

Ferroelectric BiFeO₃/TiO₂ nanotube heterostructures for enhanced photoelectrochemical performance

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ABSTRACT

Ferroelectric based heterostructures have shown great promises in solar water splitting due to unique photoelectrochemical (PEC) properties including polarization-induced charge separation and tunable electrochemical surface reaction. A highly ordered ferroelectric BiFeO₃/TiO₂ nanotube (TNT) heterostructures were fabricated by anodic oxidation and pulsed laser deposition. The microscopic morphology, optical, and PEC properties of nanostructures were characterized. The BiFeO₃/TNT photoelectrode is photoactive under visible light illumination, which exhibits higher photocurrent from greater water oxidation, compared with the pure TNT photoelectrode. The coating thickness of BiFeO₃ strongly affected the photoelectrochemical properties. The enhanced PEC performance could be attributed to the effective charge separation and the favorable band bending for water oxidation, originating from ferroelectric polarization-related internal field.

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1. Introduction

The nanostructure of semiconducting transition metal oxides (TMOs), such as TiO₂, Fe₂O₃, and WO₃, play an extremely important role in photoelectrochemical (PEC) water splitting for solar energy conversion technology [1–6]. Especially, these highly ordered nanostructures provide an effective route for enhancing PEC performances due to the substantial dimensional reduction of photocatalyst and larger specific surface area [7–9]. They allow more photogenerated charge transfer to interfaces by reducing charge-carrier diffusion length and greater water oxidation at the semiconductor/electrolyte interface. Among the nanostructures based on TMOs, TiO₂ nanotube (TNT) arrays, simply prepared by anodic oxidation, have been extensively utilized for photocatalysis applications because of their excellent chemical stability and strong surface catalytic activity [10–12]. However, for the efficiency of solar conversion, they still undergo from the limit of optical absorption in visible light region due to large bandgap and the inefficient charge collection due to high interfacial electron

recombination. Thus, there have been various efforts to improve light harvesting and efficiency by either doping the TNT arrays with various dopants, such as N, C, and B [12–15], or forming heterostructures on the basis of TNT arrays with lower bandgap semiconductors such as CdS, WO₃, and Co₃O₄ [16–19]. In spite of a significant benefit of TNT arrays with doping or surface modification, the development of advanced systems including new functional materials that feature wide light absorption and effective charge separation would greatly progress PEC energy conversion.

The photoferroelectrics that represent a ferroelectric photovoltaic materials and photocatalysts have been recently revisited with emergence of a small bandgap ferroelectric semiconductors, such as BiFeO₃ ($E_g = 2.7$ eV) [20,21], KBiFe₂O₅ (1.6 eV) [22,23], Bi₂FeCrO₆ (1.5–2.7 eV) [24,25], LaCoO₃-doped Bi₄Ti₃O₁₂ (2.65 eV) [26], and [KNbO₃]_{1-x}[BaNi_{0.5}Nb_{0.5}O_{3-δ}]_x (1.1–3.8 eV) [27]. These ferroelectric semiconductors are capable of visible light absorption with unique photovoltaic properties, for example, above bandgap generated photovoltages and efficient ferroelectric polarization induced charge separation. As a result, the application of photoferroelectrics have mainly focused on solid-state solar cells, and but their photocatalysis and PEC applications are also extremely important for solar energy conversion. However, there are still limitations of single photoelectrode to promote photoelectrochemistry by fast

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recombination of photogenerated carriers and poor electrical conduction with a short charge diffusion length. Those stimulate effort on the exploration of heterostructure photoelectrode with nanostructures. Such heterostructures can offer band engineering across interface toward efficient charge separation. Specially, ferroelectric based heterostructures further introduce favorable interfacial band structures and charge transfer properties via switchable ferroelectric polarization driven internal electric field, leading to an enhanced PEC performance. In addition, a ferroelectric polarization induces surface band bending, resulting from screening of depolarization field, so can be to tune certain electrochemical surface reactions. All these indicate that ferroelectric based heterostructure combining with advanced nanostructures potentially can be an alternative system for effective solar water splitting.

In this study, we deposited BiFeO₃ thin films on highly-ordered anodized TNT arrays using pulsed laser deposition for heterostructure photoelectrode. BiFeO₃ has shown a remarkable photo-induced oxidation capability due to visible light absorption, good chemical stability and strong ferroelectric polarization. The ferroelectric BiFeO₃/TNT heterostructures exhibits substantially higher photoelectrochemical performance than the single TNT photoelectrode. We have investigated the effects of BiFeO₃ coating thickness on the microscopic morphology, associated with PEC performance. This work provides useful information for developing highly efficient ferroelectric based heterostructures for solar water splitting and photovoltaic devices.

2. Experimental details

Highly-ordered TiO₂ nanotube (TNT) arrays with ~80 nm pore size and 5 μ m thick were fabricated by anodization of Ti foils in ethylene glycol with 0.2 wt.% NH₄F and 2 vol.% H₂O₂ for 12 h at 15 °C [28,29]. The free-standing TNT film with anatase phase was obtained by annealing the anodized TNT/Ti at 500 °C for 1 h and then detaching process in 33 wt % H₂O₂. The anatase TNT film was attached on F doped SnO₂ (FTO) coated glass using viscous TiO₂ nanoparticles (TNP) paste printed by doctor-blade method and followed by sintering at 500 °C for 1 h. Finally, we obtained the nanostructured single photoelectrode with 5 μ m thick TNT arrays/3 μ m thick TNP layer on FTO coated glass substrate, which provided high surface to volume ratios to enable a large internal surface area for PEC reaction.

