

Preparation of Superhydrophobic ZnO Surface Derived from Wood Template

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Abstract. A superhydrophobic ZnO/C surface with a carbon morphology derived from a wood template was fabricated through a solution immersion process, sintering, and modification by FAS. The distribution of zinc oxide on the carbon substrate surface was controlled by changing the mass fraction of Zn(NO₃)₂. After being modified with FAS, the as-prepared ZnO/C surface showed analogous superhydrophobic properties, with a water contact angle of approximately 151.5 °.

Introduction

Wettability is an important feature of solid surfaces that is determined by the chemical composition and microstructure of the surfaces^[1]. In general, two methods can be used to prepare a superhydrophobic surface. The first method is to create roughness on a hydrophobic material surface. The second method is to modify a low-surface-energy material on a rough surface^[2-4].

Some plants show superhydrophobic capabilities. Some biomimetic surfaces with superhydrophobicity have been fabricated in the recent years on the basis of a combination of plant surface micro- and nanostructures and chemical compositions by using some synthetic methods^[5-8]. Wooden structural ceramic has a rich, rough, and porous surface structure, and its pore size ranges from several microns to tens of microns, thus providing great possibilities for its use to prepare superhydrophobic materials. Therefore, the use of natural biological structures as templates to prepare superhydrophobic materials is a new concept.

Zinc oxide (ZnO) is an important semiconductor material, which has found numerous applications such as gas sensors, transparent electrodes, pH sensors, biosensors, acoustic wave devices, UV photodetectors, and photocatalysts^[9-12]. Moreover, ZnO is a very interesting candidate for the preparation of superhydrophobic and self-cleaning films^[13]. The development of ZnO surfaces with superhydrophobic properties can expand the range of traditional applications of these devices.

In the present work, we used natural wood lauan as a template to fabricate superhydrophobic biomorphic ZnO on a carbon substrate (ZnO/C) mainly through sintering the wood template and chemical modification. Then, the microstructure, crystal structure, bonding mode, and hydrophobicity of the obtained surface were investigated.

Experimental

Preparation of ZnO/C Superhydrophobic Surface

Natural-wood lauan was used as the biological plant template. The dried wood was cut into small pieces and sintered in a dry distillation furnace at a heating rate of 2 °C/min to 600 °C, after which the samples were kept warm for 2 h. During the sintering, the wood samples were pyrolyzed into

biomorphic carbon [7]. The biomorphic carbon was then immersed in a $\text{Zn}(\text{NO}_3)_2$ solution (3wt% aqueous solution) for 60 min under vacuum. After drying, the samples were sintered in a tube furnace in which the air was heated to 200 °C at a rate of 2 °C/min. The temperature was then increased to 650 °C at a rate of 3 °C/min. A ZnO coating was thus generated on the carbon substrates. Finally, a ZnO/C sample was modified by a fluorine silane solution with isopropanol (at a volume ratio of 1:5) for 5 days and then dried naturally in air.

Characterization

X-ray diffractometry (XRD, D8 Advance, and Germany) was used to identify the phases of the materials obtained in this study. The surface morphology of the ZnO/C samples was examined with field emission scanning electron microscopy (FESEM, Quant 250FEG). A contact angle (CA) measurement instrument (JC2000D2, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd) was used to measure the contact angle of distilled water with a droplet volume of 4 μL .

Results and Discussion

Phase Analysis

Fig.1 shows the XRD pattern of the as-prepared ZnO/C surface obtained by immersing carbon derived from lauan into a $\text{Zn}(\text{NO}_3)_2$ solution and sintering it at 650 °C. In addition to the characteristic diffraction peaks of ZnO, there are two steamed bread peaks at 24 ° and 43 °, which are the amorphous peaks of carbon. This nongraphitizable carbon was obtained from the pyrolysis of the wood during sintering. ZnO peaks appear along with carbon peaks because $\text{Zn}(\text{NO}_3)_2$ on the carbon surface decomposed to ZnO at high temperature. However, nitrogen peaks were not detected, which indicates that $\text{Zn}(\text{NO}_3)_2$ was completely decomposed. Thus, the obtained products were mixed materials, i.e., ZnO/C.

