Fabrication of nano TiO$_2$/ZnO superhydrophobic surface composite coating on steel substrate via a simple process

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The nano TiO$_2$/ZnO composite particle was prepared by means of violent stirring and modified with stearic acid, superhydrophobic nano TiO$_2$/ZnO composite coating was formed on the steel specimen via a simple process. The surface wettability and topology of coating were characterized by contact angle measurement, Scanning electron microscope, Fourier transform infrared spectrometry and thermogravimetry. The results show that composite particle is introduced into the hydrophobic methyl by stearic acid surface modification, and the formation of micro/nano double roughness structures. When the content of stearic acid was 9%, the resulting as-prepared coating surface displayed a static water contact angle of 165.3°, and a sliding angle of 4°, showing excellent temperature tolerance and self-cleaning. The presented method is fast, low-cost and has great potential value in large-scale industry production.

1. Introduction

The self-cleaning property of a superhydrophobic surface, on which the water static contact angle (CA) is greater than 150° and the sliding angle (SA) is no more than 10° [1, 2], has drawn tremendous interest recently because of its potential application in industrial areas and biological processes, such as corrosion-free coatings [3], anti-adhesive coatings [4], and self-cleaning materials [5]. After the discovery of superhydrophobic surfaces in nature, many artificial superhydrophobic coatings have been fabricated by mimicking nature. According to previous research, superhydrophobic coatings must satisfy the following two conditions: a low surface energy of the constituent materials in the coating, and the presence of surface roughness, especially hierarchical micrometer/nanometer-sized roughness. In artificial superhydrophobic coatings, such roughness has been introduced using top-down or bottom-up processes [6, 7]. Up to now, superhydrophobicity is remarkable in that many exploratory researches in this field have started with various methods, such as sol-gel processing [8], chemical vapor deposition [9], layer-by-layer assembling method [10], etching and lithography [11], etc. Researchers using nano-sized particles to increase surface roughness of a hydrophobic surface will find it to practicable approach. Recently, there has been increasing interest in studying the wetting behaviors of nanostructures of various materials, such as TiO$_2$ [12], Al$_2$O$_3$ [13], ZnO [14], SnO$_2$ [15]. Since nanostructures have inherent surface roughness, this nanowire surface enables air to be trapped more easily under water droplets, thus most parts of the water droplet sit on a layer of the air. Also, the surface energy of the material can be lowered through chemical modifications. By combining surface roughness and chemical modification, the modified nanostructure surface can prevent water penetration down into spaces between nanowires.

Nanocomposite morphology, composition, and crystal form are the main factors which determine the properties of the composite materials. Nano TiO$_2$ and ZnO are important inorganic functional materials due to their unique properties in widely used in various fields [16, 17]. The researchers have found [18, 19], complex in the UV protection, corrosion resistance and photocatalysis is superior to single material. Guo et al. described a hydrothermal approach to prepare a ZnO/CuO hetero-hierarchical nanotrees array. Hetero-hierarchical nanotrees array has a static water contact angle as high as 170°, and this substrate could be used as self-cleaning surface [20]. Houmard et al. prepared superhydrophobic particulate film using TiO$_2$/SiO$_2$ composite thin films via a sol-gel route [21]. For this paper, we designed a simple process to prepare superhydrophobic coating based on stearic acid-modified nano TiO$_2$/ZnO. We investigate the morphological and wetting properties of the coating surfaces; the superhydrophobic nano TiO$_2$/ZnO hybrid coating had a rough surface with micro/nanometer

dual-size structure.

2. Experimental details

2.1. Materials

Rutile nano-TiO$_2$ and micron-ZnO were purchased from Shanghai River Industrial Co., Ltd. Stearic acid was obtained from Guangdong Shantou Chemical Reagent Co., China. Sodium dodecyl sulfate (SDS) was obtained from Shantou Guanghua Chemical Reagent Co., Ltd. All other chemicals were commercially available and used as received.

2.2 Modification of nano TiO$_2$/ZnO

First, the pH was adjusted to 4.0 by the stearic acid dissolved in 10mL of absolute ethanol ultrasonic dispersion for 5min, then added to the solution of the TiO$_2$ (20g), ZnO (10g) and SDS (1g) well dissolved in 50mL of DI water. The solution was vigorously stirred at 40°C for 30min, and the pH of TiO$_2$/ZnO hybrid emulsion was adjusted to 4.0 by the addition of acetic acid. Thus, a homogeneous white viscous liquid was obtained.