Ferroelectric based heterostructures were fabricated by depositing BiFeO₃ (BFO) thin films on TNT/TNP/FTO glass substrates using pulsed laser deposition (KrF excimer laser, λ = 248 nm) with an energy fluence of 150 mJ/cm² and a repetition of 5 Hz. The coating thickness of BFO was controlled by deposition time. After BFO deposition, all the samples were annealed for 30 min at 500 °C in an oxygen atmosphere.

Structural properties and surface morphologies of the TNT/TNP structure and BFO/TNT heterostructures were characterized by using high resolution X-ray diffractometer (XRD, Bruker D8 discover) and field emission scanning electron microscope (FE-SEM, TESCAN MIRA-II), respectively. Ferroelectric properties of BFO/TNT heterostructures were investigated by piezoresponse force microscopy (PFM, SEIKO 300 HV). For piezoresponse image and ferroelectric domain switching, a voltage of 1 V_{ac} with 17 kHz and $\pm$ 25 V_{dc} were applied to the conductive Pt/Ir coated tips as a top electrode.

The optical absorption spectra of the films were measured using an ultraviolet–visible (UV–Vis) spectrometer (Carry 5000, Agilent). PEC measurements were conducted using a three-electrode configuration with a Pt mesh counter electrode and a saturated Ag/AgCl reference electrode. For PEC water splitting, the 1 cm² working electrode was immersed in a 1 M KOH electrolyte and

illuminated under 1 sun (100 mW/cm²) with a solar simulator (150 W xenon lamp, 1.5 air mass filter).

3. Result and discussion

3.1. Structural properties

The nanostructured photoelectrodes with BFO/TNT/TNP heterostructure were prepared by combining with anodization and pulsed laser deposition (see Fig. 1(a)). Fig. 1 (b) and (c) show FE-SEM cross-sectional images of the TNT/TNP structure and BFO/TNT/TNP heterostructure. The TNT film (5 μ m thickness) with vertically aligned nanotubular morphology was well attached to FTO glass with TNP layer (3 μ m thickness). After depositing BFO, no significant change of the nanotubular structures were observed with coating BFO on both the outer and inner TNT walls. Three different thicknesses of BFO coating samples were fabricated by controlling the deposition time of BFO: BFO1 (~90 nm thickness), BFO2 (~220 nm thickness), and BFO3 (~300 nm thickness). Note that the coating thickness of BFO on top surface of TNTs is estimated from FE-SEM cross-sectional images of samples. Fig. 1 (d) displays the morphology of TNT/TNP structure and the three different BFO/TNT/TNP heterostructures. TNT arrays are highly ordered and tight with smooth surface and an average pore diameter of ~80 nm. However, as the BFO deposition time increases from 10 min (BFO1)

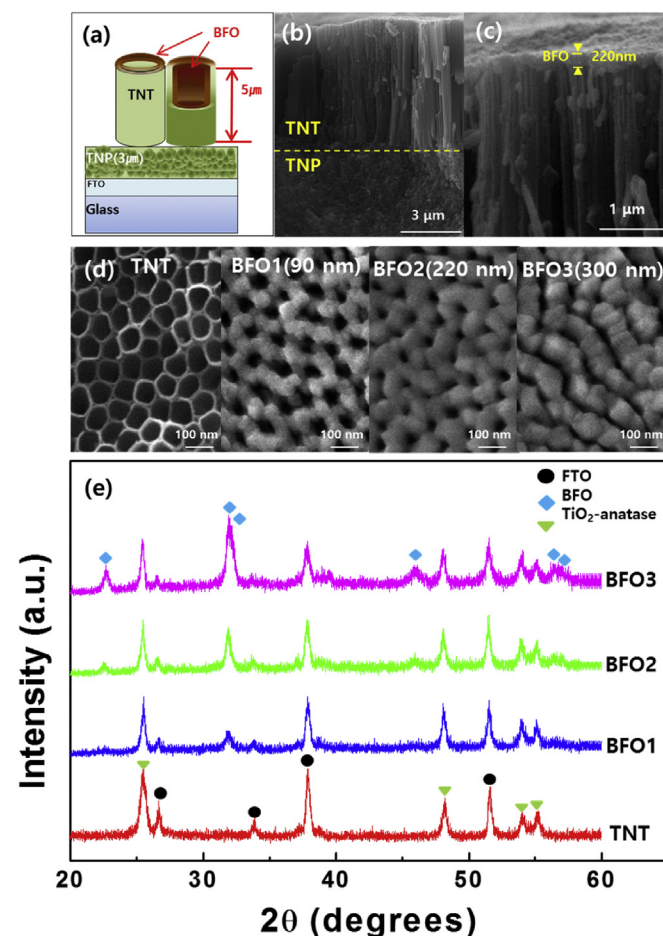


Fig. 1. (a) Schematic of BFO/TNT/TNP heterostructure on FTO glass substrate. FE-SEM cross-sectional images of (b) TNT/TNP and (c) BFO2 (220 nm thickness)/TNT. (d) FE-SEM images of the top surface of the TNT array and BFO/TNT with three different BFO coating thickness. (e) XRD patterns of TNT, BFO1, BFO2, and BFO3.

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