript{8}TMOS) showed a dramatic decrease in weight of up to nearly 35% in the temperature range 40–165 °C, as shown in Figure 5c. This change corresponds to the endothermic peak in the TGA curve, which occurs due to hydrolysis of the sample, i.e. removal of H\textsubscript{2}O.\textsuperscript{39} Then, the material maintains its weight till 290 °C, after which it showed a further drop of up to 25% weight at around 331 °C due to a small endothermic peak, indicating a further water loss. On further increasing the temperature, the material shows a very slight decrease in weight (about 2%) for the rest of the temperature range.\textsuperscript{39} The sample revealed sublimation effect, showing no phase change, indicating that prepared silica wires are stable in the mentioned temperature range.\textsuperscript{38}

Optical Properties by UV–Vis Spectroscopy. The absorption spectrum of samples containing silica wires dispersed in ethanol was recorded by UV–vis spectroscopy using a U-2800 HITACHI spectrometer in the range 200–800 nm. The UV–visible spectrum of silica wires prepared without any surfactant shows no absorption peak in the visible region (Figure 6), which is due to its wide band gap as glasses have high optical transparency or low absorptivity in the visible range.\textsuperscript{41,42}

The silica wires prepared without any surfactant show absorption bands at 235 nm (Figure 6a). The silica wires prepared by 40 and 80 μL of natural surfactant (\textit{N. nucifera}/lotus leaf extract) show absorption bands at 226 and 230 nm, respectively (Figure 6b), whereas those prepared by 40 and 80 μL of chemical surfactant (C\textsubscript{8}TMOS) show strong bands at 238 and 243 nm, respectively (Figure 6c). The observed red shift suggests a reduction in the band gap upon increasing the amount of surfactant. The reduction in the band gap is related to the increased silica particle size upon increasing the amount of surfactant,\textsuperscript{42} which is also evident by close networking of hybrid silica wires observed in scanning electron microscopy (SEM) results.

SEM Analysis. The surface analysis by scanning electron microscopy (JEOL: JSM-6480) shows the branched silica wire structure, with no cross-linked network and having smaller surface-to-volume ratios\textsuperscript{43} for the sample prepared using 40 μL of C\textsubscript{8}TMOS, as shown in Figure 7a. It is obvious that silica wires consist of a Si core (dark in color) covered by a silicon oxide shell.
This chemically inert Si oxide shell prevents the lateral growth of Si wires and thus the perpendicular growth of the wires has shaped them into a branched structure, as shown in Figure 7a. This less self-assembled structure can be attributed to the comparatively lower hydrophobicity than that of the sample prepared using 80 μL of C₈TMOS. The latter showed a more self-assembled porous network of silica having larger surface-to-volume ratios, as shown in Figure 7c. The resulting hierarchal surface is sufficient to provide superhydrophobicity in the form of microscopic air pockets. The improved hydrophobicity by increasing the amount of surfactant is also evident by the results of contact angle measurements.

**CONCLUSIONS**

Silica films were successfully synthesized in the absence of any surfactant and using green surfactant (N. nucifera/lotus leaf extract) and chemical surfactant (trimethoxycetylsilane (C₈TMOS)). Water contact angles (CA) of both hybrid silica films prepared on cellulose acetate filter paper and those on the glass substrate showed an enhancement in water repellency on increasing the amount of surfactant. However, the improvement by increasing the amount of surfactant is more prominent (up to 24° rise in CA) in the case of films over glass slides. However, overall the water repellency was outstanding in the case of films on cellulose acetate filter (CA = 154°) paper, which endowed them with superhydrophobicity, suggesting that the coatings are highly water resistant, as already reported for rough substrates such as filter paper, cotton cloths, and paper surface. TGA/DSC analysis showed that silica wires prepared without surfactant showed no phase change in the range 0–200 °C, whereas those synthesized with surfactants require the temperature up to 170 °C to change the phase. The red shift observed in UV−vis spectra of hybrid silica wires upon increasing the number of surfactants (in both green and chemical cases) indicates the increased particle size, which is evident by close porous mesh of silica wires in spectra of SEM analysis.

