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Fabrication and correlation between photoluminescence and photoelectrochemical properties of vertically aligned ZnO coated TiO₂ nanotube arrays

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ABSTRACT

We report on a study on the correlation between the photoluminescence and the photoelectrochemical properties of ZnO–TiO₂ heterogeneous nanostructure composed of anatase TiO₂ nanotubes and wurtzite ZnO coatings. Vertically aligned ZnO coated TiO₂ nanotube (ZnO/TiO₂ NT) arrays have been fabricated by atomic layer deposition of ZnO coatings on electrochemical anodization formed TiO₂ nanotubes. The obtained ZnO/TiO₂ NT arrays show higher photoresponse to shorter wavelength light than to longer wavelength light. A reduction in photoluminescence and an enhancement in photoelectrochemical activity are observed for annealed ZnO/TiO₂ NT arrays. ZnO/TiO₂ NTs with thinner ZnO coatings rather than thicker ZnO coatings have better photoelectrochemical properties. Compared with bare TiO₂ NT arrays, an increase in photocurrent of about 50 percent is obtained for the arrays of 450 °C annealed of ZnO/TiO₂ NTs with 10-cycle deposition of ZnO coatings under visible illumination with cutoff of 420 nm.

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1. Introduction

By virtue of their high surface-to-volume ratio and superior optical, electronic and photoelectrochemical properties, nanostructured TiO₂ and ZnO have recently attracted much attention because of their potential applications in photovoltaic processes, photocatalytic reactions, etc. [1–3]. Both metal oxides have also advantages of low cost, stability, nontoxicity, and ease of availability. Among various nanostructured TiO₂, highly ordered tubular nanostructures i.e. TiO₂ nanotubes (NTs) are of particular interest because of their larger surface area which increases the density of active sites for surface reactions and improves interfacial carrier transfer rates [4–6]. The aligned NT structure also dramatically improves charge transport properties, which greatly contributes to photoelectrochemical performance. TiO₂ NT arrays have therefore been extensively studied as electrodes in photocatalysts [2,7–9] and solar cells [10–12]. ZnO nanomaterials have also been demonstrated to be promising when used in photocatalysts [13–15] and photovoltaics [16–18]. Due to their large band gaps (TiO₂: ~3.2 eV, ZnO: ~3.4 eV), however, both TiO₂ and

ZnO normally only work under UV irradiation, thus restricting their practical applications.

The good compatibility between TiO₂ and ZnO allows them to be composed to form a heterogeneous nanostructure. It has been proved that heterostructures composed of nanostructured TiO₂ and ZnO can improve the quantum efficiency of photocatalysts and photovoltaics due to the combination of the high reactivity of TiO₂ and the large binding energy of ZnO. Covering of a ZnO coating on TiO₂ surface also increases the mobility of charge carriers [(TiO₂: 0.5 cm² V⁻¹ s⁻¹) < (ZnO: 200 cm² V⁻¹ s⁻¹)]. The process of electron and hole transfer between the corresponding conduction and valence bands can be improved and a better charge separation of photogenerated carriers can be achieved when compared with catalysts from a single metal oxide. In addition, an extension for spectral range of photoresponse can be expected due to the staggered band alignment of the heterostructures [19–21]. The improved electron and hole conductivity, the enhanced charged carries separation and the extended photoresponse range, all facilitate an increase of solar conversion efficiencies and are most favorable for photocatalytic reactions and photovoltaic processes [22–25]. Much work has been therefore devoted to nano-scaled ZnO–TiO₂ composites, in particular, to one-dimensional hetero-nanostructures such as ZnO modified TiO₂ or TiO₂ modified ZnO nanotubes (NTs) and nanowires [23–25].

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In the present work, we fabricated vertically aligned ZnO coated TiO₂ (ZnO/TiO₂) NTs by electrochemical anodization of Ti foil followed by atomic layer deposition (ALD) of ZnO on the TiO₂ NTs. After a detailed morphological and structural characterization, the correlation between the photoluminescence (PL) and the photoelectrochemical properties was studied by measuring PL and photocurrents to understand the suppressed radiative recombination and the enhanced charge separation of photogenerated carries in the nano-heterojunction composed of TiO₂ NTs and ZnO coatings as well as to obtain better visible-light photoreponse and higher photoelectrochemical activity.

