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Facile fabrication of superhydrophobic ZnO powders coated on polyurethane sponge for effective oil/water separation application

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ABSTRACT

Oil spills pose significant challenges to the environment, wildlife, and local economies, thus an effective method for cleaning up an oil spill is urgent. Here, superhydrophobic ZnO powder particles were synthesized using a simple and efficient method and investigated their coating on polyurethane sponge for oil/water separation application. Initially, ZnO particles were prepared through a hydrothermal reaction of $Zn(CH_3COO)_2$ and NaOH solution in an autoclave. Subsequently, superhydrophobic ZnO particles were obtained through hydrophobic modification using either stearic acid or 1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane. The results demonstrate that the ZnO particles exhibited excellent superhydrophobic properties, with contact angle of 153^o. After coating superhydrophobic ZnO particles on the polyurethane sponge, the surface became superhydrophobic/oleophilic and could adsorb oil with a capacity measured up to more than 40 times its own weight. Results demonstrate the promising application of superhydrophobic/oleophilic polyurethane sponge for oil/water separation.

1. Introduction

The creation of superhydrophobic materials has been a hot topic not only in academic research but also in industrial applications. A superhydrophobic surface or material is one that exhibits a contact angle greater than 150° [1]. Inspired by the superhydrophobic nature of the lotus leaf, scientists have come to understand that creating artificial superhydrophobic surfaces requires a combination of a rough surface or structure and control over surface energy [2-4] . Over the past decade, superhydrophobic surfaces have found a wide range of applications in various fields, including biosensors [5], anti-corrosion coatings [6], anti-wax treatments [7], self-cleaning mechanisms, anti-fog solutions, anti-adhesion technologies [8], and water/oil separation [9]. There are numerous methods for achieving artificial superhydrophobic surfaces, with most of these methods relying on two key principles: (i) creating structured surfaces to increase surface area and (ii) chemically modifying the surface to reduce its energy [3,6,10-12].

Direct modification the substate to obtain the superhydrophobic surface is suffered from fragile surface textures and poor resistance to wear[13]. In addition, for application in oil-water separation, it requires the modification the surface of porous adsorbents to be superhydrophobic for effective recycling of viscous crude oil spill [14]. On the other hand, ZnO particles exhibit excellent physical, and

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chemical properties, including electronic structure, electron distribution, crystal structure, and ease of chemical modification[15]. Consequently, ZnO particles with diverse morphologies have found widespread use in optical, magnetic, electrical, and various other fields [16]. However, the hydrophilic nature of ZnO particles significantly limits their applications in the fields of self-cleaning and superhydrophilicity [17]. To enhance the superhydrophilicity of ZnO materials, extensive works have been discovered such as varying the morphology [18] or stearic acid modification [19]. In general synthesis of superhydrophobic ZnO particles, researchers only created a solution containing ZnO particles or a superhydrophobic surface using ZnO particle deposition [20], resulting not truly superhydrophobic ZnO particles. For example, Gao, D., and colleagues successfully prepared a solution containing ZnO particles and fluoroethylene-vinylether polymer (PEVE) that could generate a superhydrophobic membrane depending on the ratio of ZnO particles and PEVE [20]. Zhang et al [21] successfully synthesized superhydrophobic Zinc-CPPs (coordination polymer particles) by controlling the morphologies of ZnO nanostructures. To form the superhydrophobic glass, the superhydrophobic particles were coated on the glass and then treated it with a layer of gold, followed by treatment with silane. The technique is suitable for preparation of flat superhydrophobic substrate [22], but not suitable for synthesis of sperhydrophobic sponge [23] .

Herein, we demonstrate a simple method to prepare superhydrophobic ZnO particles. The superhydrophobic ZnO particles were then coated on polyurethane sponge for application in oil/water separation. Firstly, the ZnO particles were synthesized in an aqueous solution by a hydrothermal method. Subsequently, the ZnO particles were continuously modified with either stearic acid or 1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane to obtain the superhydrophobic surface. Finally, the superhydrophobic ZnO particles were deposited on a polyurethane sponge for oil/water separation. We pointed out that the modified polyurethane sponge can adsorb oil up to more than 40 times its own weight, promising potential application in recovery oil spills.