2.3 Fabrication of superhydrophobic coatings

The mixture was directly coated on a steel specimen via a dip-coating process, the cleaned substrate was immersed into the sol for 10min before withdrawal, and withdrawal speed was kept at 5～10cm/min. After each dip-coating, the substrate was dried at room temperature for 2min, then the coating was heated at 200°C for 15min to remove residual solvent and solidify the coating. Finally, uniform TiO$_2$/ZnO coatings were formed after air drying and heat curing step. Fig. 1 shows the schematic illustration of preparing superhydrophobic.

2.4 Characterization

The water CA and SA were obtained using the sessile drop method by averaging the measurements on four different positions of the examined the measurements on four different positions of the examined surface. The water droplet size used for the measurements was 3.0μL. The morphological structures of the as-prepared surfaces were observed by digital scanning electron microscopy (SEM, S-3400N). Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 380 spectrometer in the range 4000～500cm^{-1}, and cured films were tested with thermo gravimetric analysis (TG).

Fig. 1. Schematic illustration of superhydrophobicity coating.

3. Results and discussion

The bionic films with hydrophobicity were fabricated by the hierarchical TiO$_2$/ZnO microspheres modified by stearic acid. The FTIR spectra of the original and modified TiO$_2$/ZnO are shown in Fig. 2. In the high frequency region, the symmetric v_a(CH$_2$) methylene and asymmetric v_{as}(CH$_3$) methyl vibration peaks appear clearly at 2852cm^{-1} and 2925cm^{-1} in stearic acid modified coating film spectra, which indicates the existence of the long chain alkyl groups on the surface [22]. In the low frequency region, the presence of the bands at 1465cm^{-1} and 1541cm^{-1} is attributed to −COO− stretching vibrations in CH$_3$(CH$_2$)$_{16}$COO− groups on the surface of hierarchical TiO$_2$/ZnO modified by stearic acid [23]. This indicates that the stearic acid is grafted on the surface of TiO$_2$/ZnO samples.
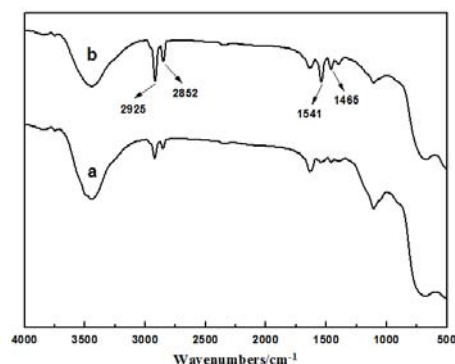

Fig. 2. The infrared spectrograms of samples (a) unmodified and (b) modified by stearic acid.

The stearic acid is a low surface energy material, which can effectively reduce the surface energy of solids, and facilitates access to superhydrophobic surface [24]. However, the stearic acid content needs further investigation as to it influences the coating's hydrophobic performance. From Table 1, it can be seen that the CA on coating first increases and then decreases. The surface of the CA up to 165.3°, when the content of stearic acid is 9%, exhibits excellent superhydrophobic property. When the content of stearic acid continues to increase, due to the

excessive surface modification of the stearic acid in the nano TiO_2/ZnO surface to form a double-layer adsorption, the stearic acid hydrophilic groups exposed on the surface of the coating, so that the surface of the CA and hydrophobicity also decreased. Therefore, we are possible to be added by changing the proportion of stearic acid, to effectively control nano TiO_2/ZnO surface hydrophobic properties.

Table 1. Effect of stearic acid content on CA and SA of coating.

