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Superhydrophobic Zn*Al* double hydroxide nanostructures and ZnO films on *Al* and glass substrates

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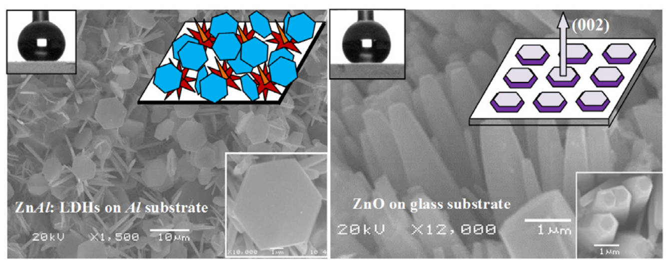
HIGHLIGHTS

- Zn*Al*: layered double hydroxides (LDHs) nanoplates are fabricated on *Al* substrate.
- ZnO nanorods are fabricated on glass substrate.
- Zn*Al*: LDHs and ZnO are characterized using XRD, SEM and FTIR.
- Superhydrophobicity is achieved by passivating the substrates using stearic acid.
- Water contact angle of Zn*Al*: LDHs or ZnO coated substrate is > 160°.

GRAPHICAL ABSTRACT



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ABSTRACT

Superhydrophobic nanostructured Zn*Al*: layered double hydroxides (LDHs) and ZnO films have been fabricated on *Al* and glass substrates, respectively, by a simple and cost effective chemical bath deposition technique. Randomly oriented hexagonal patterned of Zn*Al*: LDHs thin nanoplates are clearly observed on *Al*-substrate in the scanning electron microscopic images. The average size of these hexagonal plates is ~4 μm side and ~30 nm of thickness. While on the glass substrate, a oriented hexagonal patterned ZnO nanorods (height ~5 μm and 1 μm diameter) are observed and each rod is further decorated throughout the top few nanometers with several nanosteps. At the top of the nanorod, a perfectly hexagonal patterned ZnO surface with ~250 nm sides is observed. The tendency to form hexagonal morphological features is due to the hexagonal crystal structure of ZnO confirmed from X-ray diffraction patterns and transmission electron microscopy image. The Zn*Al*: LDHs and/or ZnO coated substrates have been passivated by using stearic acid (SA) molecules. Infrared spectra of passivated Zn*Al*: LDHs coated substrates confirm the presence of SA. X-ray diffraction pattern also corroborates the results of infrared spectrum. The contact angle of the as prepared samples is zero. The superhydrophobicity is achieved by observing contact angle of ~161° with a hysteresis of ~4° for *Al*-substrate. On the glass substrate, a higher contact angle of ~168° with a lower hysteresis of ~3° is observed. A lower surface roughness of ~4.93 μm is measured on Zn*Al*: LDHs surface layer on the *Al* substrate as compare to a higher surface roughness of 6.87 μm measured on ZnO layer on glass substrate. The superhydrophobicity of passivated nanostructured films on two different substrates is observed due to high surface roughness and low surface energy.

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1. Introduction

After a rainfall, shining of nearly spherical water drops on certain leaves is one of the most beautiful wonders of nature. Such natural phenomenon is observed not only on plants' leaves, but also on the body of several living creatures [1]. The water repellency phenomenon is well understood on lotus leaves and is called as 'lotus effect' [2]. This is considered as the basis of the studies of superhydrophobicity. The microscopic observation of the lotus leaves under scanning electron microscope show the coexistence of combined micro-nanostructured pattern which is again covered with a hydrophobic wax component. Two basic mathematical models, Wenzel [3] and Cassie and Baxter [4], are used to explain the contact angle behavior of rough surfaces. In general, a water droplet contact angle less than 90° indicates a hydrophilic surface while an angle greater than 90° present a hydrophobic one. If the water contact is higher than 150°, the surface called superhydrophobic, and on such a surface, water drops would roll off with nearly zero wetting which is also called self-cleaning surface. Study of the wetting properties of solids by liquids and interfacial phenomena are not only important in fundamental research but also significant technological issues. In many areas of technology it is required to control the wettability of surfaces. Self-cleaning property is desirable for car windshields, aircraft, solar energy cells, anti-sticking of snow on glass window [5], etc. Apart from these, superhydrophobic surfaces have several emerging applications in a large number of fields such as anticorrosive industrials parts, antibiofouling paints for boats, biomedical applications, microfluidics, textiles, current conduction, bio-chips and many others [6,7].

Generally, superhydrophobic surfaces are prepared by combining two steps that involve the creation of a rough micro-nano patterning on surface in the first step and passivation of this rough surface using low surface energy coating in the second step. Various techniques have been developed to prepare rough surface patterns, and also to control the shapes, dimensions, and regularity of the surface, such as lithography, sol–gel, plasma etching, chemical etching, chemical bath deposition (CBD) technique [8–10], etc.