2. Experimental

Materials

1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane (98%) was obtained from Aldrich. Ethanol, toluene, n-hexane, acid stearic, zinc acetate were analytical grades and were purchased from Xilong company. The materials were used as received without any further purification process.

Preparation superhydrophobic ZnO particles

In this section, ZnO particles were synthesized using the hydrothermal method, employing a solution of 0.1N NaOH and a solution of 0.1N Zn(CH3COO)2. Initially, NaOH solution was introduced into the Zn(CH3COO)2 solution with vigorous stirring at a rate of 3 mL/min.

The resulting Zn(OH)2 was subsequently subjected to a thermal treatment within an autoclave system for a duration of 6 hours. Following this, the synthesized Zn(OH)2 was collected via centrifugation and subjected to multiple rinses with distilled water. Eventually, ZnO particles were derived by thermally decomposing the Zn(OH)2 in a furnace set at 500°C for a duration of 1 hour, as outlined in the reaction.

After thermal treatment, the white powders collected are ZnO particles, those were used to prepare the ssuperhydrophobic particles. The superhydrophobic ZnO particles were prepared by following steps: Firstly, the ZnO particles were treated by a 30-minute UV/O3 to effectively eliminate any organic contaminants and promote the creation of surface hydroxyl (-OH) groups. Following this, the activated surface was directly submerged in a solution consisting of 50 mL n-hexane containing 50 microliters of 1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane (PFOS) (for a period of 6 hours) or 50 mL ethanol containing 0.50 mmol of stearic acid (for 3 hours), depending on the modification process. The resultant chemically modified ZnO particles then underwent a thorough rinsing procedure involving three successive washes with n-hexane (in the case of silane modification) or with ethanol (in the case of stearic acid modification), after which they were gently dried under a nitrogen flow. Lastly, the particles were meticulously placed within a clean oven set at 60°C for a duration of 24 hours to ensure absolute dryness and stabilization.

Materials characterization

The morphology of ZnO particles was characterized using a Scanning Electron Microscopy (SEM, JEOL 7600F with EDS, Oxford Instruments). The FTIR and X-ray diffraction (XRD) methods were used to confirm the successful grafting of chemical modifications onto the ZnO particle surface. The wetting properties of the ZnO particles were evaluated by measuring the static contact angle of water using an OCA-data physics instrument at three different positions on each surface, with a 5 μL distilled water droplet. In particular, the powder ZnO particles will be deposited onto a glass slide. Following this, a 5 μL distilled water droplet will be placed on top, and the contact angle will be measured.

3. Results and discussion

Materials characterization

Figure 1 (A) illustrates SEM image of ZnO particles prepared by using starting precursors of 0.1 M Zn^{2+} and 0.1 M NaOH. The ZnO particles have uniform hexagonal wurtzite shapes, with diameters around 1.5 μm and lengths of roughly 3.5 μm, respectively. EDS analysis of the synthesized ZnO particles is shown in Figure 1 (B). The EDS spectroscopy confirms the existence of O and Zn elements originally from ZnO particles. The atomic composition ratio of [Zn]/[O] is one, confirming the stoichiometric ZnO particles were obtained.

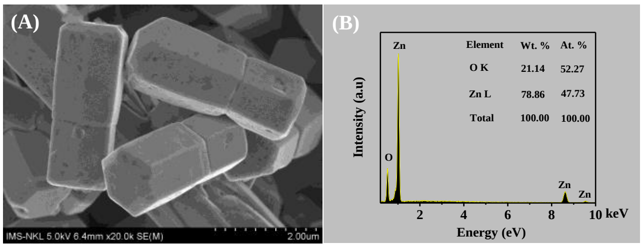

Fig. 1: (A) SEM image and (B) EDS analysis of ZnO particles

Chemical modification of ZnO particles

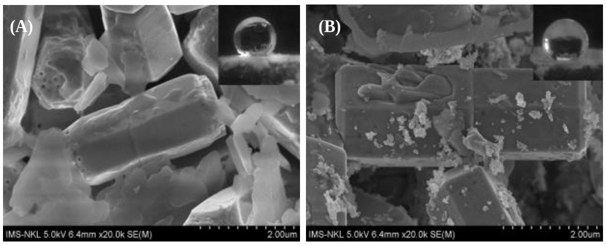

Fig. 2: SEM images of chemical modified-ZnO particles: (A) Stearic acid coated ZnO particles; (B) Silanization coated ZnO particles. Insets are photos of corresponding water droplets