Thus, the hybrid silica wires prepared exhibit good transparency, low surface energy, and superhydrophobicity. These prepared transparent silica wire assemblies provide exceptional opportunities in developing materials with hierarchical structures for multifunctionalities such as superhydrophobic coatings for waterproof electronic devices, military uniforms, self-cleaning surfaces, etc. Also, silica sieves or membranes are emerging candidates for several potential applications involving adsorption and molecular separations due to their large surface areas, high pore volumes, and tunable pore sizes. Detailed studies on using the silica wire assemblies as coatings, substrates, or sacrificial templates are in progress for numerous applications such as separation devices, nanocatalysis, sensors, biomedical applications, and fuel cells. The current work opens a new door toward nontoxic, environmentally friendly, and low-cost silica assemblies for various such applications.
Figure 7. SEM images of hybrid silica wires prepared (a, b) using 40 μL of chemical and natural surfactant (C₈TMOS) and (c, d) using 80 μL of chemical and natural surfactant (C₈TMOS).

Figure 8. Schematic process for preparing hybrid silica wires by the sol–gel method and their assembly as transparent hybrid films on cellulose acetate filter paper and glass substrate.
EXPERIMENTAL SECTION

Synthesis of Hybrid Silica Wires and Films. In a typical synthesis, 2 g of poly(vinylpyrrolidone) (C9H14NO) was dissolved in 20 mL of n-butanol in a 250 mL flask. After that, 2 mL of ethanol, 0.56 mL of distilled water, 1.36 mL of sodium citrate solution (Na3C6H5O7), and 0.40 mL of ammonia (NH3) solution were added sequentially. The mixture was shaken by hand for 2–3 min after each chemical addition. Finally, a mixture of 200 μL of TEOS and green (N. nucifera/lotus leaf extract) or chemical (trimethoxy(ocetyl)silane (C9TMOS): C13H26O5Si) surfactant was added to the above mixture for cross-linkage between water and oil medium and to provide silica. The mixture was shaken for 5 min immediately and left static for 24 h at 37 °C to grow silica wires (SiWs). The sample was then sonicated (DSA100-SK1-2.8L, three times, air-dried for 2 days, and centrifugation tube. The hybrid SiWs were washed with ethanol A) at 4500 rpm for 60 min to separate SiWs in a 15 mL 50 Hz) for 1 h and centrifuged (PLC-3, P = 220 V/50 Hz, 0.65 A) at 4500 rpm for 60 min to separate SiWs in a 15 mL centrifugation tube. The hybrid SiWs were washed with ethanol three times, air-dried for 2 days, and finally used to prepare a suspension of 20 mg/mL concentration of silica in ethanol. Two different samples were synthesized of each of the surfactant using two different amounts, i.e. 40 and 80 μL.

Silica Wire Assembly on Filter Paper. Vacuum filtration (Rocker: 300 C-VG 12) was performed to coat the hybrid silica film on cellulose acetate filter paper. In a typical procedure, the above-prepared suspension of silica wires was filtered through a cellulose acetate filter paper (pore size, 0.40 μm) to form an interwoven silica wire assembly on the filter paper. After washing with ethanol twice, the hybrid silica film on the filter paper substrate was air-dried.

Silica Wire Assembly on Glass Substrate. The dip-coating method was applied using a Dip Master TM-100 dip-coater to assemble silica wire films on the glass substrate. In a typical procedure, the already cleaned glass substrate with different amounts, i.e. 40 and 80 μL of TEOS and green (N. nucifera/lotus leaf extract) or chemical (trimethoxy(ocetyl)silane (C9TMOS): C13H26O5Si) surfactant was added to the above mixture for cross-linkage between water and oil medium and to provide silica. The mixture was shaken for 5 min immediately and left static for 24 h at 37 °C to grow silica wires (SiWs). The sample was then sonicated (DSA100-SK1-2.8L, V = 220 V, P = 100 W, 50 Hz) for 1 h and centrifuged (PLC-3, P = 220 V/50 Hz, 0.65 A) at 4500 rpm for 60 min to separate SiWs in a 15 mL centrifugation tube. The hybrid SiWs were washed with ethanol three times, air-dried for 2 days, and finally used to prepare a suspension of 20 mg/mL concentration of silica in ethanol. Two different samples were synthesized of each of the surfactant using two different amounts, i.e. 40 and 80 μL.