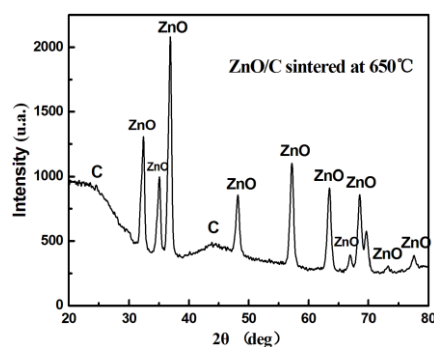


Fig.1 XRD Pattern of ZnO/C Derived from the Lauan

Surface Morphology and Composition Analysis

Fig.2 shows the surface morphology of the biomorphic carbon and the ZnO/C composite materials before and after surface modification with FAS. The surface microstructure of the biomorphic carbon is honeycomb-like, with a nearly hexagonal pore structure with pore sizes ranging from several microns to tens of microns (Fig.2a). In other words, the biomorphic carbon retained the original structure of the wood perfectly. According to the Cassie model, this rough structure facilitates preparation of a superhydrophobic surface. As compared to the original biomorphic carbon, the unmodified ZnO/C obtained by immersing the carbon derived from lauan in a $\text{Zn}(\text{NO}_3)_2$ solution and sintering it at 650 °C showed a very similar morphology, as can be seen from Fig.2b. A white ZnO thin film was formed on both the surface and the internal apertures of the pores. The EDS spectra (Fig.2d) shows a Zn peak but not a N peak. This indicates that $\text{Zn}(\text{NO}_3)_2$ on

the surface of carbon decomposed into ZnO, which agrees with the XRD analysis.

Fig. 2c shows the surface morphology of the modified ZnO/C. From its microstructure, we can see that the surface of the modified ZnO/C also retained the original structure of lauan. It can be confirmed that the FAS treatment almost has not been damaged effectively on the products microstructure. The EDS spectrum (Fig.2d) for the modified ZnO/C surface shows a peak for F, which demonstrates that FAS covered the surface of the modified ZnO/C composite.

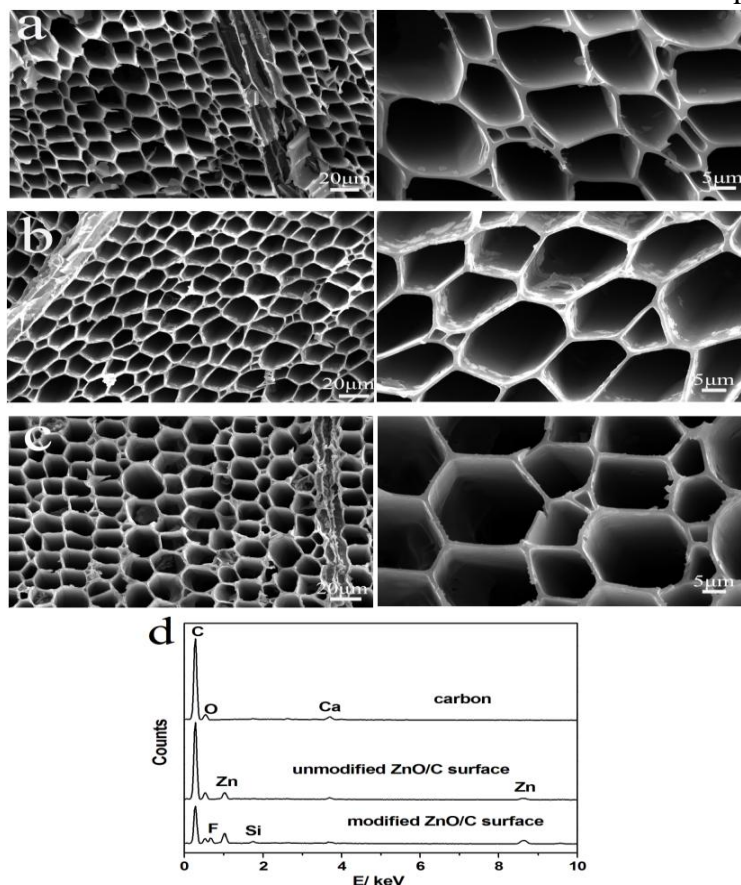


Fig.2 SEM Images of the Surfaces of (a) The Biomorphic Carbon Derived from Lauan, (b) The Unmodified Biomorphic ZnO/C, and (c) The Modified Biomorphic ZnO/C, and (d) EDS Spectra of the Surfaces of the Materials in These Figures