Before chemical modification with stearic acid and PFOS silane, the ZnO particles were activated by the -OH groups on the surface using UV ozone (UV O_3) for 30 minutes. After the chemical modification, the materials were examined using SEM, FTIR, and XRD techniques to determine their microstructure. Figure 2 illustrates the SEM of chemically modified ZnO particles with stearic acid (Figure 2(A)) and PFOS (Figure 2(B)). In comparison to unmodified ZnO particles, a thin chemical coating can be observed around the particles, while the particles themselves retain their hexagonal wurtzite shape. This indicates that the modification processes did not significantly damage the morphology of the particles, but slightly changed the surface of the particles. Insets of Figure 2 are photos of corresponding water droplets, which confirm the superhydrophobic nature of the modified ZnO materials.

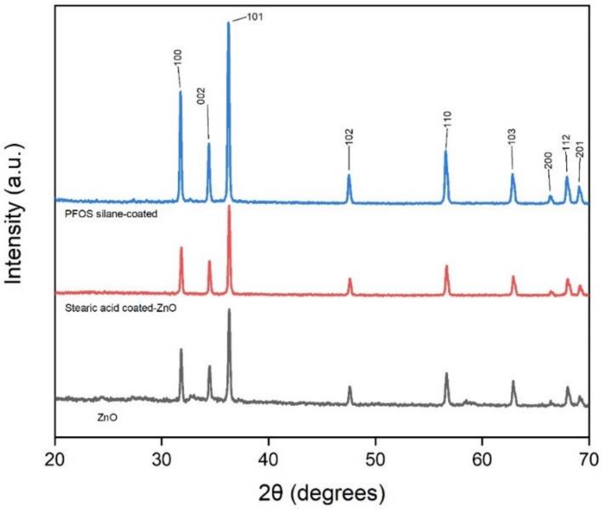

Fig. 3: X-ray diffraction patterns of pristine ZnO particles, stearic acid-modified ZnO particles, and silane-modified ZnO particles

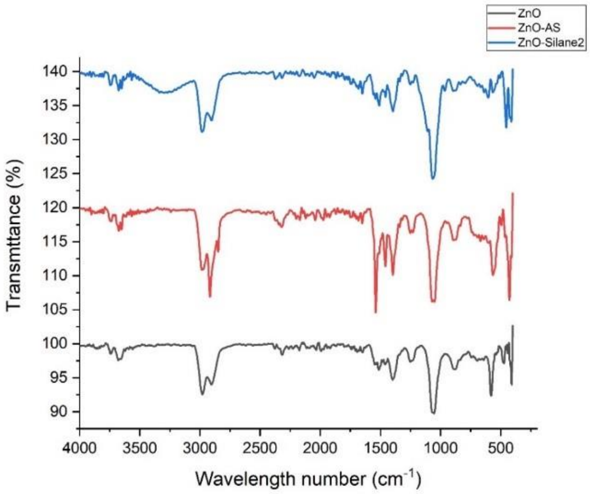

Fig. 4: FTIR spectra of as- prepared ZnO particles, stearic acid- modified ZnO particles, and silane-modified ZnO particles

The XRD pattern of the pristine ZnO particles is as displayed in Figure 3 (the grey line). The diffraction peaks at 31.79°, 34.44°, 36.27°, 47.57°, 56.63°, 62.90°, 66.42°, 68.00°, and 69.14° are indexed as (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. These match with the usually reported peak positions for hexagonal wurtzite phase of ZnO (JCPDS No: 36-145) [21][24]. Such those data confirm that the hexagonal ZnO particles were successfully synthesized by a hydrothermal method followed by thermal calcination. The XRD patterns of chemical modified ZnO particles are compared with unmodified ZnO particle, as shown in Figure 3. Firstly, there is no observation of secondary phases in the ZnO particles with the chemical coating samples. Additionally, no impurity peaks are observed in Figure 3, indicating that the synthesized ZnO particles, and chemically modified particles are hexagonal wurtzite phase. Therefore, after the chemical alternation, the XRD patterns indicate the high purity and high crystalline quality of the pristine ZnO particles, and the chemical coating ZnO particles.

