Applied Surface Science 343 (2015) 172–180

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Hierarchical ZnO particles grafting by fluorocarbon polymer derivative: Preparation and superhydrophobic behavior

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ARTICLE INFO

Article history:
Received 20 September 2014
Received in revised form 21 February 2015
Accepted 4 March 2015
Available online 11 March 2015

Keywords:
Superhydrophobicity
Hydrothermal process
Surface grafting
Contact angle
Wetting model

ABSTRACT

Superhydrophobic surfaces on the basis of hierarchical ZnO particles grafted by fluoroethylene-vinylether (FEVE) polymer derivative were prepared using a facile, mild and low-cost method. X-ray diffraction (XRD) and scanning electron microscope (SEM) revealed that the resulting ZnO particles via hydrothermal process exhibit micro–nano dual-scale morphology with high purity under a suitable surfactant amount and alkali concentration. The grafting of FEVE derivative was confirmed by Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray spectrometer (EDS), suggesting that hierarchical surface of ZnO particles was an imported monomolecular layer of fluorocarbon polymer. The obtained surface fabricated by drop-casting shows considerably high contact angle and good resistance to water immersion. The wetting behavior in this work was furthermore analyzed by theoretical wetting model. This work demonstrates that the sufficient low-wettable surface and high roughness both take a vital role in the superhydrophobic behavior.

1. Introduction

Researchers are always devoting great interest to superhydrophobic behavior in nature, in order to fabricate mimicking superhydrophobic surface, which exhibits considerable potential application in self-cleaning coatings, exterior paints and flow drag reduction [1]. According to the study on natural superhydrophobic materials, such as lotus leaf [2] and spider legs [3], it was concluded that chemical composition of low-wettable surface and topology with high roughness determine the advanced superhydrophobicity, which was valued by contact angle (CA). As a general idea, more than 150° of CA is a direct criterion to identify a superhydrophobic material. To constitute micro–nano hierarchical surface with low wettability becomes a widely applied method to realize superhydrophobic behavior [4].

To synthesize the hierarchical scale surface, a mild liquid-phase route should be selected with priority because of its low energy consumption. One widely adopted way seems to be assembling micro- and nanoscale particles with a functional group as a connection, which could be carried out via various methods, including condensation of functional groups [5–8], supermolecular self-assembly [9] and layer-by-layer assembly [10–12]. Another beneficial synthesis route is realized by the growth of nanoscale structure from microscale substrate, of which the in situ polymerization to grow polymer nanophase [13,14] and sol–gel process forming silica colloidal particles around existing cores [15–19] are mostly noticed. However, whatever type of route is performed, the connection of dual scales usually leads to inconvenience, because complicated preparation design, multi-assembly steps and limited raw material resource could rarely be avoided.

Therefore, the hierarchical inorganic particles prepared via one step show great advantages. Actually, researchers have already supplied an advanced route to prepare dual-scale particles, which usually via hydrothermal process. Numerous “chestnut” dual-scale inorganic particles can be generated by series of metal salt precursors [20], yielding microscale dimension, but with nanoscale branches. Particularly, a considerable number of reports [21–26] focused on “chestnut” ZnO particles by hydrothermal method, because this low-cost advanced material shows great properties in the field of chemical sensor and photoelectric converter. However, for superhydrophobic applications, there have been only a few reports on one-dimensional ZnO rods vertically growing on certain substrates [27–31]; dual-scale ZnO particles are rarely found in this field. In comparison to these 1-D ZnO nanorod layers, dual-scale ZnO possesses great flexibility because high roughness was carried by dual-scale “segments”, which could distribute to form continuous layer without dipping the entire substrate in reactive medium. That provides great

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http://dx.doi.org/10.1016/j.apsusc.2015.03.024

Table 1
Reagents amount (g) for hydrothermal preparation of hierarchical ZnO particles.

Sample	NaOH	PEG	Solvent EtOH/H_2O (v/v)
ZnO-1	9.0	20.0	0.5
ZnO-2	12.0	20.0	0.5
ZnO-3	10.5	20.0	0.5
ZnO-4	9.0	20.0	0
ZnO-5	9.0	10.0	0
ZnO-6	9.0	30.0	0

convenience to fabricate superhydrophobic surface with a large area.

On the other hand, to the best of our knowledge, the researched hierarchical surface is usually treated by organic molecules, such as long-chain alkyl or fluorocarbon silanes [27,28,32,33], in order to offer the low-wettable composition to high roughness structure. However, high cost and limited production of these modifiers restricted the application in the inorganic particles modification. Then a polymer-sized reagent composed of simple repeat units could be considered, fluoroethylene-vinylether (FEVE) resin, which has advantages of relative low cost and wide application. The multi-functional (—OH) substituted polymer shows significant feasibility to realize group transform [34] (—OH + —NCO → —NH—COO—). Therefore, the condensation of FEVE and isocyanate alkoxy silanes provides a multi-functional modifier for grafting on hierarchical surfaces. But up till now, rare attention has been paid to the selection of FEVE derivatives applied in surface grafting of inorganic particles.

