

Fabrication of Superhydrophobic Surface from a Supramolecular Organosilane with Quadruple Hydrogen Bonding

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Hydrogen bonds play an important role in determining the three-dimensional structure of chemical and biological systems because of their specificity and directionality.¹ In contrast to covalent bonds, which are stable under normal conditions and can only be broken by providing sufficient energy, the formation of hydrogen bonds is reversible and their strength depends on the chemical environment, such as the solvent or temperature. Further, stable supramolecular assemblies can also be obtained in more polar solvents, such as chloroform or acetonitrile, that are bound together by the combination of several such weak interactions in binding motifs with multiple hydrogen bonds.²

Motivated by a self-assembling ADAD array of quadruple hydrogen-bonding donor (D) and acceptor (A) sites,^{6,7} we synthesized a novel supramolecular organosilane (supraTES), 2-(3-(triethoxysilyl)propylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone, having quadruple hydrogen bonds (Figure 1) that can be applied as a functional coating material via hydrolysis and polycondensation, resulting in a superhydrophobic coating. Recently, a superhydrophobic surface having a water contact angle greater than 150° has attracted much attention both in fundamental research and practical applications.³ Conventionally, the wettability of a solid surface can be controlled by both the chemical composition and the geometrical microstructure of the surface; the wettability can be decreased by creating a local geometry with a large geometric area relative to the projected area. This effect can be observed in nature on the leaves of the sacred lotus.⁴

In this communication, we describe a novel method to fabricate a superhydrophobic surface by the simple sol–gel process at room temperature using a supramolecular organosilane having quadruple hydrogen bonds. This supramolecular organosilane is present in a phase-separated state in solution and even after the sol–gel process, because considerable stabilization results from the dimerization that occurs due to the linear array of four hydrogen bonds.⁵ This unique property of the supramolecular organosilane means that in a sol–gel process it provides a simple phase-separation method that does not require any other hardening process or additives.

The supraTES was synthesized in a single step from commercially available starting materials, (3-triethoxysilyl) propylisocyanate and 2-amino-4-hydroxy-6-methyl-pyrimidine (see Supporting Information). Figure 1C shows the FTIR spectra of the supraTES. The bands at 3216 and 3150 cm⁻¹ are assigned to the hydrogen-bonded NH groups of pyrimidinone.⁵ In the ¹H NMR spectrum of supraTES in CDCl₃ (see Supporting Information, Figure S1) the NH proton signals at 13.15, 11.86, and 10.15 ppm are indicative of extensive hydrogen bonding.⁵ Since they have the strong quadruple hydrogen bonds, these supraTES can trigger the phase separation in any kind of polar solvents. As reported by Meijer and co-workers,⁵ this supraTES in concentrated solution

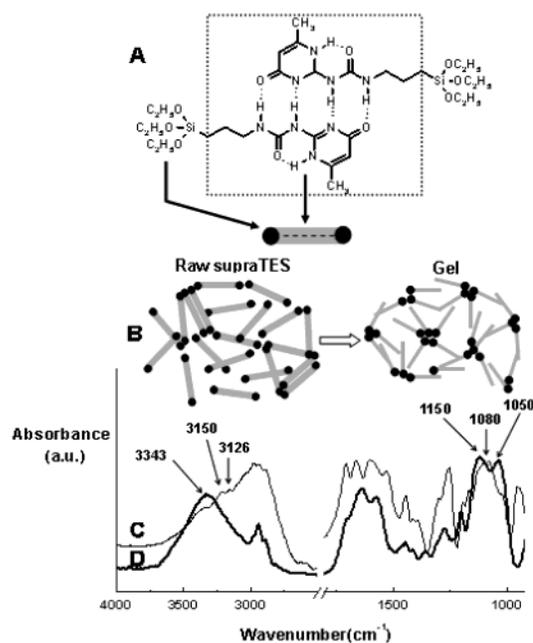


Figure 1. Possible structure of a synthesized supramolecular organosilane (supraTES) in solution (A) and the FTIR spectra of raw supraTES (C) and a gelled one (D) (hydrogen-bonded NH: 3216, 3150 cm⁻¹; free NH: 3343, Si–O: 1080, and Si–O–Si: 1050, 1150 cm⁻¹). (B) Schematic of the inner structure of supraTES in the interconnected granular structure during sol–gel process.

exists in a dimerized state. In this study, we investigate the use of this supramolecular organosilane as a functional coating material, i.e., a superhydrophobic coating with an intrinsically phase-separated structure.

