



Water-resistant surfaces using zinc oxide structured nanorod arrays with switchable wetting property



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ARTICLE INFO

Article history:

Received 12 January 2016

Revised 31 March 2016

Accepted in revised form 24 April 2016

Available online 30 April 2016

Keywords:

Super-hydrophobic

Water contact angle

Zinc oxide

Nanorod arrays

Rose petal effect

Photo-catalysis

ABSTRACT

This study presents an experimental approach for fabricating super-hydrophobic coatings based on a dual roughness structure composed of zinc oxide nanorod arrays coated with a sputtered zinc oxide nano-layer. The ZnO nanorod arrays were grown by means of a low-temperature electrochemical deposition technique (75 °C) on FTO substrates. The ZnO nanorods show a (002) orientation along the c-axis, and have a hexagonal structure, with an average length of 710 nm, and average width of 156 nm. On the other hand, the crystallite size of the top-coating sputtered ZnO layer is of 30 nm. The as-deposited ZnO nanorod arrays exhibited a hydrophobic behavior, with a surface water contact angle of 108°, whereas the dual-scale roughness ZnO nanorods coated with sputtered ZnO exhibited a super-hydrophobic behavior, with a surface water contact angle of 157° and a high water droplet adhesion. The photo-catalytic activity of the samples was investigated against the degradation of methylene blue under UV-A irradiation (365 nm). The ZnO nanorod arrays showed good photocatalytic activity whereas the superhydrophobic ZnO nanorod arrays top-coated with sputtered ZnO showed minimal activity regarding the degradation of methylene blue. The superhydrophobic films exhibited high sensitivity to UV light, with a UV-induced switching behavior from super-hydrophobic to super-hydrophilic after only 30 min of UV exposure.

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1. Introduction and background

Zinc oxide is an important n-type semiconducting material due to its wide band gap (3.37 eV at room temperature) [1] and large exciton binding energy (60 meV) [2]. ZnO is emerging as an efficient photo-catalyst due to its high surface reactivity, reaction and mineralization rates [3]. Because of the major importance of surface area and surface defects in the photo-catalytic activity of metal oxides, one dimensional structures such as nanowires or nanorods represent ideal candidate structures for photo-catalytic applications due to their large surface-to-volume ratio compared to thin films [4].

There is a big interest in growing ZnO nanorods for their potential use in different applications such as dye sensitized solar cells [5,6], anti-reflective coatings (ARC) [7,8,9], light-emitting diodes [10], photo-catalysts [11–13], and gas sensing devices [14,15]. Different processes have been reported to fabricate zinc oxide nanorods, such as

physical vapor deposition [16,17], chemical vapor deposition [18], wet chemical deposition [19,20], ink-jet printing and hydrothermal processes [21,22], surfactant assisted hydrothermal methods [23], vapor phase transport [24,25], and pulsed laser deposition [26].

Electrochemical and chemical bath depositions conducted at low temperatures [27,28] represent an easy, fast preparation and non-toxic process to prepare zinc oxide nanorod arrays. Moreover, they can be up-scaled for industrial applications.

Zinc oxide is intrinsically hydrophilic, which is due to the presence of hydroxyl groups on its surface [29,30]. However, ZnO can be used to prepare hydrophobic surfaces by creating hierarchical structures and roughening the surfaces [31,32]. There exist two types of super-hydrophobic surfaces, low and high water-adhesion super-hydrophobicity [33–35]. The first type is inspired from the lotus plant, and is observed with water contact angles exceeding 150°, and very low sliding angles (not exceeding 10°) [36]. On the other hand, high water-adhesion super-hydrophobicity is inspired from the rose-petal effect or the gecko's feet [37–39]. This type of surfaces is characterized by a high water contact angle (exceeding 150°) and a high water adhesion demonstrated by

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the firm pinning behavior of the water droplet to the surface at any sliding angle [40].

The wettability of surfaces plays an important role in different applications, and the creation of low water-adhesion super-hydrophobic coatings have attracted special interest due to their potential application for ultra-dry surfaces, self-cleaning and anti-fogging coatings. On the other hand, the high adhesive rose-petal super-hydrophobicity can be used in applications such as liquid transportation [41,42] and single molecule spectroscopy [43].

The design of superhydrophobic surfaces based on ZnO nanorod arrays needs a combination of both rough hierarchical structures as well as low surface energy [44,45]. Previous research consisted on the formation of superhydrophobic hierarchical micro-nano structures, by surface modification process using low surface free energy top-coatings [46,47]. Xue et al. [48] fabricated superhydrophobic surfaces using ZnO nanorod arrays top-coated with Cu₂O nanoparticles, which have a lower surface free energy compared to ZnO, and reported a static contact angle of 126° for the as-prepared ZnO nanorods compared to a maximum static angle of 166° after the deposition of Cu₂O top coating. Also, in order to decrease the contact area between the water droplet and the material's surface, Zhu et al. [49] reports the fabrication of ZnO nanorod arrays followed by a surface modification with n-octadecanoic acid, exhibiting a contact angle of 159°. Likewise, Gyraev et al. [50] and He et al. [51] fabricated ZnO nanorod arrays by a post-hydrophobization process using low surface energy provided by stearic acid (CA = 152°) and by surface fluorination (CA = 167°), respectively. Other research have been dedicated to study the effect of sticky super-hydrophobicity, or super-hydrophobicity with high sliding angles, due to high water adhesion using ZnO nanorods [34,49,52].

