Colloids and Surfaces A: Physicochem. Eng. Aspects 441 (2014) 298–305

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Controllable fabrication of superhydrophobic TiO_2 coating with improved transparency and thermostability

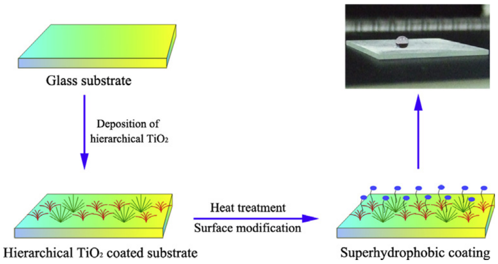
Yanfen Wang, Benxia Li*, Tongxuan Liu, Chuyang Xu, Zhiwei Ge

School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, China

HIGHLIGHTS

- TiO_2 micro/nanostructures were chemically deposited on glass substrates.
- Excellent superhydrophobicity with low roll-off angle and good rebound property.
- The double control over roughness and transparency of the coatings are achieved.
- The coatings remain superhydrophobic even heated at temperatures up to 200 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 June 2013
Received in revised form
11 September 2013
Accepted 19 September 2013
Available online 27 September 2013

Keywords:
Superhydrophobic surface
TiO_2 nanostructures
Chemical deposition
Transparent coating

ABSTRACT

Superhydrophobic surfaces generally require a combination of surface topography and low surface energy, where a thick surface coating on the substrate usually leads to loss of its transparency or color. We demonstrated a convenient and controllable strategy for fabricating the superhydrophobic TiO_2 coatings with improved transparency on glass substrates. The TiO_2 coating possesses hierarchical morphology assembled by radial nanowires, which effectively constructed a rough surface topography and sufficiently captured air pockets. After thermal annealing and modification with stearic acid, the as-prepared TiO_2 coating on glass exhibited excellent superhydrophobicity with a water contact angle (WCA) as high as 157°, low roll-off angle of 2° and good bounce performance. The growth process of the hierarchical TiO_2 coating was studied. The double control over roughness and transparency of the superhydrophobic coatings on the glass substrate are achieved by adjusting the original concentration of titanium source. Moreover, the coatings remain superhydrophobic even heated at temperatures up to 200 °C for 30 min.

1. Introduction

Superhydrophobic surfaces with a water contact angle (WCA) greater than 150° and roll-off angle lower than 10° have attracted significant attention due to their potential applications as water-repellent materials [1–3], reducing resistance of underwater vessels [4] and suppressing oxidation and corrosion on metal surfaces [5–7]. The lotus leaf with its superhydrophobicity is a typical self-cleaning plant in nature, on which rain droplets can freely roll or bounce off from the surface and remove dust particles [8,9]. It has been found that the self-cleaning property of lotus is mainly due to its hierarchical surface topography and the presence of biological epicuticular wax with low surface energy [10]. Therefore, rough surface topography and low surface energy are two key factors in realizing the superhydrophobicity of solid surfaces [11–15].

Up to now, various methods have been developed to prepare artificial superhydrophobic coatings, such as phase separation [16,17], plasma etching [18,19], sol–gel method [20,21], solution-immersing method [7,22], and electrospinning method [23,24]. However, many of techniques involve complicated procedures,

---

* Corresponding author. Tel.: +86 554 6668649; fax: +86 554 6668643.
E-mail address: libx@mail.ustc.edu.cn (B. Li).

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.09.023

special equipments or expensive reagents, and some of the methods are only applicable to small surfaces [25]. Moreover, expensive silanes or fluorides were used to decrease the surface energy of artificial superhydrophobic surfaces in many cases. Recently, Lee and co-workers reported a new method for preparing a superhydrophobic surface by stearic acid chemically adsorbed onto the ZnO nanoparticles [26]. Compared with those conventional surfactants, stearic acid is a favorable candidate for superhydrophobicity due to its low surface energy, biocompatibility, low cost and low toxicity [27,28].

From the viewpoint of further applications of superhydrophobic coatings, the transparency of superhydrophobic coatings is a very important property [29,30]. However, it is difficult to prepare transparent superhydrophobic coatings because the superhydrophobic surface generally requires high surface roughness, where a thick coating on the substrate leads to extensive light scattering and thus loss of its transparency or color. As a result, the practical application of superhydrophobic coatings on optically transparent substrates is greatly limited. Therefore, it is of much significance to develop a facile, efficient and low-cost route for fabricating the superhydrophobic coating with improved transparency and thermostability.

In this work, we demonstrated a facile low-temperature aqueous solution strategy for creating superhydrophobic TiO_2 coatings with improved transparency and low adhesion. The hierarchical TiO_2 micro/nanostructures were chemically deposited on glass substrates, followed by thermal annealing and dipping modification with stearic acid. The schematic illustration is exhibited in Scheme 1. The resulting coating exhibited excellent superhydrophobicity and improved transparency. This coating demonstrated good rebound characteristic and low adhesion, suggesting its potential application for self-cleaning materials. Moreover, the coating remains superhydrophobic even heated at temperatures up to 200 °C for 30 min.

