A Novel Method of Preparation of Superhydrophobic Nanosilica in Aqueous Solution

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(Received September 7, 2005; CL-051148)

A novel method of preparation of superhydrophobic nanosilica by surface-modification in situ in aqueous solution is reported in this paper. The silica nanoparticles modified by hexamethyldisilazane show superior hydrophobic and excellent dispersive properties in organic solvents. Wettability studies show that the film of nanosilica is superhydrophobic with a very large contact angle (167 ± 2°) and a small sliding angle (less than 2°).

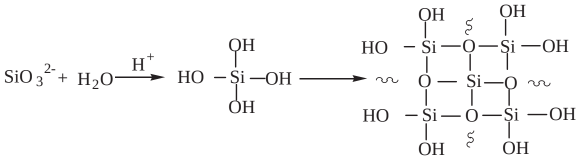
The wettability of a solid surface is a very important property and is governed by both the chemical composition and the geometrical microstructure of the surface.[1] Superhydrophobic surfaces, with a water contact angle (CA) larger than 150°, have attracted a lot of interest because of the potential in practical applications.[2]

High-quality silica nanoparticles, especially those with superior hydrophobicity and oleophilicity, are usually prepared by fuming reaction—a costly and complicated method.[3] The superhydrophobic silica aerogels prepared using methyltrimethoxysilane precursor, alkyl alkoxychlorosilane coprecursors, and their surface derivatization in organic solvents are also expensive owing to the costly materials and solvents.[4,5] Many investigators treat precipitated nanosilica with various modifiers to improve its surface properties. But it is difficult to make the nanosilica that is not only well dispersive in organic solvent but also superior hydrophobic.[6]

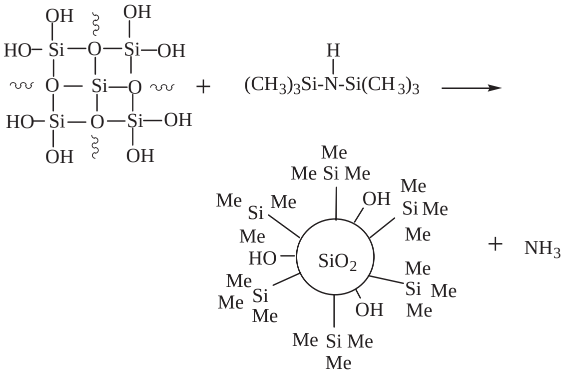
In this paper, we introduce a new route of synthesizing superhydrophobic nanoscale silica by surface-modification in situ in aqueous solution. We present the typical formula and technique used in our study in the following.

The stoichiometric amount of sodium metasilicate with a density of 0.8–1.0 g/mL was dissolved in deionized water at a certain concentration in a reactor equipped with a condensator and two isopiestic dropping funnels. A solution of hydrochloric acid dissolved in deionized water was placed into one funnel. The weighed hexamethyldisilazane (HMDS) dissolved in absolute alcohol as the modifier was placed into the other funnel. At first, we added half of the hydrochloric acid solution to the reactor with stirring at room temperature. Then, the rest of the hydrochloric acid and the modifier were added dropwise to the reactor simultaneously. When the concentration of sodium metasilicate was equal to that of hydrochloric acid, the reaction solution appeared turbid. Gradually, an amount of foam appeared on the surface of this aqueous solution. The suspension was heated to 60 °C and was stirred for 4 h at this temperature. Then, the obtained solution was put into a separating funnel. The suspension was separated into two layers quickly, and a layer of white floc floated on the top. The clear aqueous solution at the bottom was dropped out thereafter. The floc was collected by filtration and washed repeatedly using a mixed solution of deionized water and alcohol until Cl^- could not be detected using silver nitrate solution by visual examination. Here, Cl^- and Na^+ were removed at the same time. The filtered cake was redispersed into a quantity of mixed solution of deionized water and alcohol at a volume ratio of 1:1 to form emulsion. Finally, the emulsion was spray-dried and loose SiO_2 nanoparticles were obtained (with a yield rate of over 93% measured based on the Si of sodium metasilicate and HMDS). A typical formula was used as follows: 0.3 mol/L sodium metasilicate, 0.72 mol/L hydrochloric acid, and 0.05 mol/L modifier. The size of nanoparticles can be conditioned on the concentration of the sodium metasilicate and the modifier. If the concentration of the sodium metasilicate increases or the concentration of the modifier decreases, the size of particles will become bigger.

Surface-modification of such nanosilica in situ is a polyreaction-like process[7] where the hydrolysis product of sodium metasilicate is used as the monomer and HMDS as the chain terminator. The condensation polymerization of hydrolysis products is a process of chain growth and surface-modification is analogous to chain termination. We hypothesize that the condensation-like polymerization is carried through in the following mode:



(1)



(2)

where the Me stands for the $–CH_3$.