Flocculation Test. When the suspension of silica wires was prepared in distilled water, flocculation occurred, which indicated the water repellency property of the synthesized silica wires.

Preparation of Nelumbo nucifera/Lotus Leaf Extract. First, 25 g of crushed N. nucifera/lotus leaves were dipped in 100 mL of n-hexane for 24 h in a 500 mL air-tight beaker, to prevent n-hexane from evaporation. The greenish extract was then filtered and left open in air to evaporate n-hexane, and finally a yellowish green extract was obtained.

Chemical Reactions. Sodium citrate was added to the mixture to stabilize the emulsion. When it reacted with ammonia, which was used to control the pH of the chemical reaction, first, the solution got acidic due to free H+ ions obtained from H2O and the solution became slightly acidic. Then, sodium citrate turned to citric acid. When sodium citrate reacted with ammonia, ammonium citrate was formed and no free H+ ions were present in the solution.

By the sol–gel process, TEOS produced the silica nanoparticles by the following steps:

Due to anisotropic deposition, which was caused by hydrolyzed TEOS, Si nanoparticles were produced in half an hour, inside the droplets of H2O. The Si nanoparticles deposited at the edge of the water droplets to reduce the surface energy for attaining superhydrophobicity. It is important to know that superhydrophobicity and surface energy are inversely proportional to each other. One side of the Si nanoparticles was attached to the oil medium and the other side with water medium. The growth of silica by sol–gel occurred only in water medium. The hydrolyzed TEOS was stabilized by sodium citrate. TEOS was passed through sodium citrate into the water medium to react with the silica nanoparticles.

When was C9TMOS added, it was dissolved in n-butanol (oil phase) and hydrolyzed into C9Si(OH)3 when it came across water medium. C9Si(OH)3, joined itself by its hydrophilic side, i.e., the Si(OH)3 ion with water and its hydrophilic tail, i.e., C9 with n-butanol. This fact proved that it has amphiphilic character. Due to this behavior of C9Si(OH)3 as a surfactant, the surface tension of water droplets was minimized and they joined with SiO2 nanoparticles. Thus, polymerization is associated with the formation of a 1-, 2-, or 3-dimensional network of siloxane [Si–O–Si] bonds accompanied by the production of H–O–H and R–O–H species. Condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon-containing molecules by the process of polymerization. Thus, a polymer is a huge molecule (or macromolecule) formed from hundreds or thousands of units called monomers. The number of bonds that a monomer can form is called its functionality. polymerization of silicon alkoxide, for instance, can lead to complex branching of the polymer because a fully hydrolyzed monomer Si(OH)3 is tetrafunctional (can branch or bond in four different directions). Alternatively, under certain conditions (e.g., low water concentration), fewer than four of the OR or OH groups (ligands) will be capable of condensation, so relatively little branching will occur. The mechanisms of hydrolysis and condensation and the factors that result in bias toward linear or branched structures are the most critical issues of sol–gel science and technology. This reaction is favored in both basic and acidic conditions. The hydrolysis of TEOS molecules forms silanol groups. The condensation/polymerization between the silanol groups or between silanol groups and ethoxy groups creates siloxane bridges (Si–O–Si) that form the entire silica structure.

\[
\begin{align*}
\text{Si(OH)}_3 & \rightarrow \text{Si(OH)}_2\text{OH} + \text{H}_2\text{O} \\
\text{Si(OH)}_2\text{OH} & \rightarrow \text{Si(OH)}\text{OH} + \text{H}_2\text{O} \\
\text{Si(OH)}\text{OH} & \rightarrow \text{Si} + \text{H}_2\text{O}
\end{align*}
\]
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