

Photocatalytic activity enhancement of TiO₂ thin films with silver doping under visible light

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ABSTRACT

TiO₂ and silver doped TiO₂ films (photoanodes) were prepared by the sol–gel method using silver contents of 1%, 3% and 5% (w/w). Photoelectrocatalytic activity of these photoanodes was evaluated by monitoring the photocatalytic decomposition of methanol and basic orange II (BOII) in aqueous solution under visible light illumination at pH 3 adjusted with HClO₄ by the application of potential bias. Enhanced photoelectrocatalytic activity was found by the application of 0.4 V (vs. SCE) bias potential under visible light illumination. A detrimental effect was observed on the photoelectrocatalytic activity of the TiO₂ photoanodes in the presence of BOII, and is evident from the low photocurrents; however, the presence of silver in the TiO₂ films increased the photoelectrocatalytic activity. Also the photoelectrolysis of methanol removed over 80% of total organic carbon in 5 h of reaction under visible light and 0.4 V (vs. SCE) bias potential. Nevertheless, negligible TOC removal was observed for the BOII photoelectrolysis with or without bias potential and under visible light illumination or in dark. Less than 9% of discoloration was achieved at the 3% Ag–TiO₂ photoanode under visible light illumination and bias potential.

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1. Introduction

The application field of photocatalysis is broad and it has contributed in the development of new ways to prevent and remove organic pollutants. The photoelectric and photochemical properties of titanium dioxide as a catalyst have driven its research for various applications such as solar energy conversion and degradation of organic compounds in wastewater [1–6]. Moreover TiO₂ is an inexpensive, nontoxic, chemically and biologically inert semiconductor [7–10].

The use of TiO₂ powder for the removal of contaminants in water and air has shown to be efficient due to its large surface area available for the reaction [11], however, the immobilization of TiO₂ particles on solid substrates present great advantages over systems which employ colloidal suspensions of TiO₂ particles, since by this way the difficulty of recovering the catalyst from treated water can be solved [12–14]. TiO₂ may be immobilized on a variety of materials, such as glass spheres or sheets, the reactor walls, fiberglass mesh [15], polyethylene and polypropylene films, or films and transparent porous TiO₂ glass substrates [16], etc. Nevertheless, if the TiO₂ is immobilized on substrates of electrically conductive materials, it is possible to use in electrochemical techniques [3,4],

which provide valuable information regarding to the rate of contaminant destruction in comparison with the photocurrent passing through the working electrode. From this comparison, it is possible to deduce the oxidation efficiency under any potential applied [17].

Different deposition techniques have been used to immobilize TiO₂ particles, some of these are the rotary evaporation, pulsed laser deposition [18], sputtering [19], chemical vapor deposition of precursors [20], dip-coating [21], sol–gel [22], spin-coating [23], aerosol powder coating, coating electrophoretic [24], ion implantation [25], hydrothermal crystallization, etc. Among the above mentioned methods, sol–gel is the most competent due to its simplicity and low cost in the production of multicomponent uniform layers [26].

In spite of the positive properties of TiO₂, spectroscopic studies showed that ~90% of the photogenerated electron–hole (e[−]–h⁺) pairs recombine rapidly after excitation, representing a quantum yield less than 10% [27]. Besides as a wide band semiconductor, it requires the application of light with energy greater than 3.2–3.0 eV for anatase and rutile respectively for the photoactivation. The absorption threshold corresponds to the UV light spectrum, which is between ~380 and ~400 nm [28–32], causing a slow reaction rate, since according to data reported, the solar spectrum contains only about 5% of UV radiation [33–36]. For this reason researches have focused on improving its performance by modifying its surface by deposition of noble metals [37]; thus moving its absorption spectrum toward the visible region.

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In this work, we studied the photoelectrocatalytic properties of undoped and Ag doped TiO₂ films on conductive glass deposited by sol–gel method and dip-coating technique. These photoanodes were used for the oxidation of methanol and basic orange II dye as model compounds.

2. Experimental

2.1. TiO₂ and Ag–TiO₂ photoanode preparation

TiO₂ and Ag–TiO₂ thin films were prepared by the sol–gel method using optically transparent conducting glass plates (10 mm × 25 mm × 1.1 mm ITO glass, Sigma–Aldrich). The ITO plates were cleaned with an alkali free detergent, and double distilled water in an ultrasonic bath. These ITO plates were dried prior to utilization, first under a stream of air and subsequently dried in an oven at 100 °C. Silver contents of 1%, 3% and 5% (w/w) were used to prepare the Ag–TiO₂ thin films. Precursor solutions for thin films were prepared at room temperature following the procedure reported by Mathews et al. [38]; which briefly consisted of preparing two solutions separately. A solution containing 0.8 mL of deionized water, 0.5 mL of nitric acid (AR grade), 5 mL of ethanol (99.9% pure, AR grade) and silver nitrate (AR grade) was added drop wise into a homogeneous solution containing 6.5 mL of titanium butoxide (AR grade) and 17.5 mL of ethanol (99.9% pure, AR grade). Then the sol was stirred during 2 h. For film deposition the ITO plates were submerged into the titania sols, perpendicularly to the solution surface, with a speed of 0.76 mm/s and withdrawn at the same speed. The films were first dried for about 15 min at room temperature and then oven dried at 100 °C for 5 min before more coatings were applied (three coatings). After drying, the thin film electrodes were sintered at 400 °C with a stream of air for 2 h. The morphology and thickness of the TiO₂ films were obtained using a high resolution scanning electron microscope (SEM) (LEO 1450 VP). The structural characterization was carried out using Rigaku X-ray diffractometer with monochromatized CuK α radiation ($\lambda = 1.54056 \text{ \AA}$). X-ray diffraction spectra of the films were recorded by scanning 2θ in the range of 20–70°, with grazing incidence angle of 0.5°.

