



Electrochromic titania nanotube arrays for the enhanced photocatalytic degradation of phenol and pharmaceutical compounds



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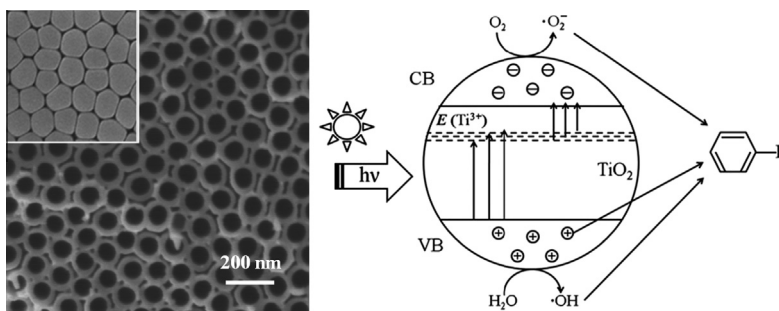
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HIGHLIGHTS

- Electrochromic titania nanotube arrays were fabricated by a cathodisation method.
- The fabricated materials exhibited enhanced photo- and electrochemical properties.
- The fabricated materials showed enhanced photocatalytic degradation of organics.

GRAPHICAL ABSTRACT



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ABSTRACT

Vertically aligned, electrochromic-coloured, amorphous titania nanotube arrays (TNAs) were fabricated using a facile room-temperature, solution-based electrochemical cathodisation method. Rapid cathodisation within 30 s converted pristine TNAs into their dark analogues. Compared to their untreated counterparts, the cathodised dark TNAs exhibited significantly enhanced optical absorbance, covering the full spectrum of visible light. Further annealing of the electrochromic coloured amorphous TNAs in a N₂ atmosphere induced their transformation into dark crystalline TNAs, which directly harnessed simulated sunlight for the photocatalytic degradation of organic contaminants, including phenol, ibuprofen, carbamazepine and caffeine. Compared to the pristine crystalline TNAs (annealed in air), the dark crystalline TNAs showed higher optical absorbance, larger charge carrier density, lower electron transport resistance, and an enhancement of 107–131% in degradation kinetics for the target organic contaminants.

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1. Introduction

The development of functional materials for the direct utilisation of solar energy has been actively pursued in many semicon-

ductor-based industries, including heterogeneous photocatalysis. Titania-based photocatalysts continue to attract considerable interest since the report of photoelectrochemical water splitting [1] and have been applied in a wide range of fields. The basic mechanism for the activation of titania involves the generation of electron/hole pairs by exciting electrons from the valence band to the conduction band through the absorption of light. The

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photogenerated electron–hole pairs can then migrate from their respective band to the semiconductor surface and initiate redox reactions with adsorbed species, such as organic compounds. Because of their inherent wide band gaps, white titania powders can only utilise a small fraction of the solar spectrum. To harness a larger portion of the solar spectrum, methods such as metal ion implantation [2], narrow-bandgap-semiconductor incorporation [3] and anionic doping [4] have been developed. Therefore, large surface areas, high optical absorption and efficient charge transport are required to accelerate heterogeneous photocatalytic reactions.

Vertically aligned, highly ordered titania nanotube arrays (TNAs), grown by the electrochemical anodisation of titanium foils [5–6], have attracted considerable attention due to their porous structures with large specific surface areas [7], strong light-scattering effects [8], and rapid electron percolation pathways for vertical charge transfer between interfaces [9]. These advantages have led to improved photoelectrical and electrochemical performances in many advanced applications. For example, amorphous TNAs have been successfully applied in oxygen sensors [10] and sodium ion batteries [11], whereas anatase TNAs have potential for water splitting [12], solar cells [13], photosynthesis [14], lithium ion storage [15], aluminium ion batteries [16], and chemical sensors [17].

Several studies have also demonstrated applications for anatase TNAs in environmental remediation processes, such as virus disinfection [18] and the degradation of contaminants [19–27]. When compared to a P25 particulate film of similar thickness, TNAs showed an enhanced long-term photocatalytic activity for the degradation of acetaldehyde because straight tubular channels allowed for the free diffusion of intermediates [23]. Many reports have demonstrated that the photocatalytic performance of TNAs is affected by their microscopic structures, crystallisation methods, and doping components. For instance, open-ended TNAs exhibited a rate constant that was ~30% higher than that of closed-ended TNAs in the photocatalytic degradation of methyl blue [24]. Vapour-thermal-treated TNAs showed better crystallisation and higher photocatalytic activity than calcined and hydrothermally treated TNAs for the decolourisation of methyl orange [25]. MoO₃-doped TNAs (7 wt% Mo) exhibited strongly enhanced photocatalytic activity in the degradation of acid orange 7 [26]. Pt and zeolitic imidazolate-loaded TNAs possessed higher optical absorbance of visible photons than Pt/TNAs, which resulted in faster phenol degradation [27].

