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Optoelectrowettability conversion on superhydrophobic CdS QDs sensitized TiO_2 nanotubes

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ABSTRACT

This work demonstrates the process of building optoelectrically cooperative surface wetting in smart and precise way. The superhydrophobic photosensitive film is constructed with TiO_2 nanotube arrays. Compared with conventional organic dyes, CdS quantum dots (QDs) as sensitizer layer are modified on TiO_2 nanotubes surface to improve photosensitivity of the composited surface in visible light region, which offer the benefit for designing and fabricating solid state hetero-junction devices. ITO glass is introduced as top electrode to apply electrical and optical stimuli and the patterned wetting is instantly obtained with masking light through ITO. The optoelectrically cooperative wettability conversion occurred on superhydrophobic TiO_2 nanotube surface at critical voltage of 12 V, which was decreased by 18 V comparing with only using electric stimulus. This study provides potential applications for TiO_2 nanotube arrays to the associated research of liquid reprography, location-controlled microfluidic device and lab-on-chip.

1. Introduction

Recently, controlling of wetting behavior of solid surfaces has attracted extensive attention due to potential applications, such as drug delivery, actuator system, and bio-separation [1–3]. External stimuli were required to overcome energy barrier for surface wettability conversion from superhydrophobic to hydrophilic state [4–19]. With adding light stimulus, the critical voltage of optoelectrowetting could be decreased [20]. Optoelectrically cooperative wettability conversion also exhibited flexible and addressable wetting behavior, which has been used for comprehensive application, such as tunable liquid mirolens, high-brightness electrowetting display, and microfluidic devices [21–25]. Tian et al. reported optoelectrically cooperative wetting for liquid reprography on superhydrophobic TiOPc sensitized ZnO nanorod arrays [26].

TiO_2 is a stable and chemically inert photoconductive semiconductor, and attracts intense interest owing to their wide applications in dye-sensitized solar cell, and self-cleaning materials [27,28]. The surface wettability conversion of superhydrophobic TiO_2 films have been reported, which could transform to hydrophilic surface with long time UV irradiation [29,30]. In order to improve photosensitivity of TiO_2, some organic dyes, such as ruthenium complex, were adsorbed. But organic dyes are generally vulnerable to the light environment and are easily photobleached or decomposed under normal light irradiation. Inorganic semiconductor QD is one of the good candidates as a light sensitizer, which absorbs light in visible region with high absorption coefficient [31–34]. Compared with organic dye, inorganic QDs as light sensitizer layer could be thin and offer the benefit of designing and fabricating solid state devices. Significantly, the absorption wavelength of QDs can be tailored by changing the size of the QDs. CdS QDs possessed unique optical properties and its energy band was matched with TiO_2. Herein, the electrowetting and optoelectrowetting of superhydrophobic CdS QDs sensitized TiO_2 nanotube arrays were investigated with ITO as top electrode. The critical voltage for optoelectrowetting was decreased by 18 V when only electrical stimulus is used. Furthermore, the diameter and the distance of tube-to-tube spacing of TiO_2 nanotube would be controllable. When light irradiated on CdS QDs sensitized TiO_2 nanotube arrays through a photo mask put on ITO electrode, the better resolution of patterned wettable region could be achieved. The improved experimental setup for wettability transition would be used for extensive nanostructures.

2. Experimental section

2.1. Highly ordered composite TiO_2 nanotube array fabrication

In a typical synthesis, the highly ordered TiO_2 nanotube arrays on Ti foil were synthesized by anodic oxidation in a NH_4F organic electrolyte [35]. Titanium foils with the thickness of 250 μm (99.7%; Alfa Aesar) were ultrasonic cleaned with ethanol before anodization. A graphite plate was used as the counter electrode. The organic electrolyte was a 0.25 wt % NH_4F (ACS reagent) in

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ethylene glycol (anhydrous) solution. The anodized voltage was accurately controlled at 60 V for 1.5 h. The following annealing process was performed at 450 °C for 1 h to crystallize the amorphous nanotube arrays for increasing the photoconductive property. Direct growth of CdS QDs on the surface of TiO_2 nanotube was then performed by chemical reaction of ionic species using chemical bath deposition method [36]. In order to improve the surface hydrophobicity, CdS QDs sensitized TiO_2 nanotubes were finally modified with fluoroalkyl silane (FAS, $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$) by solution self-assembly. TiO_2 film modified with CdS QDs were treated with 1.0 wt % ethanol solution of FAS for 5 h, and subsequently dried at 80 °C for 30 min. The composite TiO_2 nanotube on $1 \times 2\ cm^2$ Ti foil with CdS QDs as sensitizing layer and FAS acting hydrophobic layer was finally formed with the schematic diagrams being showed in Fig. 1.

2.2. Characterization and wetting experiments

The morphology of as-synthesized composite TiO_2 nanotubes was investigated by field-emission scanning electron microscopy (SEM, Hitachi S-4300) operated at 15 kV. The crystal structure was characterized by X-ray diffraction (XRD, Rigaku D/max 2500) with Cu Kα radiation. Detailed microstructure and composition of the composites were characterized using transmission electron microscopy (TEM, JEOL 2100F FEG), and energy-dispersive X-ray spectrometry (EDS) attached to the 2100F TEM. The UV–vis absorption spectra were collected with a spectrophotometer (U-3010, Hitachi).