Sample	Stearic acid (Wt%)	CA (°)	SA (°)
1	0	127.9	28
2	3	140.1	22
3	6	146.7	13
4	9	165.3	4
5	12	161.6	5
6	15	154.7	9

To test the effects of carbon chain length of fatty acids, as-prepared nano TiO_2/ZnO films were treated with different kinds of fatty acids, such as hexanoic acid (C=6), decanoic acid (C=10), myristic acid (C=14), and stearic acid (C=18). The water CA and SA of fatty acid modified nano TiO_2/ZnO films increased monotonically with increasing the carbon number of fatty acids as shown in Fig. 3.
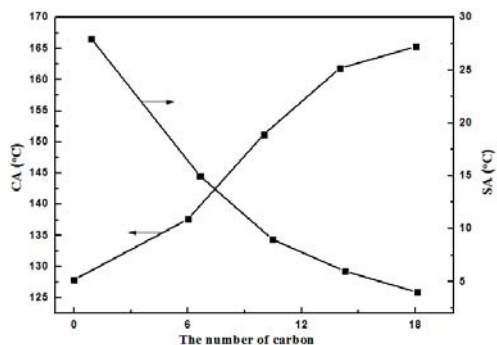

Fig. 3. Water CA and SA of fatty acid modified nano TiO_2/ZnO films as a function of the carbon number of fatty acids.

It is well established that the wettability of solid surfaces is governed by both the chemical composition and the surface morphology [25]. In our case, the as-prepared nano TiO_2/ZnO surfaces exhibit unique hierarchical micro/nano structures (Fig. 4c-d). After modification with stearic acid, these roughened structures can trap a large fraction of air within the gaps among flowerlike structures, and the microstructure of coating surface is more abundant

(Fig. 4e-f). The trapped air would dramatically increase the air-liquid interface area, preventing the penetration of water droplets into the grooves of the surface [26].

To better understand the behavior of the hydrophobized TiO_2/ZnO coatings, theoretical considerations are necessary. The Cassie and Baxter equation [27] was used to evaluate the relationship between the CA of a water droplet on a smooth surface (θ) and that on a heterogeneous surface (θ^*) composed of a solid and air in which f_1 and f_2 are the fractions of the solid surface and air in contact with liquid, respectively (i.e. $f_1 + f_2 = 1$). It is easy to deduce from this equation that increasing the fraction of air (f_2) increases the CA of the rough surface (θ^*). In other words, as the amount of air under the contact line is increased the more hydrophobic it appears.

$$cos\theta^* = f_1 cos\theta - f_2 \qquad (1)$$

In our study, the apparent contact angle θ^* on as-prepared surface is 165.3° and the contact angle on a smooth steel surface modified with stearic acid is about 75.6°. The value of f_2 is calculated to be about 0.974 according to Eq. (1). It is indicated that air occupies about 97.4% of the contact area between the water droplet and the as-prepared surface. The water droplet sits on an air cushion and suspends on the resultant rough surface, showing a high CA and a low SA (Fig. 5).
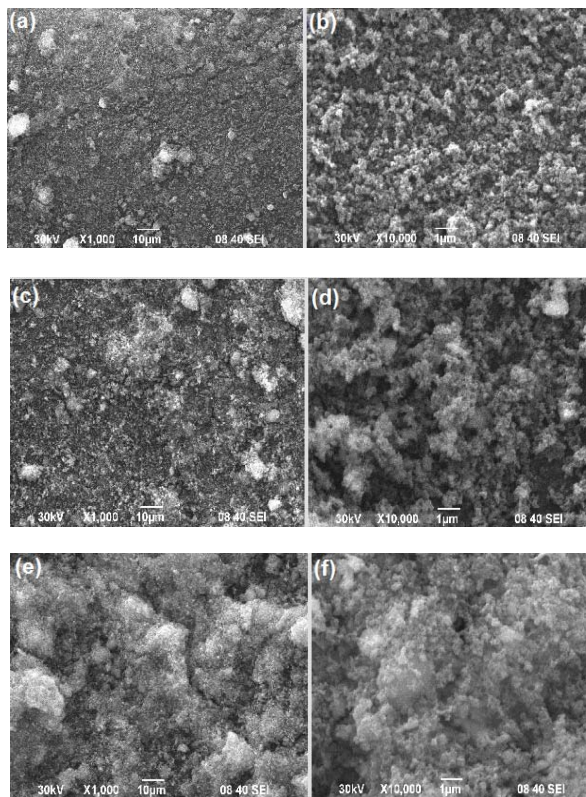

Fig. 4. SEM images of the samples: (a-b) nano TiO_2 coating; (c-d) nano TiO_2/ZnO coating; (e-f) modified nano TiO_2/ZnO coating.

Fig. 5. Pictures of water droplets on coating.

