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Deposition and super liquid repellency of fluorinated ZnO nanoparticles on carbon fabrics

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ABSTRACT

The liquid-repellent behavior of fluorinated zinc oxide (ZnO) nanoparticles deposited onto carbon fabric (CF) by a pulse microwave-assisted (MA) method followed by surface fluorination treatment was investigated. The MA process is performed at 80 °C within 10 min with different pH values of 5.5, 8 and 12. The hexagonal ZnO nanoparticles with an average size of 100 nm exhibit a well-defined wurtzite crystal structure without any heat treatment. The ZnO nanoparticles produced by MA synthesis at pH = 8 display the maximal density over CF substrate. The fluorination coating effectively imparts super water and oil repellencies on the ZnO–CF surface; i.e., the contact angles are 163° (water) and 153° (ethylene glycol, EG). The liquid repellencies toward water and EG droplets show an increasing function of surface density of ZnO nanoparticles. This result can be attributed to the fact that an air layer is confined in the nanoparticles, thereby inducing a rougher gas–vapor–solid contact line, referred to as the Cassie state. Based on the Young–Duprè equation incorporated with the Cassie parameter, the lowest work of adhesion (W_{ad}) values of the ZnO–CF surface for water and EG repellencies are estimated to be 3.16 and 4.93 mJ/m^2, respectively. Accordingly, this work sheds some light on the creation of a two-tier texture by an efficient MA route and on how the surface density of ZnO nanoparticles strongly affects the repellent behavior of the resultant ZnO–CF composites.

1. Introduction

Zinc oxide (ZnO) with a wide band gap (3.37 eV) and large excitation binding energy has a diverse range of technological applications, such as optoelectronic materials, photocatalysts, gas sensors, solar cells, transparent conductors, and piezoelectronic materials [1–3]. Pioneering efforts have focused on the fabrication of ZnO nanostructures by using various methods, including spray pyrolysis [4], electrochemical deposition [5–9], hydrothermal method [10], and templated electrosynthesis [11]. Although these successful methods exist, it is still desirable to develop efficient routes for the synthesis of ZnO materials. Recently, a microwave-assisted (MA) synthesis that offers a potential route to prepare metallic nanopowders was adopted [12,13]; the method features unique reaction effects, such as rapid heating, low reaction temperature, homogeneous transmission, and phase purity with better yield [14]. It is generally recognized that microwave heating differs from other heating processes, such as the use of heating fluid, gas, steam, or electric heating [15]. In conventional synthesis, energy is transferred to the material through convection, conduction, and radiation, inducing a temperature shift between surface and bulk. However, the MA synthesis offers a fast procedure for the synthesis of nanomaterials with uniform temperature from surface to bulk [16,17]. This study describes a simple MA deposition process for synthesizing hexagonal ZnO nanoparticles on carbon substrate at low temperature under microwave irradiation.

Wetting behavior is one of fundamental properties of nanostructural architectures, and it is strongly affected by the chemical composition (chemical factor) and geometric structure (physical factor) [18–21]. Actually, super water repellency (i.e., water contact angle > 150°) has received a great deal of attention in both fundamental research and practical applications, e.g., antifouling, anti-contamination, and biopassive technologies [22,23]. One fascinating example is the lotus leaf, which exhibits super water repellency toward water droplets. Basically, the lotus leaf possesses a two-tier micro/nanostructural surface that is textured with 3–10 μm hills and valleys coated with nanosized particles of a hydrophobic waxlike material [24]. To mimic the two-tier structure, this study adopts an efficient MA approach to deposit ZnO nanocubes onto microscaled carbon fabric (CF). In fact, various roughened surfaces, including silica stacking layers [25,26], silica-attached carbon fabrics [27], and carbon nanotubes/fabric composites [28,29], have been observed to display superior repellency toward water. However, few reports have focused on the wetting behavior of the ZnO–CF composite surface, and there is still a need for a better understanding of the water and oil repellency of ZnO nanoparticles prepared by the MA route.

Accordingly, a facile MA approach was proposed to decorate CF substrate with ZnO nanoparticles, forming a two-tier roughened surface. The surface density of ZnO nanoparticles over the CF substrate was

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adjusted by using different pH values. Two types of liquid droplets, water and ethylene glycol (EG), were used to examine the water and oil repellencies of ZnO–CF surfaces, respectively. To improve the repellency toward liquid droplets, a fluorination route was adopted to disperse the copolymer coating over the ZnO nanoparticles. The work of adhesion (W_{ad}) was calculated based on the Young–Duprè equation incorporated with the Cassie parameter. This work sheds some light on the water and oil repellency of the resultant ZnO–CF composite surface and on how the fluorination treatment affects the hydrophobic behavior of ZnO nanoparticles.

2. Experiment

All chemical agents with analytical grade were directly used without any further purification. Fig. 1 illustrates a typical procedure for growing ZnO nanoparticles over CF substrate, consisting of (a) ionic adsorption and (b) microwave synthesis. Herein, fresh CF substrate was made from fibers approximately 8–10 μm in diameter, and the surface of the carbon fiber was cleaned before the deposition of ZnO. Prior to any deposition, fresh CF samples were chemically oxidized by impregnating the carbon sample into 0.5 M nitric acid at 85 °C for 1 h. An oxidized CF sample with an area of 2×2 cm^2 was then put in a metallic solution. The Zn-containing solution used here was 1.5 M $(CH_3COO)_2Zn\cdot2H_2O$. Three pH values of the precursors were adjusted to 5.5, 8, and 12 by using 0.5 M KOH. To attain the adsorption equilibrium, the oxidized CF sample was then impregnated in the Zn^{2+} solution at ambient temperature for 12 h.