Song et al. [11] have been synthesized hexagonal, bullet-like ZnO microstructures and nanorod by a simple hydrothermal method without surfactants. Kuo et al. [12] studied on hydrothermal synthesis of ZnO microspheres and hexagonal microrods with sheet like and slate like Nanostructures. High crystalline ZnO with hexagonal dumbbell-like bipods morphology was successfully synthesized via N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB)-assisted hydrothermal microemulsion route [13]. Cho et al. [14] reported a novel method for fabrication of sub 20 nm diameter ZnO nanorod arrays on Zn sheet at room temperature and normal atmospheric condition with the presence of *Al* salt. A superhydrophobic flower like ZnO and porous Zn–*Al* LDH were synthesized on *Al* substrate by sol-gel method [15]. Cho et al. reported a method that simultaneously yield *Al*-doped ZnO nanoneedles (1D) and hexagonal Zn–*Al* hydroxide in temperature controlled microwave synthesis (95 °C and 50 W) irradiation with the presence of Zn^{2+} and Al^{3+} ions in the solution [16]. Superhydrophobic properties of *Al* surfaces by creating a certain nanoroughness using a chemical etching was reported by Saleema et al. They also studied superhydrophobic properties of ZnO coated *Al* substrate by sol-gel spin coating and they have achieved a contact angle greater than 160° [17]. In another study, ZnO nanotowers coated silica substrate fabricated by CBD technique showed highly superhydrophobic with a contact angle ~173° [18]. Sarkar et al. [19] showed superhydrophobic properties of micro-nanorough aluminum substrates upon coatings with fluorinated hydrocarbon providing a water contact angle of 165° and contact angle hysteresis below 2°. In a recent study, Yu et al. [20] has reported that superhydrophobic ZnO nanostructured materials show an important application in self-cleaning smart coatings on ITO glass substrate with a contact angle of 152°. In this article, we have fabricated superhydrophobic hexagonal structured Zn*Al*: LDHs nanoplates on *Al* substrates and ZnO nanorods on glass substrate by a very simple and inexpensive CBD technique for self-cleaning application.

2. Experimental technique

Aluminum alloy coupons (AA6061) and glass slides of rectangular shape were ultrasonically degreased in 1% Liquinox solution for 10 min. Then the substrates were washed by water followed by ultrasonication with acetone for 15 min. Finally, the substrates were washed with deionized water in ultrasonic bath and after drying at 70 °C for 10 h they were used for experimental purpose. Then, the cleaned *Al* and/or glass substrates were immersed separately in two chemical baths consisting of 40 ml of aqueous 0.1 M $Zn(NO_3)_2 6H_2O$ and 2 ml of 28% aqueous NH_4OH solution via chemical bath deposition technique. The Zn*Al*: LDHs and ZnO together were grown on *Al* substrate and only ZnO was grown on glass substrate at hot plate temperature of 75 °C. After coating the substrates were taken from the solution and ringed by deionized water. After that, the coated *Al* and glass substrates were kept for drying at an oven temperature of 70 °C. Finally, the *Al* and glass substrates were passivated separately with 0.01 M stearic acid (SA) in ethanol for 15 min by immersion for further characterizations.

The X-ray diffraction (XRD) of Zn*Al*: LDHs coated *Al* substrate and ZnO coated glass substrate were carried out using Cu Kα radiation in a Bruker D8 Discover diffractometer in order to study the crystal structure of the synthesized materials. The morphological and elemental analyses of the samples were performed using high resolution transmission electron microscope (HRTEM,JEOL JEM 2100) and scanning electron microscope (SEM, JEOL JSM-6480 L V) equipped with energy dispersive X-ray spectroscopy (EDX). The Zn*Al*: LDHs and/or ZnO nanorods functionalization with SA were analyzed by the Infrared reflection absorption spectroscopy (IRRAS, Nocolet 6700FT IR). The wetting characteristics of the samples surfaces were carried out using contact angle goniometer (Krüss GmbH, Germany). The contact angles (advancing and receding) were measured by directional movement of contact angle goniometer stage holding the sample, while a water droplet was hold by a stationary needle in contact with the sample surface. The contact angles were calculated by fitting images of asymmetric water droplet with the tangent-2 method with Krüss DSA software [21]. The surface roughness of the coated film on the two different substrates (*Al* and glass) was measured using optical profilometer (MicroXAM-100 HR 3D surface profilometer).

3. Results and discussion

3.1. X-ray diffraction of ZnO and ZnAl: LDHs

The crystal structure of the ZnO film coated on glass substrate has been characterized by X-ray diffraction. Fig. 1(a) show the XRD pattern of the ZnO prepared on glass substrate by CBD technique. All the peaks of the sample correspond to those of the standard hexagonal wurtzite ZnO structure with calculated lattice constants of about $a = 0.3258$ nm and $c = 0.5162$ nm [22]. The XRD pattern also indicates strong preferred orientation along the *c*-axis because the (002) reflection is significantly enhanced relative to the usual (101) maximum reflection. Because no other diffraction peaks were observed in the XRD patterns, we conclude that hexagonal-phase ZnO structure formed on the glass substrate. Further structural

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