It is well known that stearic acid is a compound made up of a non-polar hydrophobic alkane chain and a hydrophilic carboxyl group. When ZnO particles are mixed with stearic acid, the -OH groups on the surface of ZnO particles react with the -COOH group of stearic acid. This reaction forms a hydrophobic layer, represented as $-(CH_2)n-CH_3$, on the surface of ZnO particles[19][25]. Similarly, perfluorooctyltriethoxysilane also consists of non-polar hydrophobic groups (C-F and C-H) along with a $-Si-OC_2H_5$ group. In the process of silanization, the $-Si-OC_2H_5$ group undergoes hydrolysis to form -Si-OH, which then reacts condensation with -OH groups on the ZnO surface. This results in the attachment of $-(CF_2)n-CF_3$ groups onto the surface of ZnO particles. Both the $-CH_3$ and $-CF_3$ groups exhibit hydrophobic characteristics and provide a low surface energy. These chemical coatings collectively contribute to reducing the surface energy of the ZnO particles. The FTIR spectra of unmodified ZnO particles (the grey line of Figure 4) illustrates the strong absorption peak at 3412 cm-1 of O-H stretching vibrations, indicating that the surface of unmodified ZnO particles was coated with many O-H group and it presented hydrophilic properties. The peak of 437 cm-1 contributed the skeleton of Zn-O. The blue and red line of Figure 4 showed the FTIR spectra of chemical modified -ZnO with silane (The blue line) and with stearic acid (red line). In both the spectra, two intense peaks near 2914 cm-1 and 2846 cm-1 are observed that can be attributed to -CHn group, which confirm the existence of long alkyl group on the surface of ZnO nanoparticles. The formation of -CH3 group enables the surface of ZnO become superhydrophobic.

The surface wettability of unmodified ZnO particles, PFOS silane-coated ZnO particles, and stearic acid-coated ZnO particles was assessed by measuring the water contact angle (CA) using a 5 µL water droplet. Firstly, ZnO powder is placed on a glass slide, and then a 5-microliter water droplet is deposited on the powder surface. The CA values were measured to be about 154 ± 1° and 156 ± 1° after applying PFOS silane-coated particles, respectively. The contact angle is much larger than 150°, confirming the superhydrophobic surfaces [13]. In contrast, the CA value for glass coated with unmodified ZnO was determined to be zero. Consequently, ZnO particles chemically modified with PFOS or stearic acid exhibited remarkable superhydrophobicity with notably high CA values. When compared to PFOS, stearic acid also forms a self-assembled monolayer and creates a hydrophobic coating layer. However, stearic acid is more cost-effective, non-toxic, and harmless. In this investigation, both PFOS and stearic acid reduced the surface energy and transformed superhydrophilic ZnO particle powder into superhydrophobic ZnO particle powder.

Superhydrophobic and oleophilic sponge for oil separation

Typically, a polyurethane (PU) sponge (2×2×2 cm^3) was immersed in 15 mL of ethanol containing 200 mg of modified ZnO particles and sonicated for 15 minutes. The ZnO-coated PU sponge was dried before being immersed in 25 mL of toluene containing 2.5 g of high-density polyethylene (HDPE) for 5 minutes. Finally, the modified PU sponge was dried in an oven at 50^{o}C for 6 hours.