Pulse MA deposition was done as follows. The CF slurries were placed in the center of a household microwave oven (Tatung Co., 900 W, 2.45 GHz) in which one thermocouple had been equipped to detect reaction temperature. A pulse MA synthesis was carried out at 80 °C under 720 W microwave power, and the deposition and rest periods were set at 2 and 3 s, respectively. The pulse MA synthesis only took a total of 8 min after which the treated CF samples were dried in a vacuum oven at 105 °C overnight. The three ZnO–CF samples were designated as ZnO–CF5, ZnO–CF8, and ZnO–CF12 according to pH values of 5.5, 8, and 12, respectively. A fluorination treatment was applied to lower the surface tension of the ZnO–CF films by using a spin coater to deposit the perfluoroalkyl methacrylic copolymer (Zonyl 8740, Dupont Co.; copolymer/water ratio of 7:3 v/v) over the surfaces. The copolymer was first diluted with distilled water to 3 vol.% in this study. The spin-coating process consisted of two stages: in the first stage, the spinning speed was set at 500 rpm for 10 s in the second stage, the speed was turned up to 3000 rpm for 30 s. This coating process enabled good dispersion of the fluoro-containing copolymer onto the ZnO films [29]. After the hydrophobic coating, the fluorinated ZnO surfaces were dried in an oven overnight, inducing a fluorocarbon coating on the surface of the ZnO–CF samples.

Field-emission scanning electron microscopy (FE-SEM, JEOL JSM-5600) and high-resolution transmission electron microscopy (HR-TEM, JEOL, JEM-2100) were adopted to observe the ZnO topography and distribution on the carbon support. The deposition loading of ZnO over the CF substrate was determined by heating the ZnO–CF composites at 900 °C in air atmosphere using a thermogravimetric analyzer (TGA, PerkinElmer TA7). The relevant phase of ZnO nanocubes was identified by X-ray diffraction (XRD) using an automated X-ray diffractometer (Rigaku, D/MAX 2500). Two types of liquids, deionized water (surface tension: 72.3 mN/m) and EG (surface tension: 45.2 mN/m), were used to evaluate the water and oil repellency of the resultant ZnO–CF surfaces. An optical contact angle spectroscope was used to measure the contact angles of the liquid droplets on the films. Each droplet was dropped onto the surface from a distance of 5 cm by vibrating the syringe. A 3-μL liquid drop was deposited on the surface using a micropipette. Five drops of water were placed at different locations on a horizontal surface, and five readings were taken. All contact angle measurements were performed at ambient temperature.

3. Results and discussion

3.1. Characterization of ZnO nanoparticles

To rule out the effect of the CF substrate, the pulse MA approach was adopted for synthesizing ZnO nanoparticles in colloidal suspension. The as-synthesized ZnO powders were collected and characterized by XRD, FE-SEM, and HR-TEM. Fig. 2(a) and (b) show the typical XRD patterns of ZnO nanoparticles at pH values of 8 and 12, respectively. Herein, all the peaks are well matched on Bragg reflections of the standard wurtzite structure (JCPDS Card No. 36-1451) with the unit cell parameters $a=b=3.24$ Å and $c=5.21$ Å [16,30]. The strong and sharp peaks confirm that the hexagonal ZnO nanoparticles synthesized by the MA method are highly crystalline. This can be attributed to the fact that MA synthesis at different pH values induces a dipole change in polar molecules (e.g., water and hydration molecules) with uniform temperature distribution, thus resulting in highly crystalline ZnO.

Fig. 2(c) shows the top views of the FE-SEM image of the ZnO nanopowders prepared by the MA approach at pH = 8. The image clearly indicates that a large number of hexagonal ZnO nanoparticles are produced by the MA route. The ZnO nanoparticles were found to have an average size of 100 nm. Fig. 2(d) shows the well-defined lattice fringes of the ZnO crystal, indicating that there are no detectable crystal defects, such as micro twins or dislocations, in the ZnO nanoparticles except for unsaturated bonds on the surface or the edge. The spacing

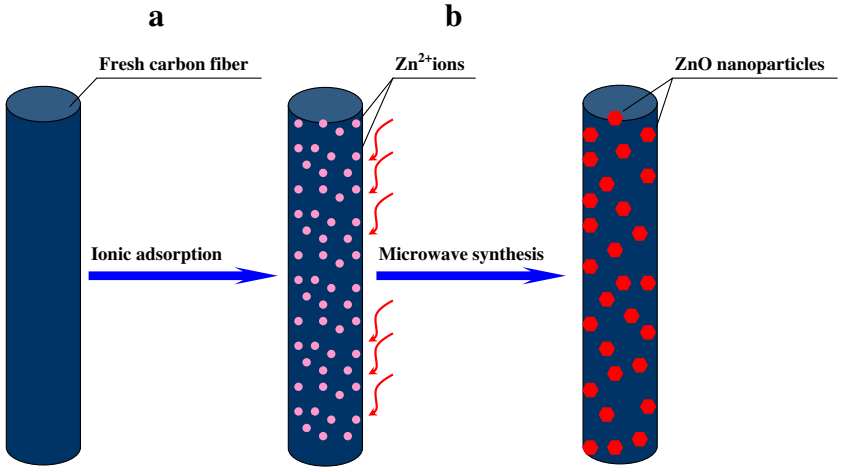

Fig. 1. Schematic diagram for growing ZnO nanoparticles onto CF substrate, consisting of (a) ionic adsorption and (b) pulse MA deposition.