Development of a simple method for the fabrication of superhydrophobic coating of nano $TiO_2/CaCO_3$ composite

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In this work, we have a facile and inexpensive method to fabricate a superhydrophobic surface with $TiO_2/CaCO_3$ composite particles. The superhydrophobic surface was prepared through mechanical stirring method of a mixture of nano-TiO_2 and nano-$CaCO_3$ suspensions on a substrate, followed by modification of a low-surface-energy of oleic acid. The surfaces were characterized by field-emission scanning electron microscopy, Fourier transform IR, thermo gravimetric analysis and differential scanning calorimeter. The results show that nano-$CaCO_3$ surfaces are physically combined with nano-TiO_2 particles，and after modified composite particle is introduced into the hydrophobic methyl, and formation of double-scale roughness structures. The as-prepared coating showed self-cleaning properties with a water contact angle as high as 162.1° and a sliding angle of 7°.

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Keywords: Composite particles, Double-scale roughness, Contact angle, Superhydrophobic

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 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], antiadhesive coatings [4], self-cleaning materials [5], and so on. The superhydrophobicity of a material depends on not only its surface morphology but also its surface energy. Commonly, there are two kings of approaches to prepare superhydrophobic surfaces: modifying the rough surfaces to lower the surface free energy or enhancing the roughness on the hydrophobic substrate [6]. Nano-TiO_2 inorganic particles have ultraviolet resistance, self-cleaning, antibacterial and anti-aging [7]. Nanosized $CaCO_3$ powder is now commercially available and can be used as a raw material for the preparation of superhydrophobic surfaces [8].

Torimoto et al. [9] reported a facile and versatile approach to fabricate hollow titania nanoparticles via core-shell structure of $TiO_2/CaCO_3$ by a sol-gel route. Okada et al. [10] prepared $CaCO_3/TiO_2$ nanoporous film by simply mixing it with TiO_2 powder during the paste preparation.

Superhydrophobic is remarkable that many exploratory researches in this filed have started with various methods, such as sol-gel [11], layer-by-layer assembling method [12], chemical vapor deposition [13], etching processing [14], etc. However, the fabrication processes of these approaches and materials were expensive and time-consuming. In this paper, a simple method using the mechanical stirring techniques is developed to achieve superhydrophobic surfaces. This inexpensive method can operate easily and eliminates elaborated equipments. Specifically, we use nano-$CaCO_3$ and nano-TiO_2 to form the composite on the surfaces and such methodology can be extended to any other inorganic salts.

2. Experimental

2.1 Materials

Nano-$CaCO_3$ and nano-TiO_2 were purchased from Shanghai. Acetic acid and γ-glycidylpyltrimethoxy trimethyloxonium silane (KH-560) were supplied from Guangdong and Nanjing, respectively. All other materials were purchased from a general store.

2.2 The preparation of superhydrophobic coating

In a typical process, the pH was adjusted to 3.0 by the oleic acid (8mL) and KH-560 (1mL) dissolved in 60mL of absolute ethanol were vigorously stirred at 40°C for 20min, then added to the solution of 3g TiO_2 and 20g $CaCO_3$ were stirred at 50°C for 30min, and the pH of $TiO_2/CaCO_3$ hybrid emulsion was adjusted to 3.0 by the addition of acetic acid. Subsequently, the reaction mixture was stirred for 12h at 40°C and aged at room temperature for 12h. Afterward, the cleaned glass slide was directly immersed into the sol 20min before withdrawal by dip-coating process, thin films can be obtained after repeated for several times. Finally, uniform coatings were formed after the coating was heated at 200°C for 15min (Fig. 1).

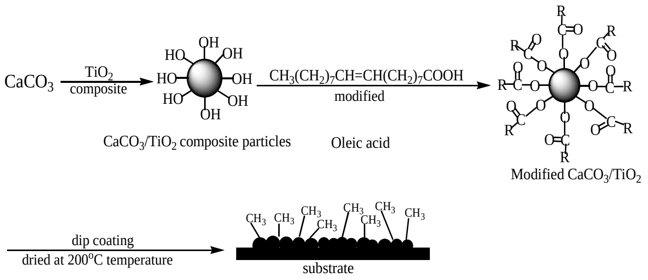

Fig. 1. Schematic illustration of superhydrophobicity coating.