2. Experimental procedure

2.1. Sample fabrication

Two processes were applied to the fabrication of ZnO/TiO₂ NT arrays. Vertical aligned TiO₂ NT arrays were first formed on Ti foil (99.99% in purity, 0.1 mm in thickness) by electrochemical anodization which was performed in a two-electrode electrochemical cell using a Ti foil as the working electrode and a graphite sheet as the counter electrode separated by 1.3 cm. Before anodization, the Ti foil was chemically polished in a mixture of de-ionized water, HNO₃ and HF with the ratio of 5:4:1 (in volume) for 30 s to remove the surface oxide layer and then rinsed with de-ionized water. The polished Ti foil was anodized in 0.5 wt% HF electrolyte at a constant voltage of 20 V for 40 min to form TiO₂ NT arrays. The arrays were then annealed in a furnace at 450 °C for 3 h in atmospheric air to convert the formed amorphous TiO₂ into anatase. The annealed TiO₂ NTs were used as the template for the deposition of ZnO coatings by ALD (TFS200, BENEQ) using diethylzinc (Zn(C₂H₅)₂, DEZ) as the metal precursor for Zn and de-ionized water (H₂O) as the reactant. DEZ was kept at 18 °C and delivered into the deposition chamber with a high purity N₂ carrier gas flow. The ZnO coatings were typically deposited by several DEZ–H₂O cycles consisting of the sequence: 0.5 s DEZ pulse, 2 s N₂ purge, 0.5 s H₂O pulse, 2 s N₂ purge. A one-cycle deposit of ZnO was approximately 0.2 nm thick when deposited on a polished plane substrate. The deposition temperature and the

working pressure were kept at 200 °C and ~1 Torr, respectively. The obtained ZnO coated TiO₂ NT arrays were rinsed with de-ionized water and annealed at different temperatures for 30 min in atmospheric air.

2.2. Structural characterization

The surface morphology of the prepared ZnO/TiO₂ NT arrays was examined by field-emission scanning electron microscopy (FESEM) with a Hitachi S-4800 microscope. The crystal structure was characterized by X-ray diffraction with a Rigaku D/max-γ B X-ray diffractometer using a rotating anode operating at 40 kV and 300 mA and Ni-filtered Cu Kα radiation ($\lambda = 0.15406$ nm). The structure was also characterized through the analysis of vibrational modes by measuring Raman scattering spectra. These measurements were performed with a Jobin-Yvon LabRAM HR 800 UV micro-Raman spectrometer using 488 nm Ar⁺ laser beam and 325 nm He–Cd laser beam to excite the samples.

2.3. Photoluminescence and photocurrent measurements

PL measurements were performed at room temperature by exciting the samples at normal incidence with a CW 325 nm He–Cd laser. PL spectra were recorded by collecting the emitted luminescence at normal direction with a 0.5 m spectrometer (Acton Research, Spectra Pro 500i) and an intensified charge-coupled device (ICCD, Andor Technology, iStar DH720) attached on the exit port of the spectrometer.

The photoelectrochemical properties were studied by measuring photocurrents in a three-electrode cell with 0.5 M Na₂SO₄ electrolyte using a CHI electrochemical analyzer (CHI 660A Instruments). With an active area of 1 cm², TiO₂ or ZnO/TiO₂ NT arrays were used as the working electrode and subjected to the irradiation of visible light with Ag/AgCl as the reference electrode and Pt foil as the counter electrode. A 500 W xenon lamp was used as the light source to provide two wavelength ranges of visible light by cutting ultraviolet light using high-pass filters with cutoff of 380 or 420 nm. The light intensity on the working electrode was 100 mW/cm².

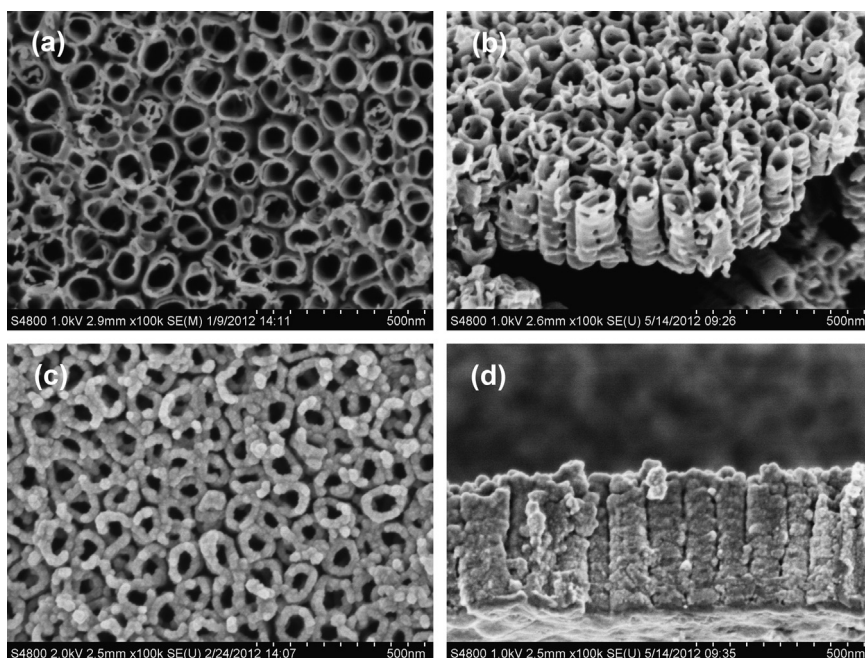


Fig. 1. (a) Top-view and (b) cross-sectional SEM images of bare TiO₂ NTs, (c) top-view and (d) cross-sectional SEM images of ZnO/TiO₂ NTs with 50 cycles of ZnO coating.

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