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Research Article

Facile Fabrication of a Hierarchical Superhydrophobic Coating with Aluminate Coupling Agent Modified Kaolin

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A superhydrophobic coating was fabricated from the dispersion of unmodified kaolin particles and aluminate coupling agent in anhydrous ethanol. Through surface modification, water contact angle of the coating prepared by modified kaolin particles increased dramatically from 0° to 152°, and the sliding angle decreased from 90° to 3°. Scanning electron microscopy was used to examine the surface morphology. A structure composed of micro-nano hierarchical component, combined with the surface modification by aluminate coupling agent which reduced the surface energy greatly, was found to be responsible for the superhydrophobicity. The method adopted is relatively simple, facile, and cost-effective and can potentially be applied to large water-repellent surface coatings.

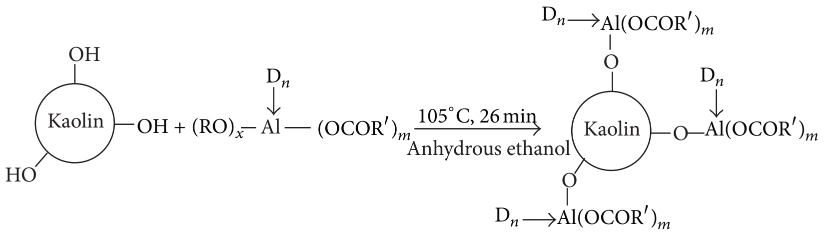
1. Introduction

Recently, superhydrophobic surfaces have drawn much attention because of the potentials for both academic research and industrial applications [1, 2]. The criteria for a superhydrophobic surface are having a water contact angle (WCA) higher than 150° and a sliding angle (SA) lower than 10° [1, 3, 4]. They show many particular properties, such as biomimicking anti-sticking, contamination prevention, water repellency, self-cleaning, anti-fogging, and anti-reflection, and so forth [2, 5, 6]. Lots of relevant reports have emerged, including oil-water separation [7–9], industrial metal cleaning [10], tunable wettability surfaces [6, 11–14], self-repairing surfaces [15], fluidic drag reduction [5], electronic devices protection [16], and biomedical instruments [17]. Despite the intense research, these surfaces are still restricted by the following problems: limited hydrophobicity with high contact angle hysteresis, failure upon physical friction, weak environment stability, substrate limitation, and high production cost, which means a significant restriction of applications [15, 18].

Kaolin is a type of clay mineral consisting mainly of hydrated aluminum silicate or kaolinite [19], which is commercially available and low in cost [20]. Kaolin is also an important industrial material, and because of its high whiteness, it was once used as the leading white pigment—in point of tonnage-consumed by North American industry [21]. Lots of applications of kaolin have emerged, such as paper coating, plastic and rubber filling, refractory, and ceramic and paint industries [19, 21–23]. Clay-polymer composites have drawn much attention because the incorporation of clay particles can lead to desirable changes in the material properties [24].

Herein, we present a very facile and simple method to fabricate a hierarchical superhydrophobic material by surface modifying kaolin particles of size 100–400 nm with aluminate coupling agent (ACA). ACA is an important surfactant. Usually, their colors show faint yellow to white, which is near to kaolin's color. It also has high activity in surface reactions and a high decomposition temperature and is environmental-friendly. The structural formula is $(\mathrm{RO})_x\mathrm{Al}(\mathrm{OCR}')_m \cdot \mathrm{D}_n$. There are two different kinds of functional groups in ACA, in which $(\mathrm{RO})_x$ are hydrophilic and $(\mathrm{OCR}')_m$ are hydrophobic. And D_n represent coordinating groups, such as N and O. The hydrophilic groups can make chemical reactions with the polar groups on the kaolin particles, making the particles coated with hydrophobic groups, which can reduce the surface energy greatly.

In this study, ACA modified kaolin was coated on commercially available glass slides to fabricate superhydrophobic



SCHEME 1: Illustration of chemical reaction between kaolin and ACA.

