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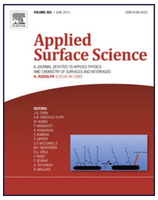

Robust superhydrophobic transparent coatings fabricated by a low-temperature sol–gel process

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ABSTRACT

A coating with robust, superhydrophobic, and transparent properties was fabricated on glass substrates by a sol–gel method at a temperature of 80 °C. The coating was formed in a solution containing silica nanoparticles and silicic acid, in which the ratio of silica nanoparticles and silicic acid was varied to tune the roughness of the coating. Subsequently, the as-deposited coating was dipped with a low surface energy material, 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichloro silane. The coated glass substrate was characterized in terms of surface morphology, optical transmittance, water- and CH_2I_2-contact angles, and its chemical as well as mechanical stability was evaluated by ultrasonication in ethanol for 120 min. The results showed that the coating had a water contact angle exceeding 160°, a sliding angle lower than 10°, a CH_2I_2 static contact angle of approximately 150°. The transmittance of the coating was reduced by less than 5% compared to that of the bare glass substrate at wavelengths above 500 nm. Moreover, the properties of the coating hardly changed after the ultrasonication test and still retained the superhydrophobicity after water dropping impact. Because the fabrication process is performed under low temperatures, it is feasible for scale-up production at low energy consumptions.

Introduction

Lotus leaf is known for its self-cleaning properties resulting from superhydrophobic surfaces with water contact angles larger than 150° [1]. It is well known that the superhydrophobic property is the result of a combination of surface roughness and low surface energy materials [2–4]. Over the past decade, mimicking lotus leaf surface morphology has led to the development of a number of artificial superhydrophobic coatings [5–8]. For the applications on glass substrates, such as touch screens, the coating requires not only transparency but also superhydrophobicity. However, hydrophobicity and transparency are two competing properties in view of the surface roughness. Increasing the surface roughness can enhance the hydrophobicity, but reduces the transparency due to light-scattering losses. Therefore, controlling the surface roughness to an appropriate value is the main task to satisfy both needs [9–11]. On the other hand, robustness and roughness are also one of the competing properties in view of the surface structure. Increasing the structure bonding strength can enhance the robust, but reduces the roughness due to surface area losses. Consequently, optimizing the tradeoff of both conditions is always a challenge.

The superhydrophobic properties are mostly determined by the trapped air layer between water and the surface. According to the Cassie–Baxter equation, the apparent contact angle (θ_{app}) can be expressed as $\cos\theta_{app} = f\cos\theta_Y - 1 + f$, where θ_Y is the intrinsic contact angle of the surface and f is the wet area fraction. A small area of contact between water and the surface apparently lowers the adhesion and ensures good mobility of water drops, qualifying the surface as superhydrophobic [12,13]. Superhydrophobic surfaces generally have an apparent contact angle higher than 150° and a sliding angle lower than 10° [14,15]. Moreover, a rough surface composed of micro- and nano-structures is a characteristic of the surface with superhydrophobicity. Such a rough surface can be fabricated by etching technique [16–19], sol–gel process [20], electrospinning [21], deposition of nanoparticles on smooth or rough substrates [22], growth of nanotubes [23], electrochemical anodization [24,25], and laser fabrication [26]. Moreover, the processing temperature generally exceeds 300 °C to from a dense structure, such as spin coating [27], electrospun nanofibers as a template [28], layer-by-layer deposition [29], and chemical vapor deposition [30]. Recently, many artificial surfaces have been investigated with regard to their chemical, mechanical [4,30,31], and thermal stability [32]. A 10 min of ultrasonication damage on a superamphiphobic coating resulted in a rapid decrease in the contact angle and an increase in the contact angle hysteresis [27]. Undoubtedly, the mechanical stability, especially the adhesive

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Table 1
The composition and pH of the sol–gel solutions studied.

Sample code	$Si(OH)_4$ (M)	Silica particle	Ethanol (ml)	pH value
15A	0.05	15 nm, 12 g	400	2.5
15B	0.09	15 nm, 6 g		2.9
15C	0.18	15 nm, 3 g		3.4
40A	0.05	40 nm, 12 g		3.1
40B	0.09	40 nm, 6 g		3.3
40C	0.18	40 nm, 3 g		4.1

strength between the coating and the substrate, determines the application of the coating. For industrial implementation, the coatings must be easily fabricated at low energy consumptions and must be durable during services. Therefore, the coatings via a low temperature fabrication having superhydrophobic characteristic and possessing mechanical stability of anti-ultrasonication damage and water dropping impact are less well studied so far [8,27,30].

In this study, a robust, superhydrophobic, transparent SiO_2-based coating was processed onto glass substrates by a sol–gel process at low temperatures. The superhydrophobic properties before and after an ultrasonication test and a water dropping impact were measured to ensure sufficient stability over impact damage.