2.3 Characterization methods

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 examined by field emission scanning electron microscopy (SEM, JSM-6010LA). 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) and differential scanning calorimetry (DSC).

3. Results and discussion

The oleic acid is a low surface energy material, which can effectively reduce the surface energy of solids, and facilitates access to superhydrophobic surface [15]. However, the oleic acid content needs further investigation how to influence the coating of hydrophobic performance, as displayed in Fig. 2 oleic acid of different proportion on coating surface hydrophobic effects. From the figure it can be seen that the trend of the CA of the coating first increases and then decreases. The surface of the CA up to 162.1° when the content of oleic acid is 10%, exhibits excellent superhydrophobic property, and when the content of oleic acid to continue to increase, due to the surface excessive modification of the oleic acid in nano $TiO_2/CaCO_3$ surface to form a double-layer adsorption, the oleic acid hydropilic groups exposed on the surface of the coating, so that the surface of the CA and hydrophobicity also decreased. Therefore, it is possible to be added by changing the proportion of oleic acid, to effectively control nano $TiO_2/CaCO_3$ surface hydrophobic properties.

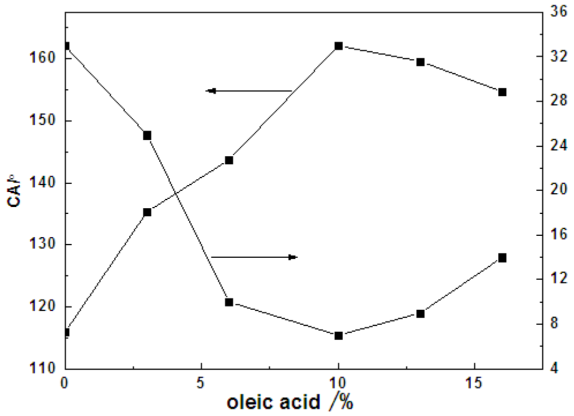

Fig. 2. Effect of oleic acid content on CA and SA of coating.

To test the effects of carbon chain length of fatty acids, as-prepared nano $TiO_2/CaCO_3$ films were treated with different kinds of fatty acids, such as hexanoic acid (C=6), decanoic acid (C=10), myristic acid (C=14), and oleic acid (C=18). The water contact angle of fatty acid modified nano $TiO_2/CaCO_3$ films increased monotonically with increasing the carbon number of fatty acids as shown in Fig. 3.

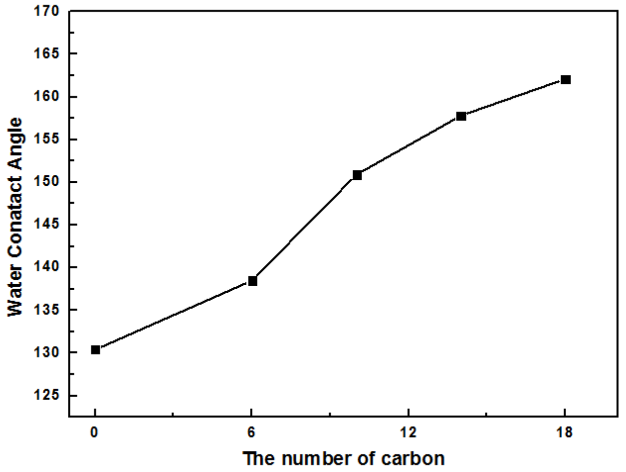

Fig. 3. Water contact angle of fatty acid modified nano $TiO_2/CaCO_3$ films as a function of the carbon number of fatty acids.