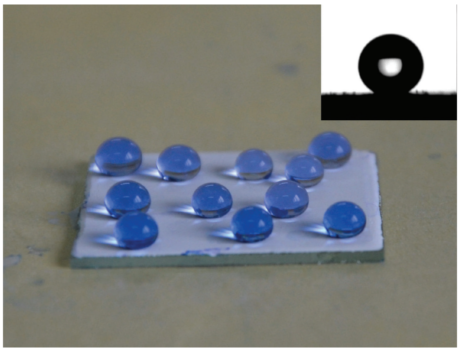


FIGURE 1: Images of water droplets dyed by methylene blue with different sizes on the ACA modified kaolin particles coating. Insets: profiles of water droplets on the surface have the contact angles of 152°.

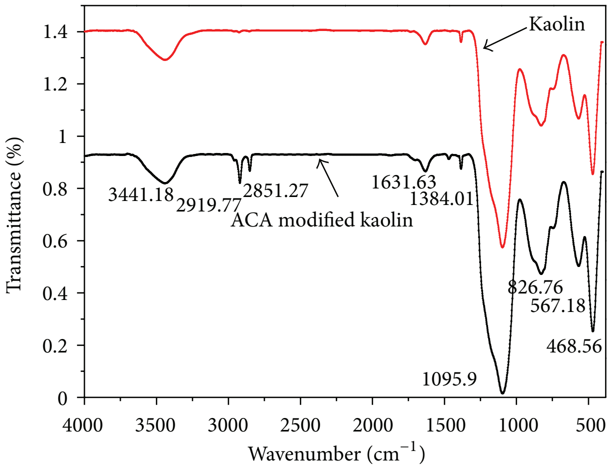


FIGURE 2: IR spectra of kaolin and aluminate coupling agent modified kaolin.

surfaces. This technique has no tedious procedures or expensive instruments and the resulting superhydrophobic material shows an excellent environment stability [25]. Because the fabricated particles were superhydrophobic, this can dramatically improve the application convenience. Furthermore, the material can be used on a variety of substrates, which can greatly expand the scope of applications. To examine the material's environmental stability, it was put outside; after three months of environmental exposure, it still shows excellent superhydrophobicity. For all the reasons above, both for academic and industrial aspects, the as-prepared superhydrophobic material is expected to be of great value.

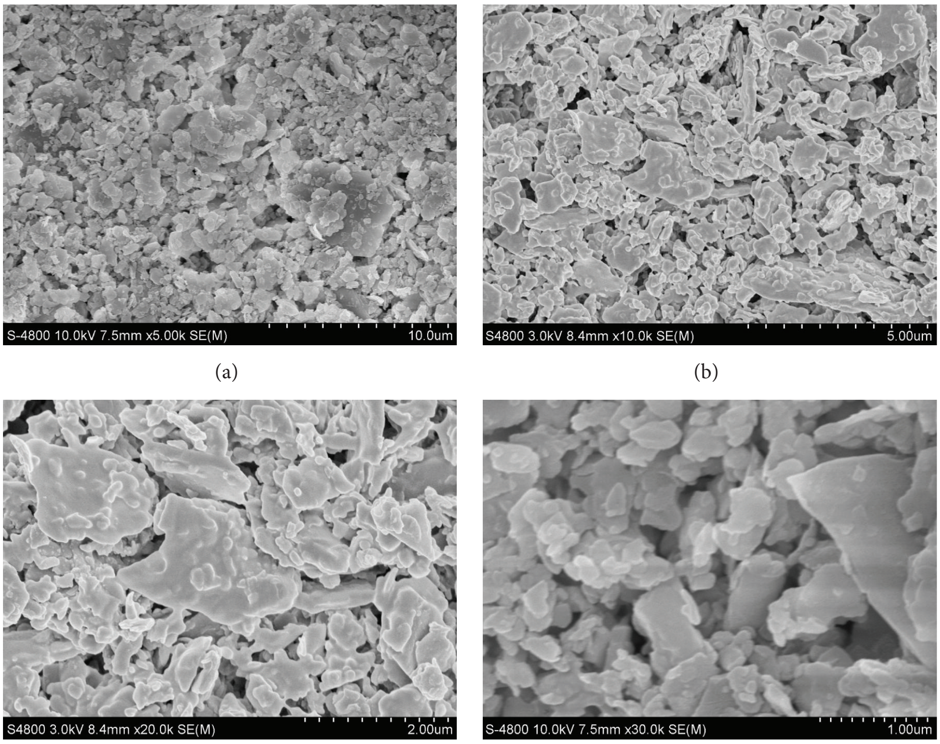
2. Materials and Methods

2.1. Materials. Kaolin particles of size 100–400 nm were purchased from Sinopharm Chemical Reagent Co., Ltd. and before used, they were dried at 120°C for 5 h to remove water. Aluminate coupling agent purchased from Nanjing Daoning Chemical Co., Ltd. was used as received. All other reagents were of AR grade and used as received.

