

Enhanced Photoelectrocatalytic Performance of Ag-deposited TiO₂ film electrodes in solution containing Cl⁻ ions

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Abstract. TiO₂ thin film electrodes were prepared on titanium sheet substrates by a dip-coating method. Ag was deposited on the surface of TiO₂ with photoreduction method. The prepared samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV-vis spectroscopy, respectively. The photoelectrocatalytic (PEC) degradation was investigated by employing methylene blue (MB) as a target pollutant. The results show that Ag-deposited TiO₂ film electrodes exhibited an enhanced PEC activity under visible light in compared with pure TiO₂, in particular in solution containing Cl⁻ ions at low pH value. Depositing process influence the catalyst's morphology and absorption performance, and then influence catalytic performance. The enhanced PEC activity observed can be attributed to the produce of photogenerated active chlorine carriers under the cooperation effect between the Ag particles on surface of TiO₂ and Cl⁻ ions in the solution.

Introduction

Semiconductor heterogeneous photocatalysis has been widely studied and recognized as a highly efficient and promising advanced oxidization technology for the degradation of environmental contaminants for several decades. TiO₂ is the most popular photocatalyst because of its high reactivity, chemical stability under ultraviolet light, nontoxicity, and low cost [1-2]. However, two major problems should be solved before the practical application of this technology on a large scale: one is the too narrow light absorption range of TiO₂ to utilize most of the sun energy; another is the low efficiency of the photocatalytic reaction (usually <1%).

Several techniques for improving the photoresponse of oxide electrodes, which have led to higher sunlight conversion efficiency, have already been proposed. For example, Ion doping [3-4] has frequently been applied to extend photo-response into the visible region. Combing TiO₂ with other materials [5] can also improve its PEC performance. Surface noble metal [6-10] modified TiO₂ exhibited higher photocatalytic activity. It was reported [6] the 1D anatase TiO₂/Ag heterogeneous composites exhibited excellent photocatalytic activity for degradation of 2,4-dichlorophenol in wastewaters. The incorporation of Ag [7] on (001) surface of anatase TiO₂ has been systematically investigated by means of density functional theory to understand the Ag effects on the electronic structure and photocatalytic properties in Ag/TiO₂ composites. It was found that the fermi level located at the bottom of conduction band, and the partial occupied states may also acted as electron trap centers which can improve the photocatalytic efficiency. Recently, a new plasmonic photocatalyst of Ag-AgCl@TiO₂ [8] exhibited efficient photocatalytic activity for the degradation of 4-chlorophenol and photoreduction of Cr(VI) ion under visible light irradiation. Its high photocatalytic activity can be attributed to the surface plasmon resonance effect of Ag nanoparticles.

It was found that active chlorine can be generated by a PEC method on a TiO₂ thin film electrode under UV light illumination [9, 10]. However, few studies [11-12] have monitored the in situ generated active chlorine during the PEC degradation of pollutants. We have reported that the photoelectrocatalytic activity of TiO₂ film electrodes in the degradation of nitrite ion is greatly enhanced in the presence of chlorine ions [12]. On the basis of similar considerations, we can expect further improvement in the PEC performance of Ag-deposited TiO₂ because of the strong cooperation

effect between Ag and Cl⁻ ions. Thus in this paper, surface Ag-deposited TiO₂ film electrode was selected as the photoanode to degrade MB in aqueous solutions containing Cl⁻ ion. The most important parameters, such as electrolytes and solution pH were investigated systematically. The PEC degradation mechanism of pollutant for the TiO₂ and Ag-deposited TiO₂ will also be discussed.

Experimental Section

Preparation and characterization. Titanium sheet was used as the substrate of photoanode, and its pre-treatment was the same as the previous reports [14]. The TiO₂ was fabricated by coating a layer of TiO₂ sol onto the titanium substrates through repetitive heat treatment, i.e., the titanium substrates were dipped into TiO₂ sol solutions for 30 s prepared by the method according to ref. 12, pulled up and then heated for 10 min at 500 °C to coat one layer, repeated this procedure for 10 times and the resulting materials were fired at 500 °C for 1 h. The annealed electrodes were electrically contacted with Cu wire on their backsides and covered with epoxy leaving a certain area of 20 cm² (5 cm × 4 cm). for use. Ag was deposited on the surface of TiO₂ electrode using photoreduction method. The prepared TiO₂ electrode was dipped into the solution containing AgNO₃ and CH₃OH and then illuminated under the UV light for 30 min. The crystalline phase of the synthesized thin film electrodes were analyzed by X-ray powder diffraction (XRD, Rigaku D/max-RA, Japan). A scanning electron microscope (SEM, FEI Sirion-200, Holland) was applied.