The formation mechanism of the surface structure on the substrate can be identified with FTIR. FTIR spectra

(Fig. 4) of TiO_2 (lina a) and $CaCO_3$ (lina b), and unmodified $TiO_2/CaCO_3$ composite particles (lina c), and modified $TiO_2/CaCO_3$ composite particles (lina d) provide evidence for the formation of oleic acid self-assembled monolayers on the as-prepared film. Compared to the spectrum of the initial coating film (line c), the symmetric $v_a(CH_2)$ methylene and asymmetric $v_{as}(CH_3)$ methyl vibration peaks appear clearly at $2850cm^{-1}$ and $2930cm^{-1}$ in oleic acid modified coating film spectra (line d), which indicates the existence of the long chain aliphatic groups on the surface [16]. In Fig. 4d, CO_3^{2-} characteristic absorption peaks at $1450cm^{-1}$ and $877cm^{-1}$, composite particles having neither new generation, nor the disappearance of the peak, compared with the FTIR spectra of TiO_2 and $CaCO_3$. It shows that both is purely physical composite action, did not produce the chemical bond.

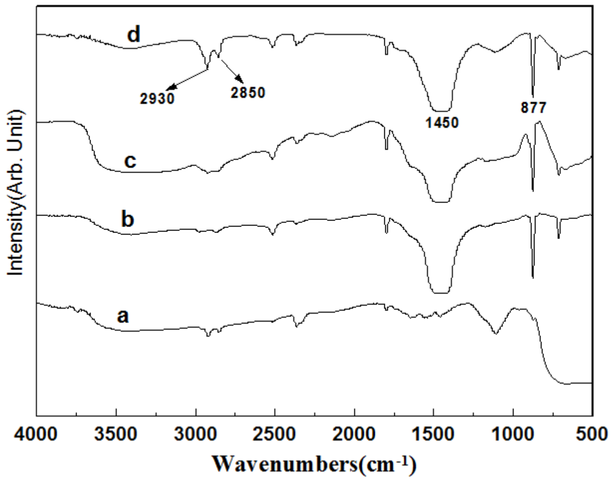

Fig. 4. FTIR spectra of (a) TiO_2; (b) $CaCO_3$; (c) unmodified $TiO_2/CaCO_3$ composite particles; (d) modified $TiO_2/CaCO_3$ composite particles.

To better understand the behavior of the hydrophobized $TiO_2/CaCO_3$ coatings, theoretical considerations are necessary. The Cassie and Baxter equation [17] 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.

$$\cos\theta^* = f_1 \cos\theta - f_2$$

Fig. 5 shows the SEM images of the $TiO_2/CaCO_3$ composite coating unmodified and modified. As it can be seen in Fig. 5, particle morphology were similar, the large particle surface is coated with a layer of small particles. The following Fig. 5b shows the larger size of the composite particles and the richer surface microstructure, similar to the lotus leaf surface micro/nano composite structure. Its surface porosity and roughness have greatly improved resulting from the scattered arrangement of the thin film structure. The surface of the coating exhibits excellent superhydrophobic properties because of complexes formed between the double-scale roughness structures.

In our study, the water droplet sits on air cushion and suspends on the resultant rough surface, showing a high CA and a low SA. As it is well known, 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).

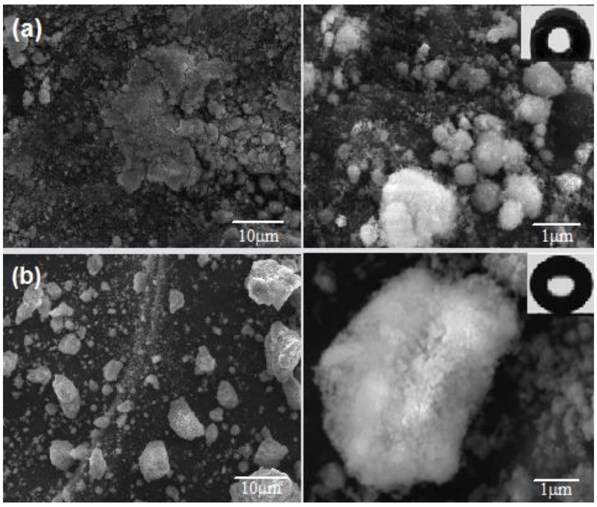

Fig. 5. SEM images of the surfaces: (a) unmodified $TiO_2/CaCO_3$ composite particles and (b) modified $TiO_2/CaCO_3$ composite particles, respectively.