As previous research shows, a surface with hierarchical roughness is considered responsible for the low hysteresis, which in turn produces the water-repellent and consequent self-cleaning properties (Fig. 6), and can be applied to the field of anti-tarnish.
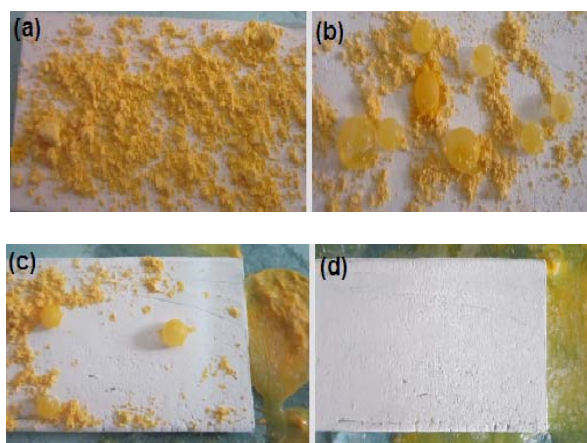

Fig. 6. Self-cleaning process of superhydrophobic composite surface: (a) chalk powder spreading on the surface; (b) chalk powder covering water droplet; (c) droplets rolling through the surface and (d) all chalk powder has been removed by water droplets.

Reacting process of the coating with temperature is understood through determining its TG curve. Heat treatment also has strong influence on the microstructure of coating; microstructure determines the roughness of the coating layer [28]. Fig. 7 shows the effect of the different heat treatment temperatures on a coating's hydrophobic angle. It is discovered that coatings attained best water-repellent property (SA=165.3°) after heating up to 200°C, the coating CA is reduced to 125° when the temperature is at 450°C. The experimental results indicated that the coating began to damage thermally, which is consistent with the thermal analysis results (Fig. 8). Because our fabrication method of superhydrophobicity uses the chemisorption of stearic acid,

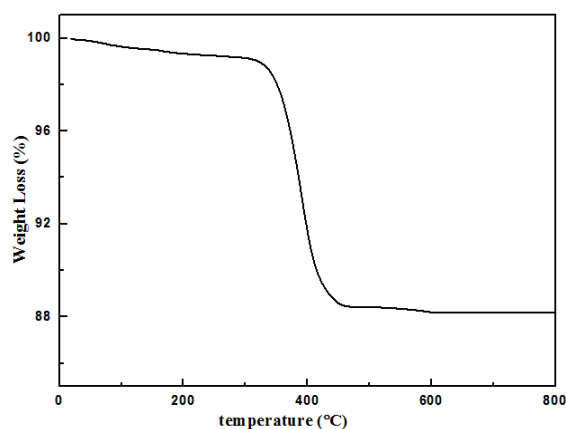the drastic SA decrease was observed resulting from thermal decomposition of stearic acid molecules.

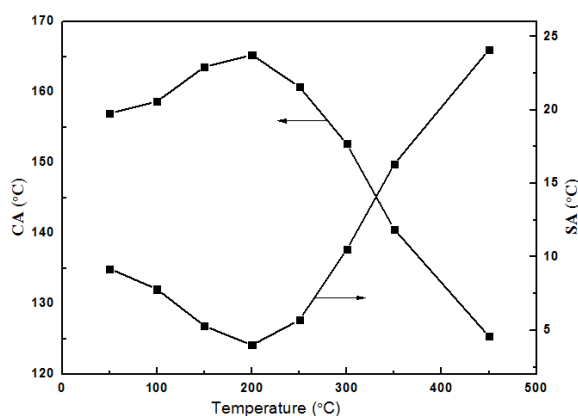Fig. 7. The thermal analysis curve of the as-prepared TiO₂/ZnO coating.

Fig. 8. Effect of heat treatment on CA and SA of the as-prepared TiO₂/ZnO coating.

4. Conclusions

In this paper, we have developed a facile and inexpensive method to fabricate hydrophobic coating by the composite nano TiO₂ and ZnO. After modifying, the CA is up to 165.3° and SA is down to about 4°. Further measurements and observations have indicated that the CA can increase and then decrease with the increase of the molar ratio of stearic acid. Moreover, the prepared surface shows a hierarchical structure in micro/nano scale. Due to its superhydrophobic property and unique micro/nano structure, nano TiO₂/ZnO coating is expected to have extensive practical applications.

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