2.2. Substrate Treatment. Glass slides were ultrasonically cleaned with water for 10 min and then immersed in ethanol for about 15 min, followed by rinsing with a copious amount of water prior to use.

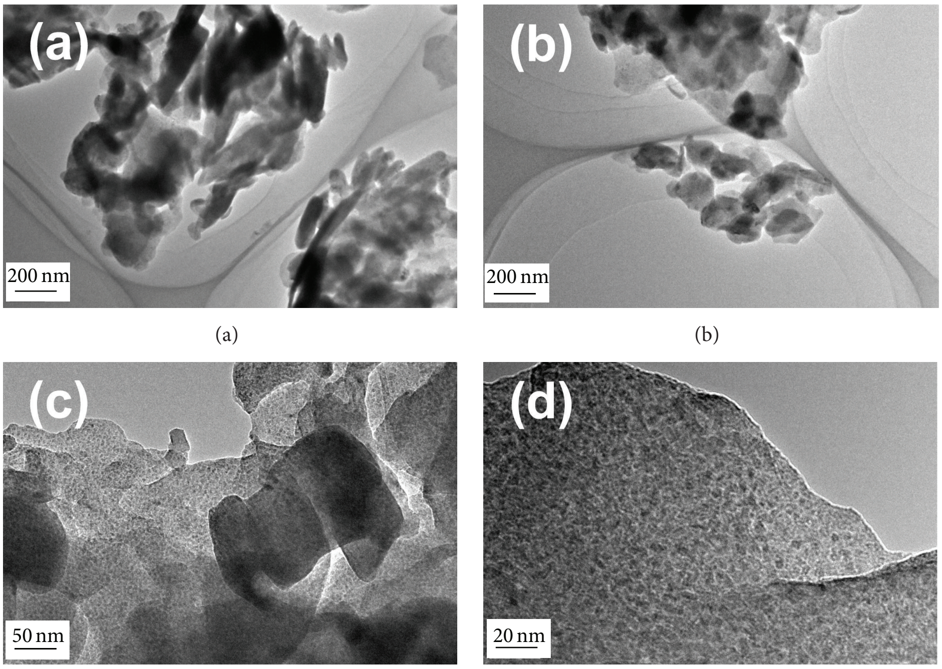
2.3. Fabrication of the Superhydrophobic Material. 0.16 g ACA was dissolved in 11 mL anhydrous ethanol at 30°C for 20 min, and then 5.0 g kaolin particles were ultrasonically dispersed in the mixture for 15 min. Then, they were heated at 106°C for 26 min. Scheme 1 showed the reaction equation. At last, the mixture was drop-coated on glass slides. Samples were dried at room temperature, covered with a culture dish to slow down ethanol evaporation, and then cured at 120°C for 1 h. Another, for the convenience of use, ACA modified kaolin particles can also be obtained. The mixture was centrifugally separated for 5 min, and then the particles were collected by suction filtration using a sand core funnel. Finally, they were dried at 100°C for 1 h. ACA modified kaolin particles (500 mg) were suspended in 1.2 mL anhydrous ethanol, subsequently, by heating for 25 min at 100°C to make a suspension. The preparation of the samples and the following treatments are the same as the stated above.

2.4. Characterization and Instruments. Infrared (IR) spectra were recorded on a Brucher Tensor 27 IR spectrometer (Brucher, Germany) with KBr as the background in the range of 4000–400 cm^{-1}. Samples were prepared by pressing the particles into KBr pellets. Water contact angle (WCA) and sliding angle measurements were performed using a SL200B instrument (Solon Tech., Shanghai, China) at ambient temperature. The volumes of probing liquids in the measurements were approximately 5 μL for the contact angle measurement and 10 μL for the sliding angle measurement. Each contact angle reported was an average value of at least



(a) (b) (c) (d)

Figure 3: SEM micrographs of the as-prepared superhydrophobic surface. The scale bars represent (a) 10 μm, (b) 5 μm, (c) 2 μm, and (d) 1 μm, respectively.