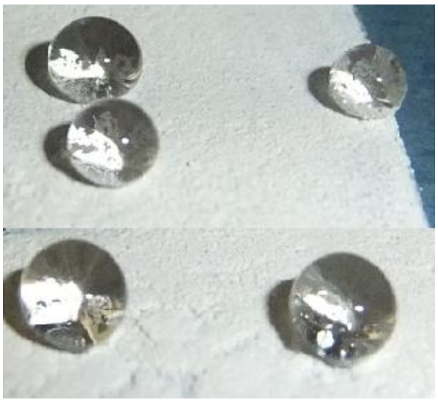

Fig. 6. Pictures of water droplets on coating.

Reacting process of the coating with temperature is understood through determining its TG and DSC curve.

Heat treatment also has strong influence on the microstructure of coating; microstructure determines roughness of coating layer [18]. Fig. 7 shows the effect of the different heat treatment temperature on coating of hydrophobic angle. It is discovered that coatings attained best water-repellent property (SA=162.1°) after heating up to 220°C. The coating CA is reduced to 143° when the temperature exceeds 350°C, the experimental results indicated that coating began to damage thermally, which is consistent with the thermal analysis results. Fig. 8 shows that $TiO_2/CaCO_3$ composite particles modified by TG-DSC cures, there is an obvious endothermic peak existing at 350°C due to the coating physically adsorbed water desorption, while the curve of TG coating begins slow thermal weight loss. Coating surface have significant quality loss at 650°C～750°C due to $CaCO_3$ thermal decomposition massive release of CO_2 gas, leading to a severe loss of quality.

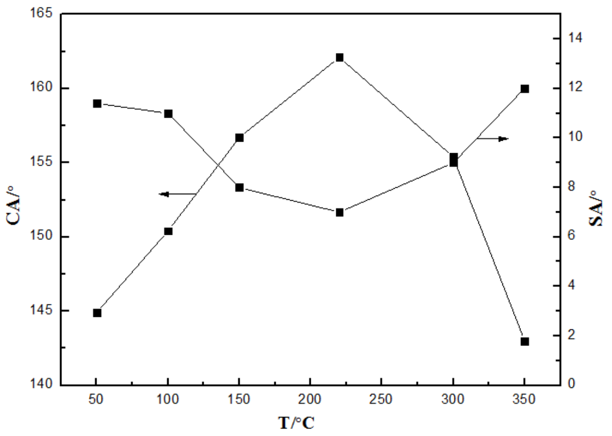

Fig. 7. Effect of heat treatment on CA of coating.

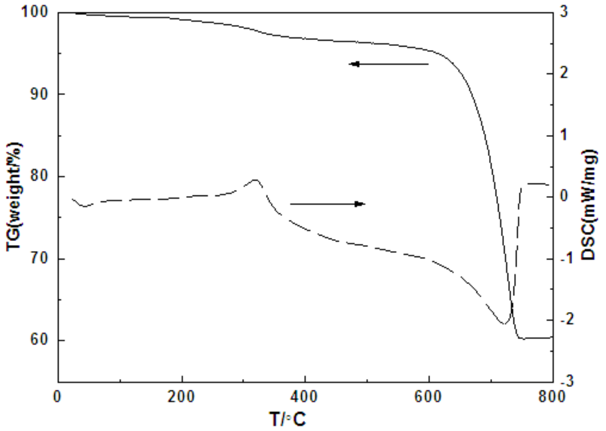

Fig. 8. Thermal analysis of coating.

4. Conclusion

In this paper, we have developed a facile and inexpensive method to fabricate superhydrophobic coating by the composite of nano-TiO_2 and nano-$CaCO_3$. After modifying, the CA is up to 162.1° and SA is down to about 7°. Further measurements and observations has indicated that the CA can increase and then decrease with the increase of the molar ratio of oleic acid. Moreover, the prepared surface shows a hierarchical structure in micro/nano scale. Due to its superhydrophobic property and unique micro/nano structure, $TiO_2/CaCO_3$ coating is expected to have extensive practical applications.

Acknowledgments

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