This present work consists on the fabrication of superhydrophobic ZnO surfaces based on dual-scale hierarchical structure based on the same material (ZnO top coated with ZnO). This is different from other research in the literature, which report the design of superhydrophobic ZnO nanorod arrays using post-hydrophobization treatment using different materials with low surface energy. The surface morphology, structure, wetting properties and switching behavior under UV light exposure, as well as the photo-catalysis ability of both hydrophobic single roughness surface, fabricated with ZnO nanorod arrays only, and super-hydrophobic dual roughness surface fabricated with ZnO nanorod arrays top coated with a layer of sputtered ZnO.

2. Experimental details

2.1. Preparation of ZnO nanorods

In this work, ZnO nanorod arrays (NRA) have been prepared by means of electrochemical deposition. The ZnO NRA are grown on 5 × 5 cm² fluorine doped tin oxide coated glass (FTO) substrates of 7 Ω/sq from Solaronix. Before the deposition, the FTO substrates were ultrasonically cleaned by successive rinsing in acetone, ethanol and ultra-pure H₂O, after the substrates were cleaned, they were subsequently blown with Nitrogen to dry.

The ZnO NRA are electrochemically grown on top of the FTO substrate using a galvanostatic seeding step prior to potentiostatic growth [53]. Previous work by Canava and Lincot [54] demonstrates that an electrochemical activation step can be used to increase the nanowire density of electrodeposited ZnO nanowire arrays. Therefore, the galvanostatic seed layer is used to control the number of nucleation sites for ZnO NR growth [53].

The ZnO nanorod arrays prepared in this work were grown on the FTO substrates from a magnetically stirred aqueous solution of 5 mM of zinc nitrate [Zn(NO₃)₂·6H₂O] and 5 mM of ammonium nitrate [NH₄NO₃] kept at a low temperature of 75 °C following the standard conditions presented by Riedel et al. [53].

The experimental set up is comprised of a three electrode system, with the substrate as the working electrode, a Platinum sheet as the counter electrode, and a Platinum wire as the pseudo reference electrode (potential remains during the deposition, −0.338 V vs. Ag/AgCl). The ZnO nanorod array growth was started with a 40 s galvanostatic step applying a current density of 0.4 mA/cm². The potentiostatic growth was subsequently conducted for 2000 s at a constant potential of −1.4 V vs. Pt.

The ZnO nanorod arrays are formed in nitrate based solutions following the reaction mechanism suggested by Izaki et al. [56–58]:



After the deposition, the prepared substrates were rinsed in water to remove residual salts and dried in nitrogen. Prior to further analysis, the samples were ultrasonically cleaned in Ethanol for 3 min, followed by pure water for 3 min, and then dried with Nitrogen to remove residual salts. The morphology of the ZnO NRA was observed using scanning electron microscopy (SEM).

2.2. Preparation of ZnO thin film using reactive magnetron sputtering

Intrinsic ZnO thin films were grown by mean of radio frequency magnetron sputtering on top of the ZnO nanorod arrays. The films were grown in pure Ar/O₂ atmosphere, with a power of 1.5 kW and a target-to-substrate distance of approx. 70 mm. The average deposition time for the intrinsic ZnO thin films was 10 min.

2.3. Photo-catalysis test

The photo-catalysis of the ZnO nanorod arrays as well as the ZnO nanorods covered with sputtered ZnO (dual roughness) was evaluated using methylene blue hydrate (MB, C₁₆H₁₈ClN₃S·xH₂O, Fluka Analytical). The photo-degradation test was conducted using 20 ml of methylene blue solution with an initial concentration of 0.01 mmol/l in the presence of FTO substrates (25 × 25 × 2 mm) coated with ZnO nanorod arrays and ZnO double structured layers. The pH value of the prepared MB solution (pH = 6.8) was measured with an SP70P/VWR pH measurement instrument.

The concentration of the MB solution was calculated from the UV–Vis measurements of the absorption spectrum using an Avantes Ava Light-DH-S-BAL spectrophotometer. 700 μl of the solution was withdrawn each time interval and its optical absorption was measured.

In order to ensure that the dye degradation is due to the UV light exposure, and not on the absorption of the dye by the surface of the ZnO films, a dark test was first conducted by adding the ZnO single roughness and dual roughness films to the MB dye solution, and storing in the dark for 1 h. The optical absorption of the dye after the dark test was taken as a baseline for the photo-catalysis test under UV illumination.

The photo-degradation test was conducted during a time interval ranging from 1 h to 5 h, the irradiation was provided by 2 × 15 W UV lamps (NU-15 KL) with a radiation power of 2 mW/cm² and major emission at 365 nm. The MB solution was magnetically stirred during the experiment, with a rotation of 115 rpm.

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