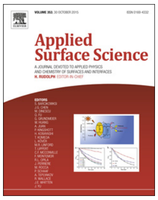
Applied Surface Science 353 (2015) 735–743

Contents lists available at ScienceDirect

Applied Surface Science

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



Photoinduced switchable wettability of bismuth coating with hierarchical dendritic structure between superhydrophobicity and superhydrophilicity

Chunping Su, Zhong Lu, Huiping Zhao, Hao Yang*, Rong Chen*

Key Laboratory for Green Chemical Process of Ministry of Education and School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Xiongchu Street, Wuhan, 430073, PR China

ARTICLE INFO

Article history:
Received 13 March 2015
Received in revised form 24 June 2015
Accepted 27 June 2015
Available online 10 July 2015

Keywords:
Bismuth
Dendritic nanostructure
Switchable wettability
Superhydrophobicity
Superhydrophilicity

ABSTRACT

Special wettability such as superhydrophobicity and superhydrophilicity has aroused considerable attention in recent years, especially for the surface that can be switched between superhydrophobicity and superhydrophilicity. In this work, hierarchical bismuth nanostructures with hyperbranched dendritic architectures were synthesized via the galvanic replacement reaction between zinc plate and $BiCl_3$ in ethylene glycol solution, which was composed of a trunk, branches (secondary branch), and leaves (tertiary branch). After being modified by stearic acid, the as-prepared bismuth coating shows superhydrophobicity with a high water contact angle of 164.8° and a low sliding angle of 3°. More importantly, a remarkable surface wettability transition between superhydrophobicity and superhydrophilicity could be easily realized by the alternation of UV–vis irradiation and modification with stearic acid. The tunable wetting behavior of bismuth coating could be used as smart materials to make a great application in practice.

1. Introduction

Solid surface with switchable wettability between superhydrophobicity and superhydrophilicity has aroused great interest and has been extensively investigated due to their potential applications in sensors [1,2], separators [3], microfluidic devices [4–6], and chemical valves [7]. Fabrication of superhydrophobic surfaces is usually achieved by modifying rough surfaces with low surface energy materials or creating nanostructures on hydrophobic surface [8,9]. For instance, hierarchical dendritic nanostructure is one of the optimal constructions to fabricate superhydrophobic surfaces [10,11]. Meanwhile, some superhydrophobic surfaces can transform from superhydrophobicity to superhydrophilicity under diverse external stimuli, such as light irradiation [12–14], pH value [15–17], temperature [18–20], electrical potential [21–23], solvent [24,25], or counterions [26–28]. Among the different stimuli, light irradiation has received special attention because it can be controlled easily and quickly that make wetting switch individually addressable [13]. It is also found that photo-responsive surface wettability is closely related to the photocatalytic properties of materials upon UV light irradiation, such as TiO_2, ZnO, WO_3, V_2O_5 and SnO_2 [29–35]. Therefore, the development of novel materials to fabricate photoinduced switchable wettability surface is meaningful and significant.

As one of the typical semi-metals, bismuth has been attracting extensive interest due to its unique electronic properties such as highly anisotropic Fermi surface, low carrier density, small carrier effective mass and large magnetoresistance (MR) effect. Recently, different dendrite bismuth nanostructure has been synthesized by electro or electroless deposition. For example, branch-like bismuth was prepared under the protection of highly pure N_2 by electrodeposition [36]. Dendritic bismuth nanostructures were fabricated via an electrochemical deposition route [37]. Li's group reported an electroless deposition and electrodeposition synthesis of Bi/Bi_2O_3 surfaces with dendritic structures [38]. However, the photo-responsive property of bismuth has been seldom reported. Zhang et al. reported the photocatalytic oxidation of NO and its mechanisms of bismuth [39]. In our previous work, it was found that bismuth nanospheres exhibited photocatalytic activities for Cr(VI) reduction upon both UV and visible light irradiation [40]. Therefore, it was believed that the photocatalytic activity of bismuth makes it feasible to prepare bismuth coating with photo-responsive wetting behaviors.

---

* Corresponding authors. Tel.: +86 13659815698; fax: +86 2787195680.
E-mail addresses: hyangwit@hotmail.com (H. Yang), rchenhku@hotmail.com (R. Chen).

http://dx.doi.org/10.1016/j.apsusc.2015.06.180

In this work, dendritic bismuth coating was prepared by electroless deposition using zinc plate as substrate in ethylene glycol solution. To obtain superhydrophobic bismuth coating, reaction parameters were optimized via varying reaction temperature and deposition time. In addition, switchable wettability between superhydrophobicity and superhydrophilicity was realized by alternative UV–vis irradiation and modification with stearic acid. To the best of our knowledge, few studies have been reported on the switchable wetting behavior of dendritic bismuth coating, and it is believed that such smart coating would expand its applications in many fields.

2. Experiment

2.1. Materials

Bismuth chloride ($BiCl_3$), ethylene glycol (EG, 99%), ethanol (99.7%), and stearic acid (SA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Zinc plates were cut into 1.5 cm × 2 cm, and cleaned with ethanol via ultrasonication to remove surface contamination, and then dried in an oven before use. All reagents were analytical reagents and used without further purification.