Experimental

Materials

Tetraethoxysilane, TEOS, $C_8H_{20}OSi$, 99.96% from SHOWA Chemical Co. Ltd., Japan. Hydrochloric acid, HCl, 37% from Fisher Chemicals, USA. Ethanol, C_2H_5OH, 99.5% from ECHO Chemical Co. Ltd., Taiwan. Silica powder, 40 nm and 15 nm, SiO_2, 99.9% from UniRegion Bio-Tech, Taiwan. 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichloro silane, PFOTS, $CF_3(CF_2)_5(CH_2)_2SiCl_3$, 97% from Sigma-Aldrich, USA.

Preparation of sol–gel solutions

Hydrochloric acid was added to deionized (DI) water for preparing pH 2 HCl aqueous solution. TEOS and pH 2 HCl aqueous solution were mixed together at a molar ratio of 1:4.6 with a magnetic stirrer for 2 h, giving rise to silicic acid, $Si(OH)_4$. Then, 40 nm or 15 nm silica powders were dispersed in 400 ml ethanol at different loadings (A: 12 g, B: 6 g, C: 3 g) using a magnetic stirrer and ultrasonic vibrator for 30 min. Silicic acid was then added to the silica/ethanol solution using a magnetic stirrer and ultrasonic vibrator for 2 h. The composition and pH of each sol–gel solution are listed in Table 1.

Dip coating process

The substrate used for this study was transparent plain glass (Microscope slides) of 25 × 75 × 1 mm. The slides were rinsed with deionized water and ethanol. Then, the substrate was ultrasonically cleaned in ethanol for 2 h. After drying using a stream of room temperature air, the slide was dipped in the sol–gel solution for 60 s and then withdrawn at a speed of 2.8 mm/s to create a liquid film on the slide. The thickness of the coating was related to that of the liquid film, which depended on the composition of the sol–gel solution, the immersion time, and the withdrawn speed of the slide. All dip coating processes were conducted in ambient atmosphere (approximately 25 °C, 70% relative humidity). The coated glass was then cured in a box oven at 80 °C for 20 min. This curing step was used to form a dense three-dimensional structure by thermally-induced self-condensation reactions within the coating material as hydroxide groups were removed from the remaining silanol molecules and the structure was bonded to the underlying substrate. Finally, PFOTS was deposited on the coated substrate by dip coating in 1 wt% PFOTS ethanol solution. The coated glass substrate was then cured in a box oven at 80 °C for 20 min.

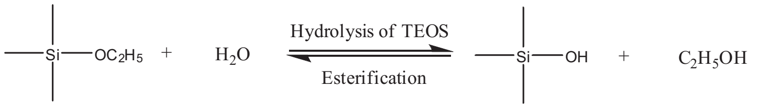
Characterization

The surface morphology of the coating was investigated using scanning electron microscopy (SEM) via a Leo 1530 field-emission gun SEM. Before imaging, the surface was sputtered with a thin layer of Pt. The contact angle of the coated glass substrate was measured using a contact angle goniometer Sindatek Model 100SB drop shape analysis system with a computer-controlled liquid dispensing system. Droplets of DI water and diiodomethane (CH_2I_2) in a volume of 3 μl were used to measure the contact angle. The experiments were performed under normal laboratory ambient conditions (25 °C and 70% relative humidity). Each contact angle measurement was repeated five times at different places on each sample and the mean value was reported. UV–vis spectroscopy measurements of the coated glass substrate were conducted using an Ocean Optics USB2000 fiber optic spectrometer. Adhesion of the coating on the glass substrate was evaluated using a 50 kHz and 150 W ultrasonicator. The sample was vertically immersed in ethanol solution while the coating was impacted by ultrasonic shock wave for different times. The thickness of the coating was measured by an α-step of Veeco Dektak 150 with software line scanning.

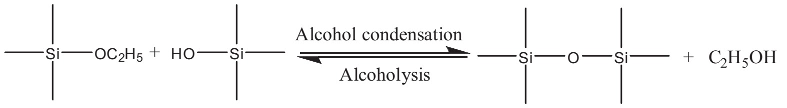
Results and discussion

Reaction mechanism in coating soluations

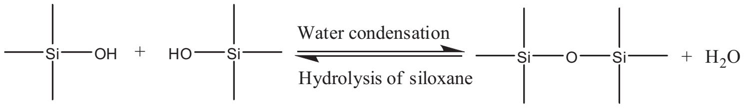
The fabrication process of the coating on the glass substrate is shown in Fig. 1. The first step of the whole process was hydrolysis of TEOS to form silicic acid. The reaction characteristics of TEOS with water can be described at the level of the functional groups, as shown in Eqs. (1)–(3) [33]:



$$\equiv Si-OC_2H_5 + H_2O \underset{\text{Esterification}}{\overset{\text{Hydrolysis of TEOS}}{\rightleftharpoons}} \equiv Si-OH + C_2H_5OH \tag{1}$$



$$\equiv Si-OC_2H_5 + HO-Si\equiv \underset{\text{Alcoholysis}}{\overset{\text{Alcohol condensation}}{\rightleftharpoons}} \equiv Si-O-Si\equiv + C_2H_5OH \tag{2}$$



$$\equiv Si-OH + HO-Si\equiv \underset{\text{Hydrolysis of siloxane}}{\overset{\text{Water condensation}}{\rightleftharpoons}} \equiv Si-O-Si\equiv + H_2O \tag{3}$$

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