Desalination 253 (2010) 88–93

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Photocatalytic activity of metal (Pt, Ag, and Cu)-deposited TiO_2 photoelectrodes for degradation of organic pollutants in aqueous solution

Chun He [a,*], Dong Shu [b,*], Minhua Su [a], Dehua Xia [a], Mudar Abou Asi [a], Long Lin [a], Ya Xiong [a]

[a] School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, China
[b] Key Lab of Electrochemical Technology on Energy Storage and Power Generation in Guangdong Universities, School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, China

ARTICLE INFO

Article history:
Received 30 August 2009
Received in revised form 17 November 2009
Accepted 18 November 2009
Available online 16 December 2009

Keywords:
Photoelectrocatalytic
Metal (Pt, Ag, and Cu)
Deposition
TiO_2 photoelectrode
Formic acid

ABSTRACT

A series of metal (Pt, Ag, and Cu)-deposited TiO_2 films with nanocrystalline structure was prepared. Compared with TiO_2 film, the degradation efficiency of formic acid for the metal-deposited TiO_2 films was significantly higher in both photocatalytic (PC) and photoelectrocatalytic (PEC) processes, the enhanced order in PC and PEC activity for the metal-deposited film is Pt–TiO_2>Ag–TiO_2>Cu–TiO_2. However, the electrochemical dissolution of deposited metals (Ag, and Cu) on TiO_2 film would be a technical problem in PEC processes, an alternate PC and PEC processes intermittently provide a positive approach to maintain deposited metals (Ag, and Cu) on the TiO_2 films well.

1. Introduction

In past decades, TiO_2-mediated photocatalytic (PC) oxidation of organic compounds has attracted increasing attention in the field of environmental research for the degradation of undesirable organics in aqueous phases [1–3]. However, this technique has not yet come up to a satisfied extent with sufficient efficiency for the application in practice due to the rapid recombination between the active electrons and holes after photoexcitation [4,5]. In order to improve the efficiency of PC oxidation reaction, TiO_2 catalyst can be modified with addition of various impurities. For example, metals or metallic oxides can be added either into the TiO_2 structure by doping, implanting or coprecipitating or onto the TiO_2 surface by coating or photodepositing as metal islands [4,6–16]. Among them, one approach is the deposition of precious metals such as Pt [11,13] and Au [9,12,14,15] on the surface of TiO_2 catalyst through photoreduction reaction. For example, Bamwenda et al. reported that the presence of deposited Au on the surface of TiO_2 could significantly improve its PC activity and achieved the best PC efficiency with 1.0 wt.% Au [12]. However, it was worthy of note that TiO_2-based PC oxidation techniques need to be eventually applied in water and wastewater treatment. In practice, it will be more attractive to employ some low-cost or environmental-friendly metals instead of noble metals to modify TiO_2 films. Recently, Ag, Cu and Fe were selected as promising metals to modify TiO_2 films [13,17–23]. Although there are some references about the PC oxidation performance in Ag–TiO_2 [13,17,18], Cu–TiO_2 [19–21] and Fe–TiO_2 [22,23] powder systems by different researchers, the PC oxidation performance in the form of immobilized film systems has not too much reported.

Recently, the development of photoelectrocatalytic (PEC) oxidation processes with an externally applied anodic bias has been of interest to many researchers [24–28]. So far, most studies were relevant either to the PC processes with the metal-loaded TiO_2 powders or to the PEC processes with the ordinary TiO_2 films [24–28]. Although electrochemically assisted PC degradation of organic pollutants was carried out on a transparent conductive oxide (TCO) glass electrode loaded with a TiO_2 film [24–28], the PEC oxidation of organic pollutants on metal-loaded TiO_2 film has been rarely reported still to date.

In this contribution, the aim of this study was to compare the effect of the metal (Pt, Ag, and Cu) deposition on their properties, especially on the PC and PEC activities for the degradation of organic pollutants in aqueous media. The metal-deposited TiO_2 films with nanocrystalline structure were prepared by a procedure of photo-deposition and subsequent dip-coating. The photocatalytic activity of the metal-deposited TiO_2 films were evaluated in the PC and PEC processes to degrade formic acid as a model chemical in aqueous solution, since formic acid has no light absorption in the range of 320–400 nm and has no spontaneous evaporation from aqueous solution [24]. Furthermore, formic acid not only exists in some actual industrial wastewaters such as the effluents from tanners, dye workshops, and printed fabrics mills [29], but also is one of stable intermediates in the mineralization of

* Corresponding authors. Tel.: +86 20 39332690.
E-mail addresses: hechun@mail.sysu.edu.cn (C. He), dshu@scnu.edu.cn (D. Shu).

0011-9164/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2009.11.028

many organic pollutants [30–32] with resistance to further oxidation [33].

2. Experimental

2.1. Materials

TiO_2 (Degussa P25) powder with an average particle size of 30 nm and surface area of 50 $m^2 g^{-1}$ was purchased from Degussa AG Company as a regular TiO_2 catalyst. The indium-tin oxide (ITO) conductive glass plates with a thickness of 1.3 mm were obtained from Shenzhen Nanya Technology Ltd. in China. Other chemicals with analytical grade were obtained as reagents and used without further purification. Deionized distilled water was used throughout the experiment.

2.2. Preparation of metal-deposited TiO_2 films

A TiO_2 film was first prepared according to the procedure described in the literature [25]. In which, 40 g of TiO_2 powder was added into 500 ml of distilled water. The TiO_2 slurry was sonicated for 30 min to break the loosely-attached aggregates up and then vigorously agitated to form the fine TiO_2 suspension. Then the TiO_2 suspension was loaded on the ITO glass plate (10.0 cm × 4.0 cm) by a procedure of dip-coating, drying and sintering. The TiO_2-coated ITO film was dried for 15 min on a hot plate at 100 °C and subsequently sintered in a muffle furnace at 400 °C for 2 h to obtain the TiO_2 film. The quantity of TiO_2 loading was about 1.07–1.10 mg cm^{-2}.