2. Experimental

2.1. Surface treatment of glass substrates

All reagents were of analytical grade, purchased from Shanghai Chemical Company and used without further purification. Glass slides chosen as transparent substrate materials were ultrasonically precleaned using 30% HCl solution for 10 min, followed by sonication in deionized water, acetone and absolute ethanol for 10 min, respectively. The treated glass slides were dried at 60 °C in vacuum.

2.2. Preparation and modification of hierarchical TiO_2 coatings

Potassium titanium oxalate (PTO, 1.0 mmol) was dissolved in 30 mL of deionized water, followed by the addition of 30% H_2O_2 (1 mL) under vigorous magnetic stirring at room temperature, and then the pH value was adjusted to 1–2 by the addition of hydrochloric acid solution (37 wt%). The mixed solution was transferred to a glass vial with 50 mL, and the treated glass slides were immersed into the solution. The mixed solution was heated at 80 °C for 24 h, and then the glass slides turned yellow after being uniformly covered with TiO_2 nanoparticles. The resulting glass films were washed with deionized water to remove the possible residues, and dried at 60 °C. Finally the as-obtained films were placed in a crucible and heated from the room temperature to 500 °C at a rate of 10 °C/min and then maintained at 500 °C for 2 h in air to solidify the coating. After the calcination procedure, the glass coatings became more transparent. In order to decrease surface energy, the annealed glass coatings were immersed in a stearic acid/ethanol solution for 6 h at room temperature, and then taken out from the solution, subsequently washed with deionized water and placed in vacuum at 60 °C for drying.

2.3. Characterization

The X-ray diffraction patterns (XRD) were recorded on a Japan Shimadzu XRD-6000 equipped with graphite monochromatized high-intensity CuKα radiation ($\lambda = 1.54178$ Å), and the field emission scanning electron microscopy (FESEM) was performed on JEOL JSM-6700F. The water contact angle on the thin-films was measured at ambient temperature by a contact angle meter C20 (Kono, USA). In order to measure the roll-off angle, a water droplet was first placed on the horizontal glass substrate with superhydrophobic coating, and then the horizontal sample stage was tilted until the droplet rolls off. The tilted angle of sample stage was recorded and read by the contact angle meter. The water contact angle and roll-off angle values were averages of measurements recorded on five different areas of the sample surface. The transparency of the coatings was detected using the UV–vis spectrometer (UV-5100, Yuanxi, China), and the bare glass slide was used as standard reference.

3. Results and discussion

3.1. Morphologies and structures characterization of the TiO_2 coating on glass substrates

The microstructure morphology of the TiO_2 coating deposited on the glass substrate has been observed by FESEM. From Fig. 1a, it is evident that the surface of glass substrate is covered with a large number of hierarchical TiO_2 micro/nanostructures. The hierarchical TiO_2 micro/nanostructures present two representative assemblies constructed by nanowires grown radially into bundles which are confirmed by the magnified SEM images in Fig. 1b and c. The TiO_2 nanowire-bundles shown in Fig. 1b account for the majority of TiO_2 micro/nanostructures, which makes up “lawn” on the glass substrate. Besides, there are a few larger nanowire-assemblies (Fig. 1c) scattered on the “lawn”. Such interesting hierarchical TiO_2 micro/nanostructures on the glass possess lots of grooves and large roughness, which would be benefit for absorbing air and preventing the penetration of water droplets into the grooves of the material to enhance the wettability according to the Wenzel and Cassie–Baxter theory [31–33]. Fig. 1d shows XRD pattern of TiO_2 coating deposited on the glass substrate after calcination at 500 °C. It can be seen that the diffraction peaks of the sample were very sharp and strong, implying that the TiO_2 coating has well crystalline. All diffraction peaks are in good agreement with those of the standard patterns of rutile TiO_2 (JCPDS Card No. 21-1276). No peak for other types or impurities was observed.

To understand the formation of the TiO_2 hierarchical micro/nanostructures, a time-dependent morphological evolution was examined by FESEM. Fig. 2 shows the FESEM images of the TiO_2 coatings obtained at different growth stages. It can be seen that after 6 h reaction, the TiO_2 coating seems not to deposit on the surface of glass substrate, and we could hazily observe some tiny nanoparticals (Fig. 2a) which may provide the growing points for TiO_2 nanowire-bundles in the next stage. As we all know, the formation of crystals could be divided into two stages: nucleus formation and crystal growth [34,35]. In the initial stage, TiO_2 initial crystal nucleus was formed on glass surface as hydrolysis and condensation reactions of titanium peroxocomplexes proceed. Subsequently, the preferential growth along the oriented directions resulted in specific hierarchical TiO_2 structure on the surface of the TiO_2 initial nuclei, as shown in