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Photoelectrocatalytic property of microporous Pt-TiO_2/Ti electrodes

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ABSTRACT

This study investigates the photoelectrocatalytic (PEC) property of microporous WO_3-loaded TiO_2/Ti layer, prepared via micro-arc oxidation (MAO) of Ti plate, followed by sputtering deposition of a thin Pt layer as a Pt-TiO_2/Ti electrode. The WO_3-loaded TiO_2 layer which is associated with a more acidic surface forms many local electrochemical cells on its micro-pores immersed in cationic dye solution. The electrocatalytic (EC) reactions can take place in the local cells by the applied electrons. A low resistivity that is accomplished by MAO technique and by platinization offers an easy path for the electron motions in the Pt-TiO_2/Ti electrode. All these features make the EC oxidation of aqueous dye pollutants practically feasible without using counter electrodes and supporting electrolytes. Our experiments demonstrate that, under PEC condition, the Pt-TiO_2/Ti shows the highest degradation rate constant of 0.83 h^{-1} at an applied bias of 1.0 V and exhibits significantly high PEC and EC oxidation activities at a low applied bias of 0.25 V. This is attributable to high anodic currents generated in the Pt-TiO_2/Ti even at low bias. The modified microporous electrodes conclusively reveal a very interesting EC property as a two double-sided device that functions the PEC and EC oxidation simultaneously without a need of supporting electrolyte and expensive Pt cathode.

1. Introduction

Photocatalysis is recognized as a very useful method for degrading a wide range of contaminants in air or water. Titanium dioxide (TiO_2) is one of the most suitable semiconductors for several environmental applications [1,2]. The surface area reportedly dominates the photocatalytic (PC) activities of the porous anodized TiO_2 oxides [1]. The nanopore TiO_2 arrays which are synthesized by anodization have shown superior PC and photoelectrocatalytic (PEC) activities in the degradation of organic compounds against the counterpart arrays, as a result of their network-framed structure that increases the carrier transport routes of the photogenerated electron–hole pairs [3]. Recently, micro-arc oxidation (MAO) has been used to prepare porous TiO_2 layers coupled with various metal oxides on Ti substrates [4,5]. MAO process has been considered a facile method for fast fabricating porous oxides [4–6]. The porous network is regarded as an open, wormlike structure on the surface of the film, with randomly orientated channels. This feature makes MAO process as one of most promising methods to synthesize micropore template of low-cost dimensionally stable anodes (DSA) [6].

The application of an external anodic bias is capable of enhancing the electron–hole separation and hence increasing the organic mineralization rate. This is because an applied bias can pull the photogenerated electrons away from electron–hole recombination, hence rendering an increase in the PEC activity for dye oxidation [7]. Alternatively, the effectiveness of electrocatalytic (EC) oxidation technique for wastewater treatment has received great interest because of its characteristics of environmental compatibility, versatility, energy efficiency and amenability of automation in the past decade [8]. In EC oxidation, the aqueous organic pollutants are initiated by absorbing on the anode surface and then oxidized by the electrons [7,9]. Since the electrons are the only reagents in the process, an effective control of electron transfer rate and the operation conditions of current density and applied potential can be controlled.

The nature of electrode material strongly influences the efficiency of the oxidation [9,10]. Platinum (Pt) anodes have a long history of use as electrode materials because of their good conductivity and chemical stability even at high potentials. In addition to its foil and grid, Pt has been adopted in various forms in EC applications. For instance, platinized titanium (Pt/Ti) anode has been reported for the wastewater oxidation [10]. And, photogenerated electrons diffuse effectively from the n-type TiO_2 into the p-type Pt region in a p–n Pt-TiO_2 system. This is because it can form a Schottky barrier between the Pt and TiO_2 for a better separation of carriers. Recently, Pt/TiO_2/Ti anodes prepared by the galvanostatic anodization of Ti sheets followed by galvanostatic deposition of underlying Pt have shown comparatively the same electrocatalytic activity as the bare Pt foils. This has ascribed to an increase in the active surface area as a result of hemisphere-shaped Pt deposits formed on the porous anode surface, as compared with the bare metal [6]. Deposition of

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Pt on TiO_2/Ti is a possible method for obtaining an inexpensive electrode that electrochemically behaves like a pure Pt electrode.

All the aforementioned studies have performed EC or PEC oxidation of various aqueous pollutants with supporting electrolyte under relatively high bias (>3 V vs. SCE) at which oxygen or chloride evolution yields for accelerating oxidation [6,9–11]. Furthermore, types of electrolytes used in EC oxidation have a significant and yet complicated effect on the degradation kinetics of parent pollutants. For example, a non-active Sb-SnO_2 anode was much superior to an active RuO_2 for oxidizing various dye solutions with Na_2SO_4 electrolyte at an applied bias higher than 2.0 V, but the relative superiority was reversed in order when the same reactions were performed in NaCl electrolyte instead [11]. A few PEC devices were built to demonstrate the characteristic feature of planar TiO_2 electrodes without a counter electrode. For example, Shang et al. used a PEC device consisting of two working electrodes in parallel without a counter electrode, in which a planar TiO_2 film supported on a patterned indium tin oxide (ITO) substrate was prepared as the working electrode [12]. Though using supporting electrolyte with care can highly increase the degradation kinetics [11,12], the presence of supporting electrolyte can potentially draw an extra operational uncertainty in the system. Here, we proposed an environmental friendly scheme with microporous Pt-TiO_2/Ti electrodes for facilitating PEC oxidation of aqueous dye pollutants without supporting electrolyte. The proposed scheme is different from the conventional one; a system uses a low applied bias (<1.0 V) with no explicit cathode.