A method of photoreduction reaction was employed to prepare the metal-deposited TiO_2 electrode. The photoreduction reaction was conducted in a PC reactor system as shown in Chamber A of Fig. 1, which consists of a 500-W high-pressure mercury lamp equipped with a double-walled quartz glass cooling tube and a rectangular quartz reactor (11.6 cm × 5.8 cm × 0.8 cm). The prepared TiO_2 film (10.0 cm × 4.0 cm) was positioned inside the quarts reactor and immersed in aqueous solution containing H_2PtCl_6 (2.2 mmol L^{-1}), $AgNO_3$ solution (2.0 mmol L^{-1}) and $CuSO_4$ (2.0 mmol L^{-1}), respectively, and then subjected to UV illumination, resulting in Pt–TiO_2, Ag–TiO_2 and Cu–TiO_2 films, respectively. The amount of metal deposition was controlled by the illumination time. An energy dispersive spectroscopy (EDS) analysis was carried out to further determine the amount of the metal deposition in the TiO_2 films.

2.3. Characterization of metal-deposited TiO_2 films

The prepared TiO_2 and metal-deposited TiO_2 films were first analyzed by X-ray diffraction (XRD) method using a diffractometer (Philips, Xpert system) with radiation of Cu target (K_α, $\lambda = 0.15406$ nm).

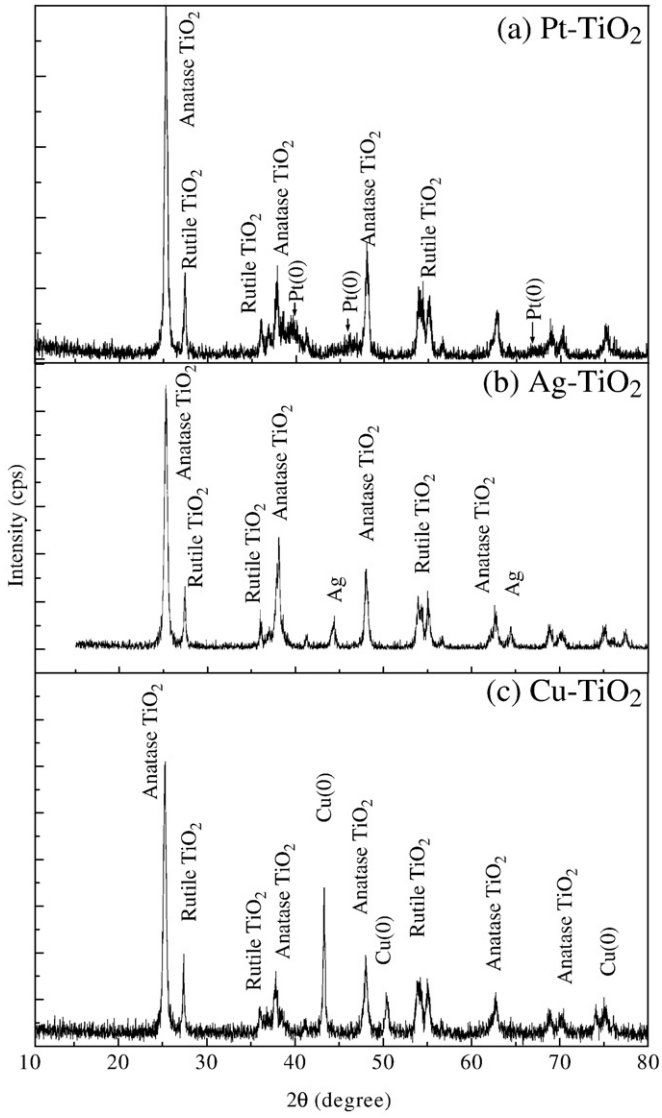

Fig. 2. XRD pattern of TiO_2 and metal–TiO_2 films.

Both the TiO_2 and metal-deposited TiO_2 films were then examined by a scanning electron microscopy (SEM) with a secondary electrons detector (Leica, Stereoscan 440). EDS was also obtained through the SEM equipped with a link analyzer (Oxford, ISIS-300) to determine the amount of metal deposition in the metal-deposited TiO_2 films.

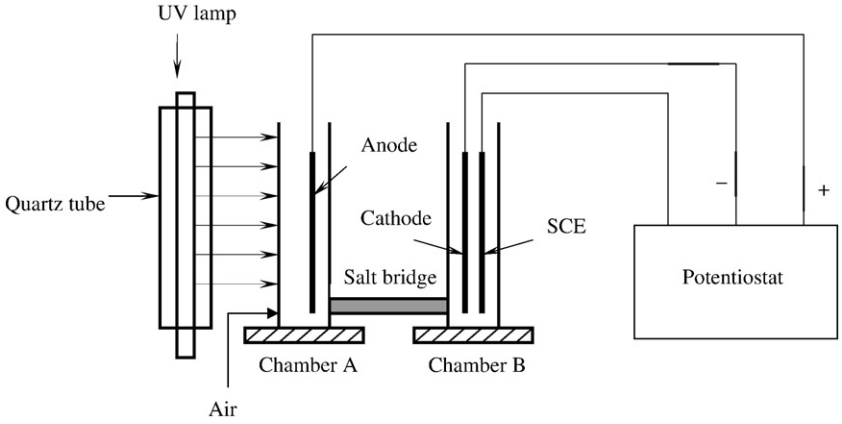

Fig. 1. Schematic diagram of PC and PEC photoreactor systems.