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Fabrication and characterization of transparent superhydrophobic thin films based on silica nanoparticles

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ABSTRACT A simple method, which was based on self-assemble of silica nanoparticles and heptadecafluorodecyl trimethoxysilane, was used to fabricate a transparent superhydrophobic thin film with a water contact angle higher than 146°. The film has a uniform thickness of about 200 nm and a certain surface roughness about 20 nm, which makes it both transparent and superhydrophobic.

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Wettability and repellency are important properties of solid surfaces for both fundamental research and practical applications. Given the limited contact area between the solid surface and water, chemical reactions or bonding formation through water are limited on a superhydrophobic surface. Accordingly, various phenomena such as the adherence of snow, oxidation, and current conduction are expected to be inhibited on such a surface. Transparent superhydrophobic films have a wide range of applications, and may be used not only to resist water and fog condensation, but also to prevent contamination [1]. Recently, transparent superhydrophobic thin films with a water contact angle higher than 150° have attracted great attention. Various methods have been developed so far for the processing of superhydrophobic transparent thin films [2–12]. According to the literature, lowering the surface free energy and increasing the surface roughness can greatly enhance the surface hydrophobicity. However, the methods used to fabricate transparent superhydrophobic films are either complicated or the film fabricated not hard enough to satisfy the request of applications. In this article, a simple method was developed to fabricate a hard transparent thin film with a surface roughness about 20 nm and water contact angle above 146°, which was based on the self-assembly of silica nanoparticles and heptadecafluorodecyl trimethoxysilane [$CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$] (HFTS).

The thin films based on silica were fabricated by the self-assembly of silica nanoparticles made as follows: An alcohol-based silica sol was prepared by mixing tetraethyl orthosilicate (TEOS) and ethanol with NH_4OH (30% in water). First 3 mL of NH_4OH were added into 50 mL of ethanol and stirred vigorously at 60 °C for 30 min, then 3 mL of TEOS were added dropwise, then stirring for 90 min. The particles of silica in the sol prepared were observed by a JEM-2010 transmission electron microscope. As shown in Fig. 1, the sol was consist of particles about 50 nm.

The silica thin film was made by dip-coating the silica sol on a glass slide, with a withdrawal speed of approximately 14 cm/min. The glass substrates were completely cleaned by sonication in ethanol for 10 min and then rinsed with deionized water before coating. After coating, the samples were dried under room temperature for 20 min, then heated at 120 °C for 1 h. After that, the surface of the silica film was modified by dipping the sample into an ethanol solution of HFTS for 8 h to gain a monolayer of HFTS film through self-assembly and then was heated at 120 °C for 20 min. The water contact angles on the thin films were determined on a DM-300 solid–liquid intersurface analysis system. The contact angle for water has been strongly strengthened up to 146° showed in Fig. 2. It was indicated that a superhydrophobic thin films has been accomplished with a much simpler method. The film prepared was transparent which makes it useful in a wide range of application fields.

The thickness of the film was determined by the across section SEM morphology observed using a JSM-5600 scanning electron microscope (SEM) and the experimental results

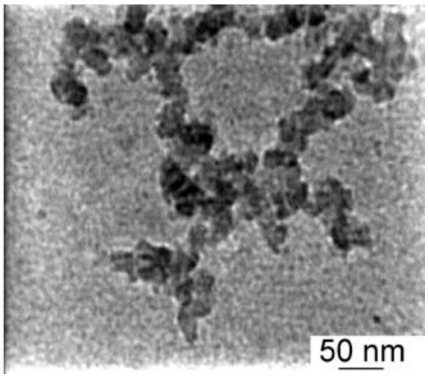

FIGURE 1 The TEM image of the silica sol prepared. The size of silica particle is about 50 nm

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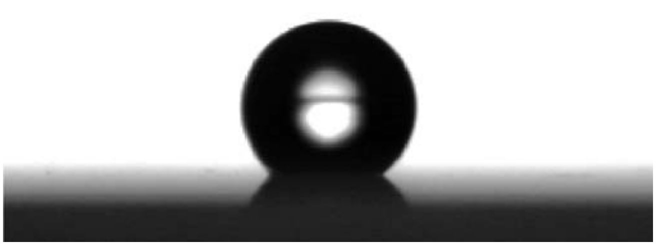

FIGURE 2 The water contact angle on the surface of thin film as prepared. Contact angle of water 146.8°