(a) (b) (c) (d)

Figure 4: TEM micrographs of kaolin particles. The scale bars represent (a) 200 nm, (b) 200 nm, (c) 50 nm, and (d) 20 nm, respectively.

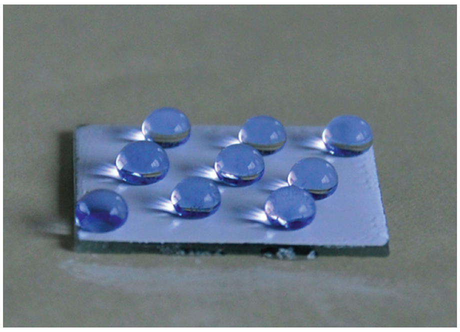


Figure 5: Images of water droplets dyed by methylene blue with different sizes on the ACA modified kaolin particles coating after three months of exposure to outdoor conditions.

five independent measurements on different positions. A scanning electron microscopy (SEM) (Hitachi S-4800) was used for examining the sample surface morphology in top-view or in cross-sections. Before the SEM investigations, all the samples were coated with gold cluster. Transmission electron microscopy (TEM) measurements were carried out using a JSM-1200EX transmission electron microscopy.

3. Results and Discussion

As noted above, the application of superhydrophobic surfaces is greatly hampered for the problem of high contact angle hysteresis, failure upon physical friction, weak environment stability, substrate limitation, and high production cost. Our work is to prepare a coating, which is superhydrophobic, using a very facile and cost-effective method, and can be applied on various substrates. Such a superhydrophobic coating was obtained by surface modification of kaolin particles using ACA as a surfactant. After the samples were cured in the oven, the as-prepared ACA modified kaolin particles surface had a static WCA of 152°, as shown in Figure 1; compared to the WCA of the unmodified kaolin, which was almost 0°, it had demonstrated an outstanding superhydrophobicity. The SA was only 3° and water droplets on this superhydrophobic coating surface easily rolled off even when there is only little tilt of the surfaces and made it very difficult to measure the WCA.

The coupling reaction was confirmed by IR analyses of ACA modified kaolin. In Figure 2, the dark and red lines are the modified and unmodified kaolin particles, respectively. For the ACA modified kaolin particles, the characteristic peaks of the asymmetric and symmetric CH_2 stretching vibration at 2919.77 and 2851.27 cm^{-1}, respectively, suggested a complete alkylation reaction between ACA and kaolin.

To further analyze the morphology of the surface, SEM was applied. The SEM images in Figure 3 showed the morphography of the coating surface. In Figures 3(a) and 3(b), it can be seen that the kaolin particles of different sizes were distributed evenly in the coating. Figures 3(c) and 3(d) revealed that the particles formed a micro-nano hierarchical structure, which, combined with the hydrophobic groups introduced by ACA modification, is supposed to be essential for superhydrophobicity [26–29]. All these features endowed the coating superhydrophobicity. The images exhibited an evident morphology of the surface roughness, which explained the prominent superhydrophobicity.

The modified kaolin particles were also analyzed by TEM (Figure 4). The TEM images revealed that the size of kaolin particles was in a range of 100–400 nm and that the surfaces of the particles were not smooth, which were composed of many overhang and re-entrant structures. Both the different particle sizes and the rough surface were contributed to the construction of hierarchical structures, so as to potentially render the particle coating superhydrophobic.

To estimate the durability of the superhydrophobic coatings, an environmental stability experiment was carried out. The coatings were exposed to environmental conditions by keeping them outdoor. The results indicated that, after three months of exposure to outdoor conditions, no superhydrophobicity decrease was found. Water drops still kept a spherical shape in the surface with a WCA of 151° and were also easily rolling off, taking dusts away in their paths (see Figure 5). We also coated the material on a variety of other substrates, such as commercial marble, limestone, plank, and plasterboard, and all the samples showed good superhydrophobicity. The results indicated that the coating can be applied on a variety of substrates.