An interconnected granular structure is obtained by casting the supraTES solution (ultrasonically dispersed in a volatile polar solvent such as ethyl acetate without H₂O) onto a flat solid surface, as shown in Figure 2A; the diameter of the granules in this structure was found to be approximately 500 nm. We were also able to obtain the same interconnected granular structure by evaporating the solvent mixture. This kind of phase-separated granular structure can also be obtained with alkylsilanes by a sol–gel phase-separation process. However, the method requires some kind of hardening process to freeze a phase separation.⁸

Compared with other template syntheses, this approach to fabricating a phase-separated continuous material is a very simple way of producing a superhydrophobic coating and is made possible by the supramolecular characteristics of our novel organosilane. The fabrication procedure involves a single step in which the supraTES solution is cast onto a solid surface and a small amount of low molecular weight poly(dimethyl siloxane) (PDMS) (*M*_n = 583 g/mol) is added to the supraTES solution to minimize the

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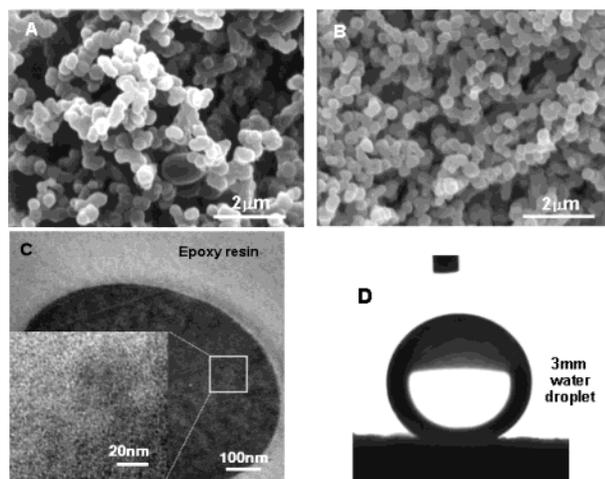


Figure 2. SEM (A, B) and TEM (C) images of a phase-separated supraTES. (A) As cast with supraTES/ethyl acetate solution onto a glass. (B, C) Suprates foam made by supraTES/ethyl acetate/HCl/H₂O/PDMS mixture via sol-gel process. (D) Shape of water droplet (diameter = 3 mm) on B.

contact area; this layer acts in a manner analogous to the waxy layer on the leaves of the sacred lotus.⁴ The mixture was stirred at 25 °C for 12 h, then cast on glass substrates and air-dried at room temperature for 2 days.

Figure 2B shows the typical picture of the cross-linked supraTES; the gelled supraTES consists of strings of globules around a network of pores with a granule size of approximately 500 nm, which is similar to that of raw supraTES (Figure 2A). The small amount of PDMS added to the supraTES solution does not affect the structure because PDMS is soluble in ethyl acetate, the solvent used in this study. During the evaporation of the solvent, the hydrophobic PDMS should tend to be localized at the surface, thereby lowering the free energy of the system.

The FTIR spectra in Figure 1 demonstrate the effect of the sol-gel process on the chemical structure of supraTES. After the sol-gel process, the Si-O band from Si-O-C₂H₅ at 1080 cm⁻¹ is no longer present and Si-O-Si bands have appeared at 1050 and 1150 cm⁻¹. Further, after the sol-gel process it is noticeable that the bands due to hydrogen-bonded NH groups have disappeared and bands due to free NH groups have emerged at about 3300 cm⁻¹. These results show that the four hydrogen bonds in supraTES play a significant role in the formation of an intrinsically phase-separated structure and are disrupted by hydrolysis and polycondensation during the sol-gel process. From the TEM image (Figure 2C) and FTIR spectra (Figure 1) of a supraTES, we speculate that a dimerized supraTES acts as a difunctional rigid organosilane with the general formula of (R'O)₃Si-R-Si(OR')₃(R, R' = organic groups),⁹ which, due to the steric hindrance, make a complete isotropic organization with no preferential orientation of the molecule as shown in Figure 1B. Although after the sol-gel process, the hydrogen bonds are disrupted by hydrolysis and polycondensation, the supramolecular silane retains its macroscopic granular structure. However, comparison of Figure 2A and 2B reveals that the size of the grains in the granular structure appeared to be more uniform after the sol-gel process. The discovery of this property of intrinsic phase separation of supraTES in solution motivated our investigation of the fabrication of a superhydrophobic surface using supraTES. As shown in Figure 2B, the surface of the phase-separated supraTES is sufficiently rough that air can be

present in the troughs between the strings of granules. The surface of this supraTES can therefore be regarded as a composite surface consisting of interconnected granules and air.

Figure 2D shows an image of a water droplet (diameter = 3 mm) on the surface of the phase-separated supraTES; the water contact angle is more than 150°. This is in stark contrast to the PDMS with a smooth surface, on which a water contact angle of only (109 ± 0.8)° is observed. These results indicate that the phase-separated structure due to the supramolecular characteristics of our organosilane with a quadruple hydrogen bonding is responsible for the superhydrophobicity. This topographical effect on superhydrophobicity corresponds well to the Wenzel and Cassie models.^{10,11}

In conclusion, we synthesized a supramolecular organosilane having quadruple hydrogen bonds, and the fabrication of a superhydrophobic surface was achieved by using this material and low molecular weight PDMS. The supramolecular organosilane possesses an intrinsically phase-separated structure in solution, which is retained even in the gel state. To the best of our knowledge, this is the first attempt to fabricate a superhydrophobic surface using a supramolecular organosilane material through a simple sol-gel process.

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Supporting Information Available: Experimental details and NMR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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