2.2. Photoelectrochemical cell

The photoelectrochemical cell (PEC) was comprised by one compartment three-electrode cell made of Pyrex glass, fitted with a quartz glass window, and a visible light lamp. The area of the photoanodes (working electrodes) in contact with the solution was 2 cm². The counter electrode was a 3 cm² platinum mesh and a saturated calomel electrode (SCE) was used as a reference electrode. A potentiostat (Epsilon BAS) interfaced with a PC (Dell, Intel Pentium 4) was used to measure the current–voltage data. The visible light source used was a 35 W Xenon lamp (8000 K). The components of the PEC were enclosed inside a wooden black box to prevent the light from the surroundings.

2.3. Photoelectrocatalytic activity

In order to study the photoelectrocatalytic activity of the thin films, methanol and basic orange II (BOII) were used as model compounds. All compounds and chemicals were used as received without further purification. The pH of the solutions was adjusted with HClO₄ or NaOH (AR grade). 30 mL of solutions containing different concentrations of the model compounds under constant pH were used. The solution in the photo reactor was mixed with an electromagnetic stirrer. The distance between the vessel and the 35 W Xenon lamp was fixed at 1 cm. The current (photocurrent) was recorded as a function of the applied bias potential (–0.5 to

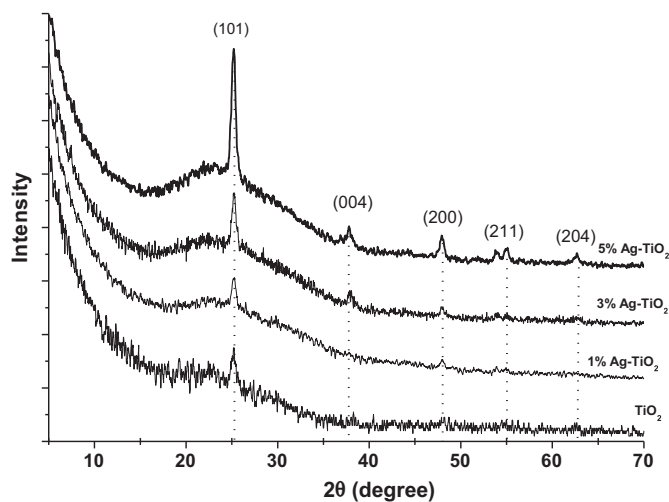


Fig. 1. XRD patterns of the TiO₂ nanocrystals with different content of Ag.

0.5 V vs. SCE) under dark and illumination conditions for the different solutions containing the model compounds. Oxidation of the model compounds was also carried out by applying a bias potential of 0.4 V vs. SCE under 5 h of illumination. Total organic carbon (TOC) was analyzed after the photoelectrocatalytic oxidation. TOC analysis was carried out using standard methods and standard reagents (20 mg L⁻¹ and 150 mg L⁻¹ TOC).

3. Results and discussion

3.1. Characterizations of the thin film structure

The XRD patterns for undoped and Ag doped TiO₂ films are shown in Fig. 1, indicating that the major phase of TiO₂ and Ag–TiO₂ films is an anatase structure. For Ag–TiO₂ films, it can be seen that the peak intensity increases with the increase of Ag concentration and no peaks of silver oxides were observed. Nevertheless, it was reported the existence of Ag and Ag₂O [39,40], and Ag, Ag⁺ and Ag²⁺ [40,41] on TiO₂ surface after doping the TiO₂ with silver ions. It has also been reported the presence of Ti³⁺ species on the TiO₂ surface which resulted from the incorporated materials of Ag or Ag₂O on the TiO₂ coatings [39–41]. The Ti³⁺ species (vacancy sites) on the Ag–TiO₂ surface enhance the photooxidation of organic compounds because these species can trap the photogenerated electrons [39].

Kuo et al. indicated that the major role of silver or silver oxide incorporated on TiO₂ could be attributed to accelerate the formation of superoxide radical anion O₂⁻ and also decrease the probability of recombination of electrons and holes by scavenging the electrons in the conduction band by silver dopants [39]. Wang et al., reported that the chemical states of Ag⁺ and Ag²⁺ are benefit to the photocatalytic ability of TiO₂ films since doping the TiO₂ with silver ions (Ag⁺ and Ag²⁺) may lead to the formation of space-charge layer [41]. Thus, depending on the optimum dopant content the e⁻/h⁺ pairs are efficiently separated by the large electric field before recombination [42].

The crystallite size (Table 1) was calculated by Scherer's equation using the FWHM from the main anatase peak (101) at $2\theta = 25.22^\circ$; the crystallite size of Ag–TiO₂ films tends to increase with the increasing amount of Ag ions. These results indicate that during the drying and annealing processes the Ag⁺ ions spreading on the surface of anatase grains would gradually be reduced to Ag⁰ which increases the crystallite size [43,44]. It can be observed that for 5% Ag doped TiO₂ the peaks (004), (211) and (204) are clearly more defined.

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