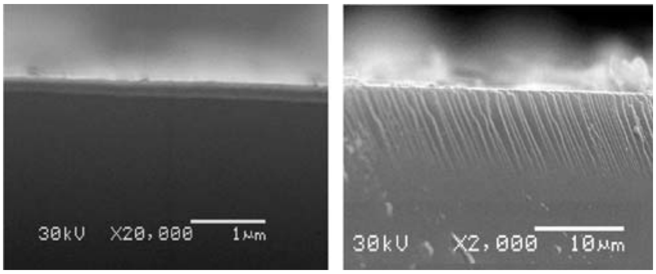

FIGURE 3 The across sectional SEM image of glass slide coated by a superhydrophobic thin film with a thickness about 200 nm. (*left*): amplified 20 000 times. (*right*): amplified by 2000 times

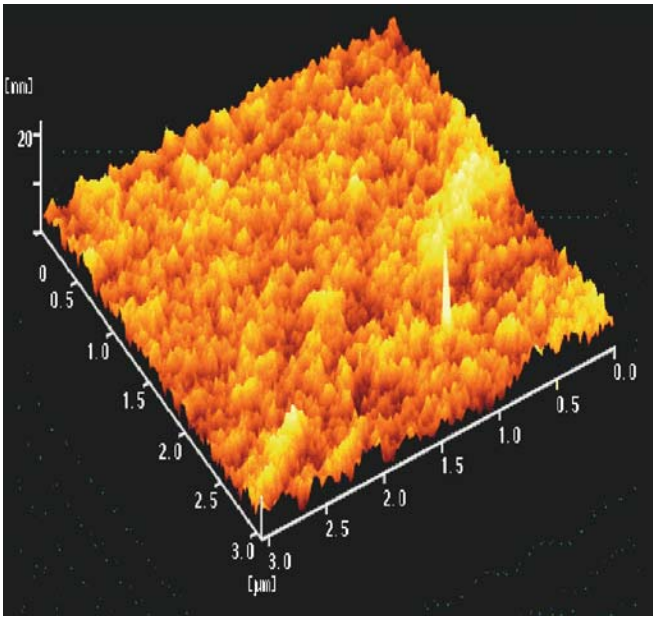

FIGURE 4 The AFM image of the film as prepared

were shown in Fig. 3. The cross-section SEM image indicates a uniform thickness of the film in nearly 200 nm.

The surface morphology of the silica-based superhydrophobic thin film was observed using an SPA-400 atomic force microscope (AFM). As shown in Fig. 4, the average surface roughness was estimated to be about 20 nm over a length span of 3 µm. This means that the films prepared have a certain surface roughness which makes it both transparent and superhydrophobic.

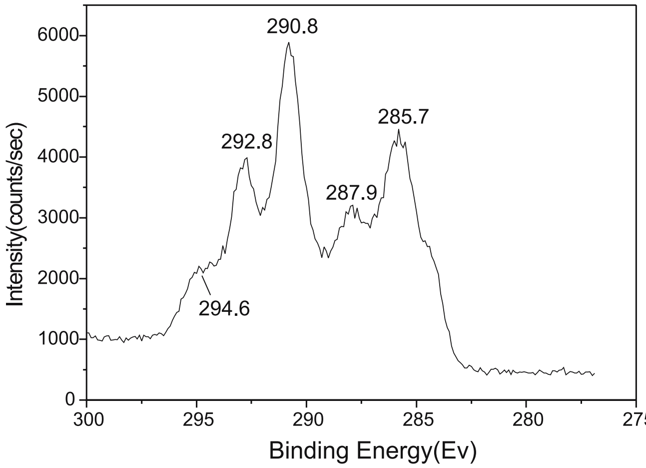

FIGURE 5 XPS spectrum of C_{1s} of the thin film as prepared

To confirm the existence of fluorine containing groups on the outermost layer of the film as prepared, X-ray photoelectron spectroscopy (XPS) spectrum was obtained on an axis ultra multi-technique electron spectrometer (Kratos, UK) with an Al K_α X-ray source and a pass energy of 40 eV. Using a least-square curve fitting program installed in the spectrometer, the C_{1s} for the thin film surface was split into several subpeaks of functional groups. A typical splitting of the spectrum of C_{1s} was shown in Fig. 5. The peaks in the spectrum can be ascribed to groups as follows, $\underline{C}$ at 292.8 eV and 290.8 eV may be attributed to $\underline{C}F_2$, $\underline{C}F_3$ at 294.6 eV, $\underline{C}{=}O$ at 285.7 eV and $\underline{C}H$ at 287.9 eV can be assigned to contaminant carbons, as shown in spectrum.

The transparent superhydrophobic thin film made is hard and it adhere strongly to the glass substrate, which makes it useful in a wide range of applications.

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