2.2. Preparation of superhydrophobic bismuth coating

1.5 cm × 2 cm clean zinc plate was immersed into 10 mL EG solution of $BiCl_3$ (20 mM) for 5 min at 10 °C, 30 °C and 60 °C, respectively. Then, bismuth coating was washed with ethanol and dried at 60 °C in the oven for 2 h. After that, the as-prepared coating was immersed in ethanol solution of stearic acid (20 mM) for 5 min, and then washed with ethanol and dried at ambient temperature. For comparison, different bismuth coatings were prepared via identical process by varying the deposition time from 10 s to 40 min.

2.3. Switchable superhydrophobicity - superhydrophilicity transition

The transition of as-prepared bismuth coating from superhydrophobicity to superhydrophilicity was conducted upon UV–vis light irradiation by using a 500 W Xe lamp for 50 min. Then, the superhydrophilic coating could recover its superhydrophobicity by being re-modified the irradiated bismuth coating with 20 mM stearic acid ethanol solution for 3 min. The recycle experiment was performed through the alternation of stearic acid modification and light irradiation process.

2.4. Characterization

Scanning electron microscope image (SEM) was taken on a Hitachi S4800 operating at 5.0 kV. The corresponding element distributions of the surface were determined by energy dispersive X-ray spectroscopy (EDX). Powder X-ray diffraction (XRD) was carried out on Bruker axs D8 Discover (Cu Ka = 1.5406 Å) at a scan rate of 2° min^{-1} in the 2θ range of 20° to 80°. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were recorded on a Philips Tecnai G2 20 electron microscope, using an accelerating voltage of 200 kV. The Fourier transform infrared spectroscopy (FTIR) spectra were collected by a Nicolet Impact 420 FT-IR spectrometer (Nicolet, USA) in a range of 600–4000 cm^{-1} using an attenuated total reflectance (ATR) system. X-ray photoelectron spectra (XPS) were performed in a VG Multilab2000 spectrometer by using Al K α (1486.6 eV) radiation as the source. Static contact angles (CAs) and sliding angles (SAs) of the as-prepared coatings were measured by KRŰSS DSA 100 (Germany) contact angle measuring instrument. A distilled water droplet (drop volume 5 μL) was used as the indicator in the experiment to characterize the wetting property of the as-prepared bismuth coating. The average CA value was obtained by measuring several different positions of the same sample. The digital photographs of water droplets on surfaces were obtained by a digital camera (Sony, from Japan).

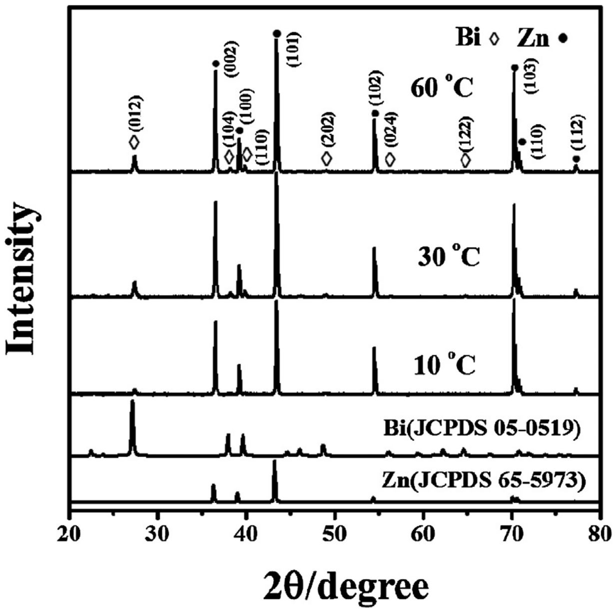


Fig. 1. XRD patterns of bismuth coatings obtained at different temperature.

3. Results and discussion

3.1. Structure and morphology of the bismuth coating

Powder X-ray diffraction (XRD) patterns were used to characterize the chemical composition of the bismuth coatings. Fig. 1 shows the XRD patterns of bismuth coatings obtained at different temperature. The characteristic peaks at 36.50°, 39.21°, 43.42°, 54.54°, 70.24°, 70.90° and 77.16°, were corresponding to crystal plane of zinc (0 0 2), (1 0 0), (1 0 1), (1 0 2), (1 0 3), (1 1 0), (1 1 2), respectively, which was in good agreement with the hexagonal crystalline zinc (JCPDS 65-5973). The diffraction peaks locating at 27.44°, 38.19°, 40.05°, 49.03°, 56.41°and 65.01° could be indexed to (0 1 2), (1 0 4), (1 1 0), (2 0 2), (0 2 4) and (1 2 2) plane of rhombohedral bismuth structure (JCPDS 05-0519), respectively. It indicates that bismuth coating was successfully deposited on the zinc plate at different temperature. Furthermore, the formation of bismuth was also verified by the strong bismuth signals in the EDX spectrum of bismuth coating (Fig. S1, Supplementary Material).

The morphology of bismuth coating surface obtained at different temperature was characterized by SEM images, as displayed in Fig. 2. The surface morphology of bismuth coating prepared under given immersion time and $BiCl_3$ concentration varied significantly at different temperature. At lower temperature (10 °C), only scattered nanoplates with irregular shapes were observed on the zinc plate (Fig. 2a). The nanoplates were about several tens to hundreds nanometers in size (Fig. 2b). When the temperature was 30 °C, mass dendritic products were observed in SEM image of Fig. 2c. The hyperbranched dendrites present a hierarchical structure composed of a trunk, branches (secondary branch), and leaves (tertiary branch). The magnified SEM image shows that subbranch was comprised of abundant spindly nanoparticles with a size ranging 100–500 nm, which protruded out of subbranches towards defined directions (Fig. 2d). This special morphology implies that