Superhydrophobic Properties

Fig.3 shows photographs of water drops on the various surfaces. The water droplet CA on the unmodified biomorphic carbon surface derived from lauan wood is 120° , as shown in Fig.3a, indicating some hydrophobic properties. In this case, the porous structure of the carbon reduces the contact area between the droplet and the substrate. The unmodified ZnO/C surface was hydrophilic, showing a water droplet CA of approximately 77° (Fig.3b). These results indicate that the chemical composition also plays an important role in the hydrophobicity. However, the modified ZnO/C surface showed significant wettability. After having been modified with the former low-energy FAS coating, the initial hydrophobic sample reached a very high water CA of approximately 151.5° (Fig.3c). As expected, the modification of a low-surface-energy material can affect its wettability. The water CA of the modified smooth carbon was only 114° , as shown in Fig. 3d. Thus, surface roughness also plays an important role in the generation of superhydrophobicity. The water droplet was almost spherical on the modified ZnO/C, as seen in Fig.3e.

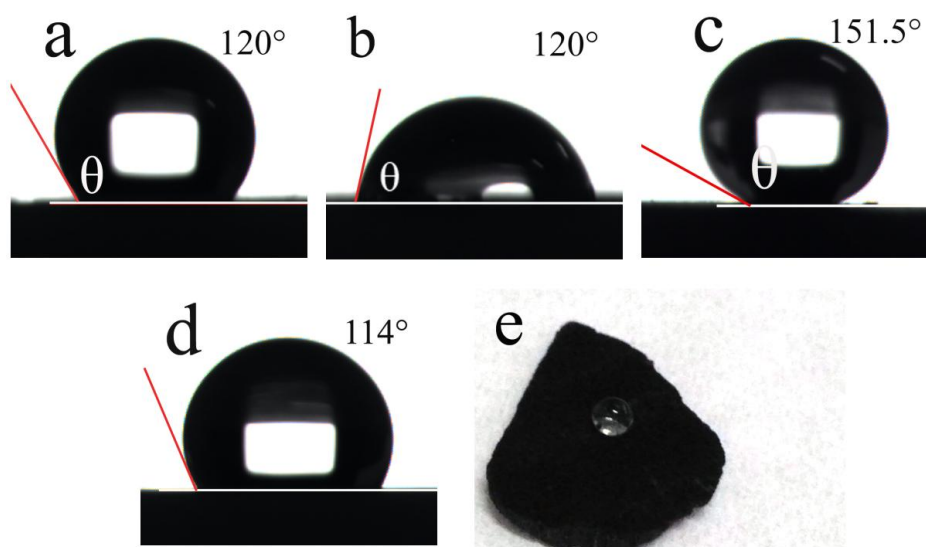


Fig.3 Images of Water CA of the (a) Biomorphic Carbon Derived from Lauan (120 °), (b) Unmodified ZnO/C (77 °), (c) Modified ZnO/C (151.5 °), (d) Modified Smooth Carbon (114 °), and (e) Macro-photograph of Droplet on the Modified ZnO/C

Conclusions

A stable superhydrophobic ZnO/C surface was obtained by a chemical solution method, sintering, and effective modification. The biomorphic carbon surface showed a honeycomb-like porous structure, which directly increased the surface roughness. The unmodified ZnO/C surface can be tailored into a superhydrophobic surface by further fluoride treatment, which decreases the surface free energy significantly. The modified ZnO/C surface exhibited excellent superhydrophobic properties, with a water CA of 151.5°. As compared to artificial imitation or other preparation method, this approach can be used to prepare superhydrophobic ceramics with high fidelity to the surface structure of the original wood. The use of a lauau template in the present study may provide a new way to fabricate superhydrophobic surfaces.

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