4. Conclusions

In the present work, a coating from ACA modified kaolin was fabricated to render the surface with superhydrophobicity. The superhydrophobic surface exhibited a highly rugged structure with micro-nano hierarchical particles randomly distributed all through the coating. Both the hierarchical structure and the ACA modified kaolin furnished the surface with superhydrophobicity. Furthermore, the as-prepared superhydrophobic material showed very good environmental durability and practicability. The technique utilized here is cost-effective, environmental-friendly, and the coating can be prepared easily on various substrates; we expect that this technique can considerably expand the range for various applications, examples of which may include fabricating large water-repellent surface coatings.

Acknowledgments

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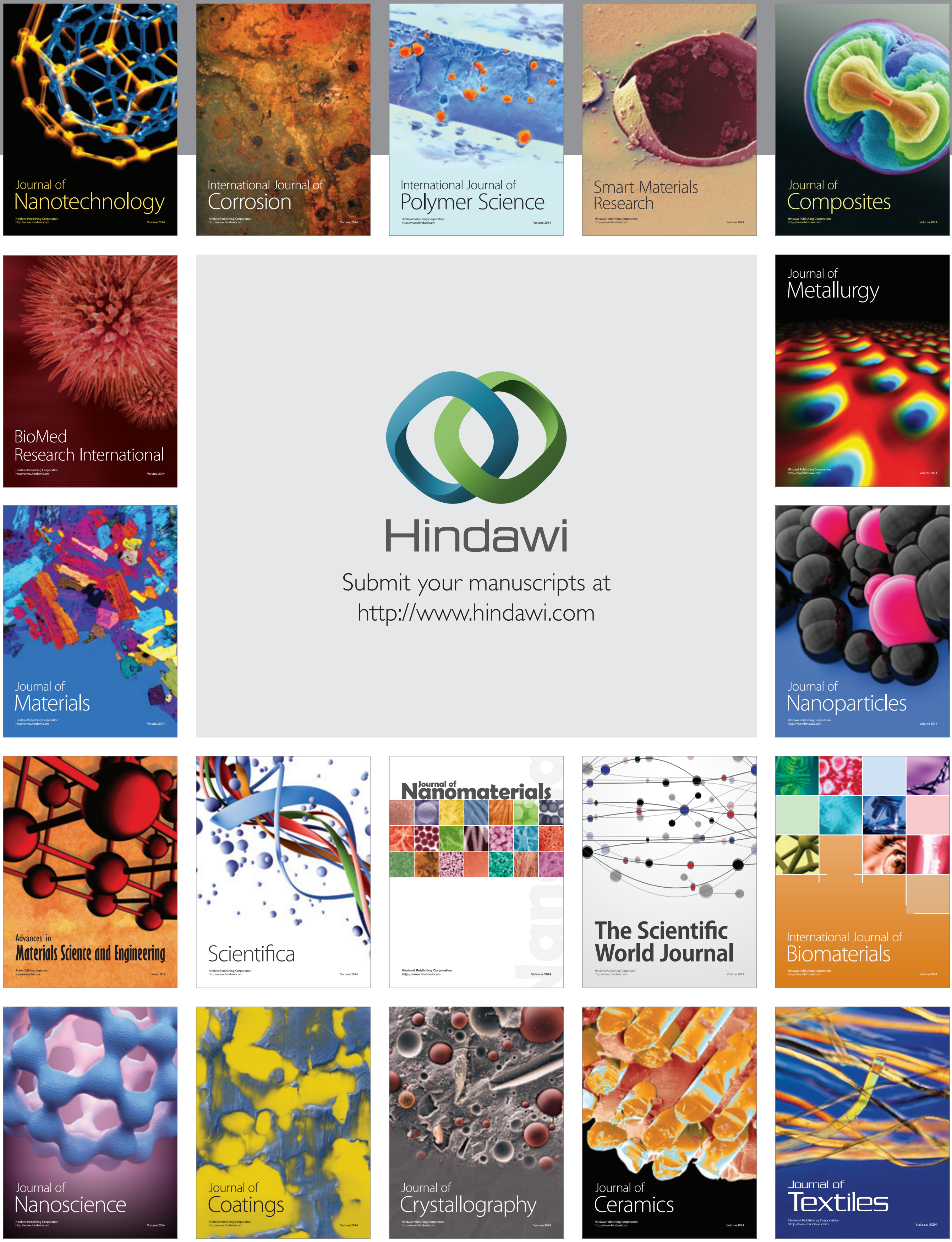
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