Our study involves the preparation of hierarchical ZnO particles via hydrothermal process, and their surface treatment using FEVE derivative, which yields dual-scale particles with fluorocarbon layer with low surface energy. Furthermore, the particles dispersions were drop-cast on glass slide, forming a superhydrophobic surface with high CA values. We have also analyzed the wetting state in our work using a special theoretical model.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($ZnAc_2{\cdot}2H_2O$, 99%) and isocyanate propyl triethoxysilane (IPTES, 96%) were purchased from J&K Chemical Co., Ltd. Sodium hydroxide (NaOH, 96%) was provided by Beijing Chemical Works. Poly(ethylene glycol) (PEG, molecular weight = 17,000–22,000) was obtained from Tianjin Guangfu Fine Chemical Research Institute. Ethanol (EtOH) and xylene were purchased from Beijing Yili Fine Chemical Co., Ltd. Triethylamine (Et_3N) was purchased from Tianjin Fu Chen Chemical Reagents Factory. All Chemicals listed above were used without further purification. Fluoroethylene-vinylether (FEVE) polymer (number-average molecular weight = 14,000, hydroxyl value = 63.8 mg KOH/g, acid value = 4.1 mg KOH/g, solid content = 65 wt%) was supplied by Daikin Fluoro Chemicals (China) Co., Ltd.

2.2. Preparation of hierarchical ZnO particles

The quantities of reagents are listed in Table 1. In a typical process, NaOH was added into a three-neck round bottom flask with mechanical stirring, and was dissolved by deionized water or ethanol/water solution (200 mL). Under vigorous stirring, PEG was prudently added into the mixture, producing a transparent solution in several minutes. The solution of $ZnAc_2{\cdot}2H_2O$ (6.02 g, 0.027 mol) in deionized water (40.0 g) was dropped into the reaction mixture via a dropping funnel for 20–30 min at 20–25 °C. After that process, the mixture was transferred into a Teflon-lined autoclave, and heated at 180 °C for 12 h. After the autoclave cooling, white products were separated by vacuum filtration and washing with ethanol. The products were dried at 80 °C for 6–8 h under vacuum.

2.3. Import of FEVE derivative

FEVE (1.0 g) was injected to a three-neck round bottom flask with a condenser and magnetic stirrer, and was diluted by xylene (20 mL). The solution was added by using Et_3N (2.0 mL) as a catalyst, followed by IPTES (281 μL, 1.14 mmol) at ambient temperature. The reactive mixture was subsequently refluxed at 140 °C for 12 h. This process yields a dark yellow solution (FEVE-IPTES).

The grafting procedure was performed according to a relative report [34]. Prescribed amount of FEVE-IPTES solution was extracted, placed in a three-neck round bottom flask with a condenser and magnetic stirrer, and was diluted by xylene, so that the total amount of solvent reached 4.5 mL. ZnO products were added into the solution, generating a turbid dispersion. The mixture was refluxed at 140 °C for 8 h. After the reaction process, the products were washed with additional xylene (40 mL) to prevent unreacted IPTES. Then the mixture was placed for at least an hour and the clear liquid in upper level was poured out. The remaining particles were well dispersed by stirring. Then the dispersion (~2 mL) was immediately drop-cast onto glass slides, dried naturally for 24 h, and prepared for contact angle (CA) measurements.

2.4. Characterization

X-ray diffraction (XRD) was performed on a D/Max 2500V/PC diffractometer (Rigaku Corporation, Japan) and Cu Kα targets (λ = 0.154 nm) were used, at a scanning rate of 0.0202 s^{-1}. The functional groups of specimen were tested by Fourier-transform infrared (FTIR), which were measured on a Bruker Vector22 infrared spectrophotometer. Samples were prepared on a KBr pellet and were scanned at wave number range of 4000–400 cm^{-1} at 25 °C, with a resolution of 2 cm^{-1}. The morphology and micro-nanostructures were analyzed by a field emission scanning electron microscopy (SEM, Hitachi S-4700). The surface chemical composition was analyzed by an energy-dispersive X-ray spectrometer (EDS) on SEM. Contact angles (CA) measurements were used to exhibit the hydrophobicity of specimen, and were performed on a JGW-360A instrument (Chengde, China) at 25 °C, with 5–10 μL droplet of ultrapure water. A static CA value is obtained by measuring the angle between both solid–liquid–air cross-sections and top of the droplet, to derive corresponding CA assuming the droplet is accurately spherical. The resulting CA value was averaged over 10 measurements.

3. Results and discussion

3.1. Preparation of hierarchical ZnO and its surface treatment

To show the complete preparation process, Scheme 1 represents all steps involved in this study. As seen in Scheme 1, hierarchical ZnO particles are synthesized by hydrothermal route with the aid of OH^- and surfactant. The surfactants are considered as soft directing agents, which could assemble to generate micelles. Afterwards, Zn (II) precursor and OH^- are enriched into the micelles. As a result, the subsequent nucleation and growth of ZnO crystal occurred in these soft templates [20,35]. Hydrothermal process obviously further enhances the formation of ZnO particles and promotes to obtain products with special morphology. The producing metal oxide particles include abundant hydrophilic —OHs and quite a few —COOHs on surface. For exhibiting low surface energy, a polymer with a great quantity of F atoms, FEVE was grafted onto the particle surface. However, because of almost no reaction activity for the functional group —OHs in polymer side chains and rare