2. Experimental procedure

Microporous TiO_2/Ti electrodes were synthesized on Ti substrates (25 × 75 × 1 mm) using an in-house MAO system, in which the Ti substrate was applied as an anode, and a stainless steel container was used as a cathode, operating at an applied potential of 300 V for 10 min. The TiO_2/Ti electrodes were fabricated in electrolyte solution consisting of Na_2WO_4 (15 g L^{-1}), $NaOH_3$ (2 g L^{-1}) and NaF (2 g L^{-1}) solutions. The as-oxidized samples were rinsed with distilled water and then dried in air at room temperature without post annealing [5]. Pt thin layer was subsequently deposited on the as-oxidized samples, denoted as Pt-TiO_2/Ti electrodes.

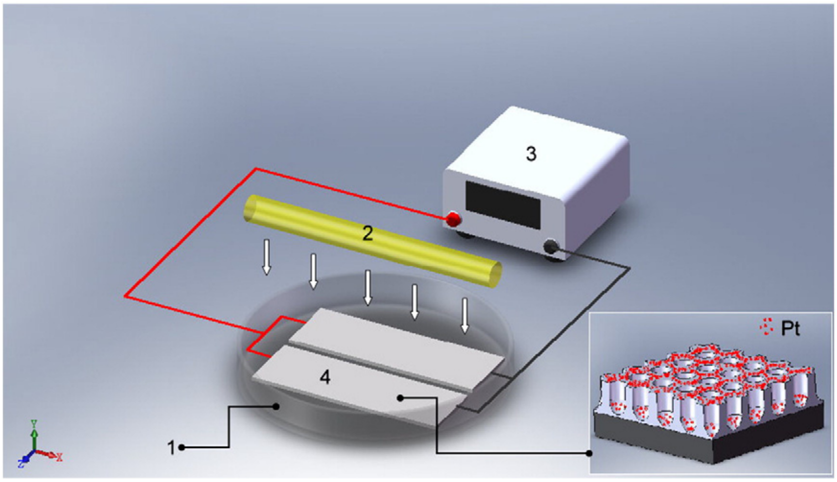
The crystal structures of the samples were analyzed using a high-resolution X-ray diffractometer (XRD, Rigaku ATX-E) operating with Cu Kα radiation at 40 kV/30 mA. The XRD patterns were scanned at a step width of 0.02°/2θ and an integration time of 1.2 s. The microstructures of the films were investigated using a scanning electron microscope (SEM, JEOL JSM-6700F) at an operating voltage of 15 kV. A high-resolution transmission electron microscope (HRTEM, Philips Tecnai 20, operated at 200 kV) was employed for microstructure characterization which was equipped with an energy dispersive spectrometer (EDS). TEM cross-sectional specimen of the sample was prepared using a focused ion beam (FIB, FEI Quanta 3D 200) with Ga liquid metal ion source at an operating voltage of 30 kV. Resistivity measurements were carried out using a four-point probe.

Cyclic voltammograms (CV) of sample electrodes were obtained with a potentiostat (CHI 610C) that was connected to saturated calomel electrode (SCE) and Pt wire in 2.0 M Na_2CO_3 solution (pH ~ 11) under AM 1.0 solar light illumination. The experimental set-up for the methylene blue (MB) oxidations is illustrated in Scheme 1, where the sample electrodes could not be used to perform the cyclic voltammetric tests without supporting electrolyte. The electrode couples were electrically connected in parallel and faced towards the light source. The photocatalytic activity was evaluated by immersing each coupled electrode (an active area of 2 cm × 5 cm × 2) in MB solution (pH ~ 6.8, 10 mg L^{-1}, 30 mL) without supporting electrolyte. A constant voltage was applied to the electrodes using a DC power supply for performing EC and PEC tests. The loop current of system, shown in Scheme 1, was measured with a digital multimeter. The degradation rate constants of MB over electrodes were assumed first-order reaction under UV (λ ~ 365 nm) irradiation. Prior to every MB degradation test, the samples were soaked in another beaker of aqueous MB solution for 10 min in darkness for equilibrium surface adsorption. Details of the MAO process and MB degradation tests were described elsewhere [5].

3. Results and discussion

3.1. Microstructures

Fig. 1 shows the XRD patterns of TiO_2/Ti and pt-TiO_2/Ti along with commercial DSA anode for comparison. The XRD patterns of Pt-TiO_2/Ti and TiO_2/Ti reveal a dominant anatase TiO_2 phase along with a crystalline WO_3 peak at $2\theta = 23.67°$ and two strong Ti peaks at $2\theta = 38.4°$ and $2\theta = 40.2°$ from a not well-anodized TiO_2 oxide. As seen in the inset of Fig. 1, the diffraction (101) plane is shifted slightly towards a lower 2θ value, suggesting possible distortion of the crystal lattice of TiO_2 by the W and F ions and/or other dopants. This suggests that the WO_3 phase could be largely loaded onto the TiO_2 matrix [5,13]. The relative high amount of WO_3 has been attributable to high PC ability [14]. Alternatively, the XRD patterns of DSA show mostly IrO_2 and Ti with a little anatase TiO_2 phase.



Scheme 1. Schematic representation of photocatalytic and photoelectrocatalytic reactor systems; 1. glass beaker, 2. UV light sources, 3. DC power supply and 4. Pt-TiO_2/Ti electrode; the inset is a close view of an idealized Pt-TiO_2/Ti electrode where the overlying Pt flakes are represented by the red-shed areas.