Electrochromic colouration/bleaching of semiconductors, which is achieved by field-assisted intercalation/extraction of monovalent cations, causes a change in the electronic states in the band gap of the host material, which is useful for the engineering of light absorption or reflection in the visible spectrum [28]. Several methods have been used for the fabrication of titania-based electrochromic films, including sol–gel [29], magnetron sputtering [30], chemical solution deposition [31], hydrothermal treatment [32], doctor blade [33], and anodisation [34–38]. The results show that TNA-based electrochromic films possess a stronger switching contrast than P25 particulate films [38], and further enhancement can be achieved by coating TiO₂ platforms with viologen [39], polyaniline [40], WO₃ [36], Al₂O₃ [41], and MoO₃ [42]. However, to the best of our knowledge, the use of cathodization-induced coloured TNAs for photocatalytic degradation of contaminants has not been examined. Moreover, limited investigations were conducted for the photocatalytic degradation of ibuprofen, carbamazepine and caffeine. Here, we demonstrate an easily scalable electrochemical method for preparing electrochromic amorphous TNAs and their further transformation into dark crystallised analogues for the photocatalytic degradation of organic contaminants.

2. Experimental

2.1. Fabrication of TNAs

Potentiostatic anodisation of Ti foils (99.7% purity, 0.25 mm thickness, Aldrich) was conducted at 50 V in an ethylene glycol electrolyte, which contained 0.1 mol dm⁻³ NH₄F, 1 wt% lactic acid and 5 wt% deionised water, using a platinum cathode [43]. After 2 h of anodisation, the developed film was ultrasonically removed in 10 wt% ethanol. The second anodisation step was performed under the same conditions for 2 h to obtain vertically aligned, highly ordered pristine TNAs (P-TNAs). After naturally drying the P-TNAs in open air, electrochemical cathodisation was performed at 5 V in a 0.5 mol dm⁻³ NaOH solution using Ti as the anode and the P-TNAs as the cathode. Because the formation of an oxide layer on the Ti anode resulted in a drop in current, the anode was replaced with a new Ti foil or regenerated in a 6 wt% HF solution for 1.5 min over a cathodisation interval of 5 min. Cathodised TNAs (C-TNAs) were obtained after 1 h of cathodisation. To obtain the crystalline TNAs, the P-TNAs and C-TNAs were annealed in a muffle furnace (JEIO Tech, MF-32G) at 450 °C for 1.5 h in a N₂ atmosphere at a flow rate of 9.0 cc min⁻¹ (P-TNAs-N₂ and C-TNAs-N₂). For comparison, the P-TNAs were also annealed in air at 450 °C for 1.5 h (P-TNAs-Air). The heating and cooling rates of the furnace were set at 2 °C min⁻¹.

2.2. Characterisation of TNAs

An FE-SEM (Hitachi, S-4800) was used to analyse the top and cross-sectional morphologies of the thin film samples. High-resolution TEM (JEOL, 2100F) was used to observe the morphology of the samples in detail. Optical reflection spectra were measured using a UV–Vis–NIR spectrophotometer (VARIAN, Cary 5000), with standard polytetrafluoroethylene powder as the reference normalised to 100%. XRD patterns were recorded with a diffractometer (Bruker, D8 Advance) using a Cu target ($\lambda = 1.5418 \text{ \AA}$). XPS was performed using a spectrometer (Thermo, K-Alpha) with a focused monochromatic Al K α X-ray source.

2.3. Photoelectrochemical measurements

The transient current, Mott–Schottky performance and electrochemical impedance of the samples were measured using a potentiostat (Biologic, VSP). The recording interval of the transient current was set to 0.1 s. The Mott–Schottky performance of the TNAs was evaluated at a fixed frequency of 5 kHz using a three-electrode configuration with a TNA working electrode, Pt counter electrode, and a saturated Ag/AgCl reference electrode. The electrochemical impedance measurements were performed over the frequency range of 100 kHz–10 mHz using an excitation signal with a 10 mV amplitude at the open-circuit potential. All of the electrochemical measurements were performed at room temperature.

2.4. Photocatalytic degradation of organic contaminants

Four organic compounds (phenol, ibuprofen, carbamazepine and caffeine) were selected as target contaminants. Phenol, which is widely used as a precursor for plastics and drugs, is a representative contaminant from industrial wastewater effluents. Ibuprofen, carbamazepine and caffeine are pharmaceutical compounds that are currently recognised as emerging water contaminants due to their increasing use [44]. The photocatalytic setup consisted of a glass reactor and a 500 W xenon lamp (DTX Corp.) equipped with an AM 1.5 G optical filters. The glass reactor was filled with 15 cm³ of a solution containing 0.1 mol dm⁻³ NaH₂PO₄ as the

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