Zahner IM6e impedance analyzer (Germany) with a two-electrode cell was used for measuring the electrochemical impedance in the frequency range of 0.02 Hz–100 kHz. The electrolyte solution was composited of 0.02 mol/L LiI, 0.02 mol/L I_2 and methyl cyanide solvent. A solar simulator (CMH-250, Aodite Photoelectronic Technology Ltd., Beijing) was used as light source for impedance and wetting measuring under the same irradiation condition. The light intensity of ≈400 mW/cm^2 was checked using a portable power meter (Model FZ-A, Beijing).

The contact angles were measured by Dataphysics OCA20 CA system, which was carried out on composite TiO_2 nanotubes surface as shown in Fig. 1. We introduce indium tin oxide (ITO, Solaronix) glass as the top transparent electrode with the surface facing downwards. ITO glass (2 cm × 3 cm, <15 Ω/square) was sequentially cleaned with detergent, deionized water, acetone, ethanol, and then modified with FAS by chemical evaporation deposition with the pressure of 0.1 Pa to improve the hydrophobic behavior of ITO surface. A 10 μL water droplet (γ_{LV} = 72 mN m^{-1}) was used in all measurements of water contact angles. The commercial red ink from Tianjin Ostrich Ink Co. Ltd. was used to demonstrate liquid reprography. Compared with composite nanotube film, ITO smooth surface is hydrophilic state. So, liquid droplet was firstly hanged on modified ITO electrode surface in our experimental setup. The composite nanotube film placed on 3D sample stage was accurately controlled to touch the liquid. The solid–liquid interface was formed with water droplet and the surface of composite nanotube film. ITO electrode was used as the cathode and the voltage was applied between ITO glass and Ti substrate. Light irradiated on composite nanotube array surface through a photo mask put on ITO electrode.

3. Results and discussion

3.1. Morphology, structure and optoelectrical properties of composite nanotube arrays

The as-fabricated CdS QDs sensitized TiO_2 nanotube arrays on Ti substrate were investigated by SEM. Fig. 2a is a typical SEM image of the top surface, which shows the hexagonal packed nanopores on the whole film. The TiO_2 nanotubes have uniform size distribution with the outer diameter about 160 nm and the wall thickness about 20 nm. The inner diameter of TiO_2 nanotubes is about 120 nm. The distance of tube-to-tube spacing is 10–15 nm on average. The top surface of nanotube is rough because of uneven oxidation etching. The cross-sectional SEM image (Fig. 2b) indicates TiO_2 nanotubes grow vertically on Ti substrate. The length of the TiO_2 nanotube is about 5 μm on average. In Fig. 2b, the broken tubes reveal no block of the pores and no morphology changes of the nanotubes after modification with CdS on the surface of TiO_2 nanotubes. Detailed microstructure and composition of the composites were characterized using TEM (Fig. S1†) and EDS. Fig. 2c is a high-resolution TEM image of a nanotube. We can clearly see several CdS QDs have been deposited into the pore of the TiO_2 nanotube. The size of CdS QDs was about 10 nm. The cubic CdS has the lattice fringes of (1 1 1) with *d*-spacing of ~0.335 nm. The wall of the nanotube is the anatase TiO_2. The in situ EDS elemental analysis of the nanotube in Fig. 2d indicated that the composites contain Ti and O with an atomic ratio about 1:2, and Cd and S with an atomic ratio of 1:1. The Cu and C signal come from the TEM grid and supporting C film. These results further confirm that the composites are composed of TiO_2 nanotubes and CdS QDs.

The crystal structure of TiO_2 nanotube arrays with (black curve) and without (red curve) CdS QDs modification was analyzed by XRD (Fig. 3a). The letters of A, T and C in XRD results represent the peak belonging to TiO_2, Ti substrate, and CdS QDs, respectively. The TiO_2 nanotubes (black) are agreement with anatase TiO_2 (JCPDS: 21-1272). The red curve indicated the modification of cubic CdS (JCPDS: 80–0019) on TiO_2 nanotube surface. Several XRD peaks on both curves come from Ti substrate. TiO_2 nanotube have the absorption band at UV region around 300–390 nm (Fig. 3b). After CdS QDs was modified on TiO_2 nanotube surface, the absorption intensity of the composite nanostructures was enhanced (red

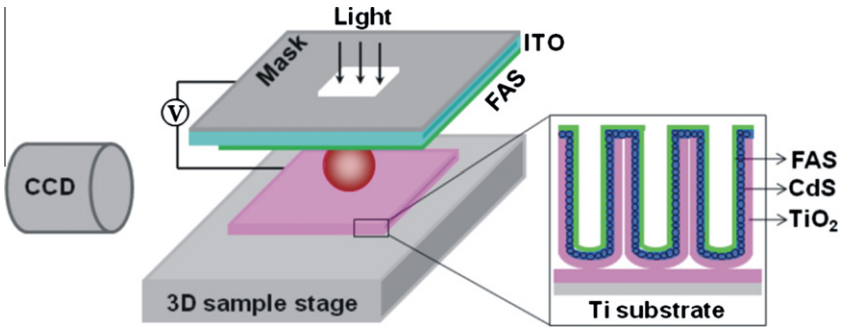

Fig. 1. Experimental setup for contact angle measurement on surface of TiO_2 nanotube arrays coated with CdS QDs and FAS.