First, sodium metasilicate is hydrolyzed to form the silicic acid under the existence of HCl. Condensation polymerization happens by anhydration among the hydroxyls of silicic acids at three dimensions and the Si and O are bonded to each other to form nanosilica clusters. Large numbers of hydroxyls are left on the surface of the nanoclusters. In the mean time, HMDS is hydrolyzed to produce trimethylsilyl and ammonia. As soon as

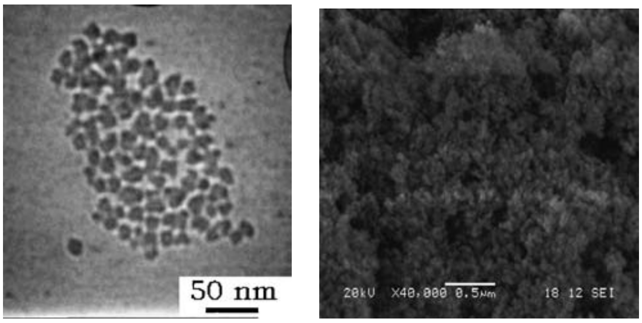


Figure 1. TEM (Left) and SEM (Right) photographs of nanosilica.

the nanoclusters are formed, the trimethylsilyl reacts rapidly with the hydroxyl of nanosilica to form the modification layer on the surface of the clusters. Here, the trimethylsilyls substitute a majority of active groups of SiO_2 and result in a steric hindrance, which prevents SiO_2 from continuously growing up or agglomerating. These reactions are competitive to each other. By controlling the reaction conditions, we can obtain nanosilica particles "capped" with organic compound.[8,9]

The left photograph in Figure 1 shows the transmission electron microscope (TEM) photograph of the nanosilica dispersed in alcohol. These uniform particles are about 20 nm in size. And the "capped" nanoparticles show strong hydrophobic properties. After the particles are mixed with water under ultrasonic waves, the white nanosilica rapidly rises and floats on the surface, and the interface becomes very clear. The nanosilica's wettability was further observed by measuring the water contact angle (CA) of the nanosilica film. We prepared the film in the following steps. After the nanosilica was dispersed into a toluene solution, a microscope slide was dipped in the solution. After the toluene volatilized, a film was formed on the slide surface. A scanning electron microscope (SEM) photograph of the film made of such nanosilica particles is presented on the right of Figure 1. The formed film has a rough surface where the white parts indicate silica particles and the black parts are void. The CA was measured on a JY-82 Contact Angle Measuring Instrument. The shape of water droplet with a diameter of 1–2 mm on the nanosilica film is shown in Figure 2. Strictly speaking, a superhydrophobic surface presents both a large static contact angle and a small sliding angle (the difference between advancing CA and receding CA). A very small sliding angle implies that the water droplet can move easily when the surface is tilted a little bit. The measured CA is $167 \pm 2^\circ$ and the sliding angle less 2°. So, the nanosilica shows excellent hydrophobic property.

The hydrophobicity, mainly, results from the surface property of the nanosilica. The bulky $-CH_3$ that is conjoint to Si makes the methyl groups to repulse each other and displace, which leads to larger freely rotating volume. And the hydrogen atoms of $-CH_3$ are repulsive to those of water, which makes the water molecule difficult to approach the hydrophilic oxygen. Besides, it is surmised that such excellent superhydrophobic properties might also come from the microstructure of silica film.[10,11] The rough surface of microvoid can store more air and, therefore, form a layer of stable air film, which prevents water drop from wetting the surface.[12,13] The joint effect of the trimethylsilyl as surface modifier and the rough microvoid surface leads to the superior hydrophobic property.

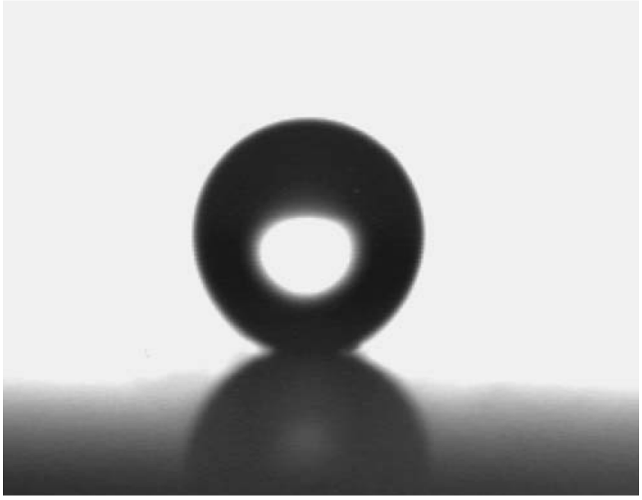


Figure 2. The shape of water droplet on nanosilica film.

The nanosilica can be well dispersed transparently in organic mediums such as CCl_4, liquid paraffin, propanediol, and diesel oil. In CCl_4, it can be dispersed transparently at a concentration of 17%. These oily solvents could rapidly spread over the films made of such SiO_2 nanoparticles when we measure their CA, which shows superior lipophilicity. Such excellent dispersibility is thought to come from two characteristics. One is the small size of the nanosilica. The other is the low energy surface that makes the organic solvent molecules to easily immerge into the interspaces among nanoparticles and wet the surface of these nanoparticles.

The nanosilica with superhydrophobic and excellent oleophilic properties is expected to be very useful in many important applications such as the separation of oil and water.

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Published on the web (Advance View) December 21, 2005; DOI 10.1246/cl.2006.94