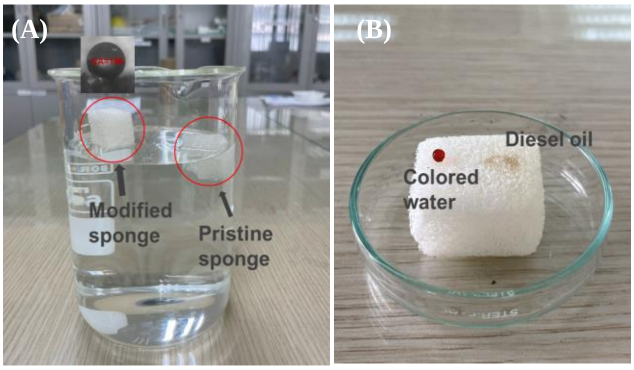

Fig. 5: Photograph of sponge to test the hydrophobic and oleophilic behavior: (A) Sponge coated with modified ZnO particles vs. Pristine sponge on the water surface; (B) Water droplet and diesel oil droplet on the sponge coated with modified ZnO particles

To compare the hydrophobic properties between the pristine sponge and the modified sponge, both samples were deposited on the water surface, as shown in Figure 5(A). The results show that the sponge coated with modified ZnO particles floating on the surface of water, whereas the pristine sponge is completely submersion. This is because the sponge becomes superhydrophobic with a contact angle of approximately 156°± 2 degrees when coated with modified ZnO particles. On the other hand, when a diesel oil droplet is deposited on the superhydrophobic sponge, the diesel oil completely spreads, as shown in Figure 5 (B). The result is opposite with colored water droplet, which stay on the surface of the sponge due to the superhydrophobic properties. Therefore, after coating with modified ZnO particles, the sponge becomes both superhydrophobic and superoleophilic. This implies that the modified sponge exhibits high selectivity for oil/water separation.

To test the capability of absorbing oil from the water surface of the modified sponge, we put the sample into the beaker contained water and oil. As shown in Figure 6(A) the beaker contained water and oil before introducing the superhydrophobic/ superoleophilic sponge. The water and oil are separated into two layers, with the oil on the top. Once modified sponge was added, the oil on the water's surface was adsorbed, resulting in oil/water separation. To calculate the absorption capacity of the sponge, the weight of the sponge before and after absorption oil was measured as m0 and m1, respectively. The absorption capacity is calculated by following equation (1):

$$C = (m_1 - m_0)/m_0 \qquad (1)$$

In this case, the PU sponge coated with modified ZnO particles has an outstanding absorption capacity of more than 40 times. Such result suggests the potential application of our modified PU sponge for oil/water separation in application of oil extraction or oil spills cleanup as shown in Figure 6.(B).

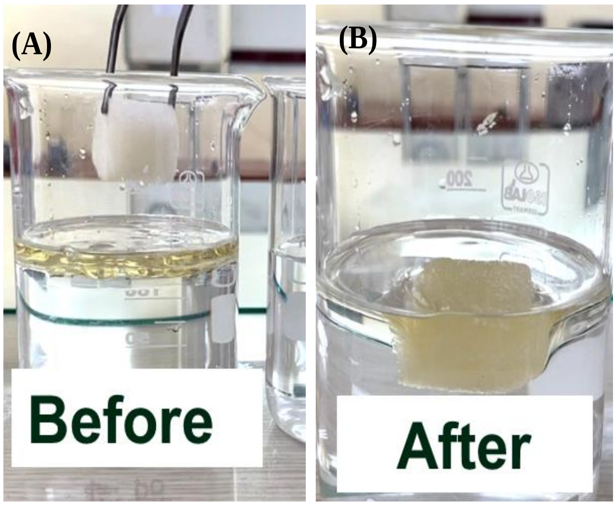

Figure 6: Photos of sponge (A) before and (B) after absorbing oil from the water surface

4. Conclusion

We have successfully achieved superhydrophobic ZnO particles using a simple and cost-effective synthesis method. The ZnO particles were prepared from readily available chemical materials (zinc acetate and sodium hydroxide), resulting in the formation of uniform hexagonal wurtzite shapes. These particles were then modified with perfluorosilane or stearic acid, resulting in superhydrophobic ZnO particles with a contact angle of greater than 154°. Our investigation also shows that after coating superhydrophobic ZnO particles on substrates, the substrate become superhydrophobic and could separate oil/water. These results hold significant potential for advancing industrial processes that create superhydrophobic surfaces with innovative attributes such as self-cleaning. Additionally, they have diverse applications, including corrosion resistance, antibacterial properties, and oil/water separation.

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