PEC degradation measurements of MB. All the photodegradation of MB experiments were carried out in a two-compartment Teflon cell equipped with a quartz window. The light source was a 250W Xe lamp. The PEC measurements were controlled by a CHI660D potentiostat (Chenhua company, Shanghai). A TiO₂ electrode was used as the working electrode, with an area of 5 cm × 4 cm exposed to the light, the counter electrode and reference electrode was a large area specpure graphite sheet and saturated calomel electrode (SCE), respectively. The potential used in the text was referred to SCE. The supporting electrolyte was 0.5 M Na₂SO₄, diluted H₂SO₄ and NaOH for pH adjustment, and NaCl was used as a source of Cl⁻ ion. Unless otherwise specified, 10 mg L⁻¹ MB was used. Prior to illumination, all the solutions tested were stirred at least for 15 min by bubbling with air to obtain adsorption equilibrium, and kept purging during the experiments. Samples were periodically taken from the anodic compartment for analysis. The concentration of MB was analyzed spectrophotometrically.

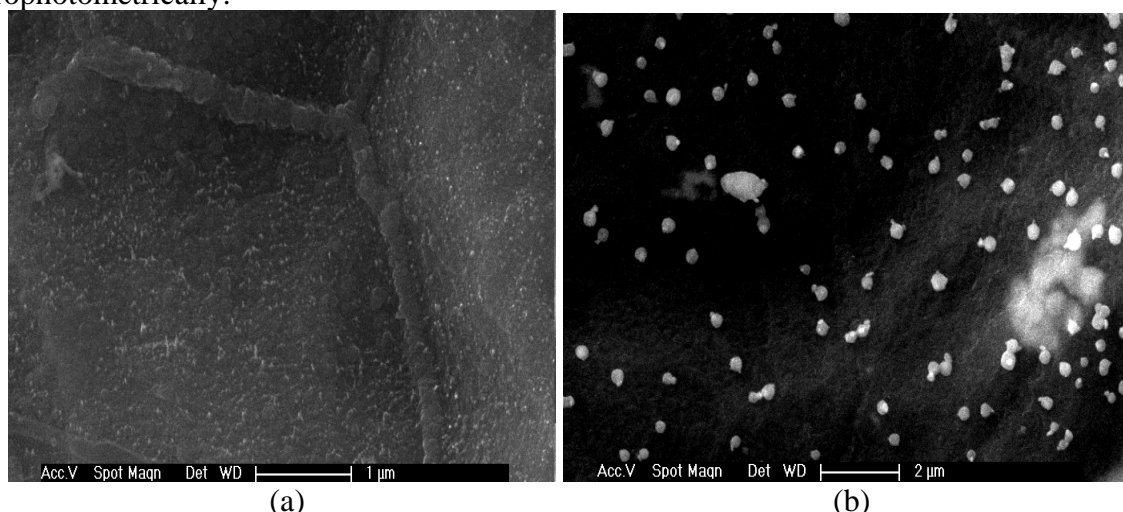


Fig. 1. SEM images of TiO₂(a) and Ag-deposited TiO₂ (b) thin film electrodes

Results and discussion

Morphology and Crystal Structure. Fig. 1 shows typical SEM micrographs for the TiO₂ and Ag-deposited TiO₂ film electrodes. It can be seen that the TiO₂ film surface is compact and uniform. After photoreduction, Ag nanoparticles were deposited on the surface. EDX spectra (Fig.2) shows

that Ag element was detected on the surface of deposited TiO_2 and a quantitative analysis of Ag was found to be about 3.2 at%.

The XRD patterns of TiO_2 and Ag-deposited TiO_2 films are shown in Fig. 3. It can be seen that the XRD patterns of the Ag-deposited TiO_2 samples exhibits similar phase to TiO_2 , which demonstrates that the crystal form of TiO_2 films did not change after depositing process. No new diffraction peaks appeared for the 3.2 at% Ag-deposited TiO_2 .

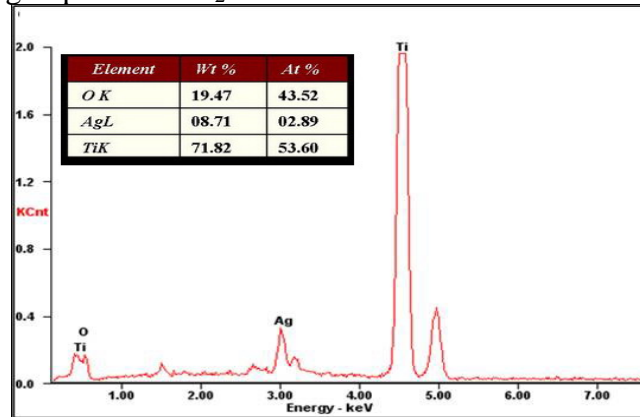


Fig. 2 EDX spectra analysis Ag-deposited TiO_2 film electrode

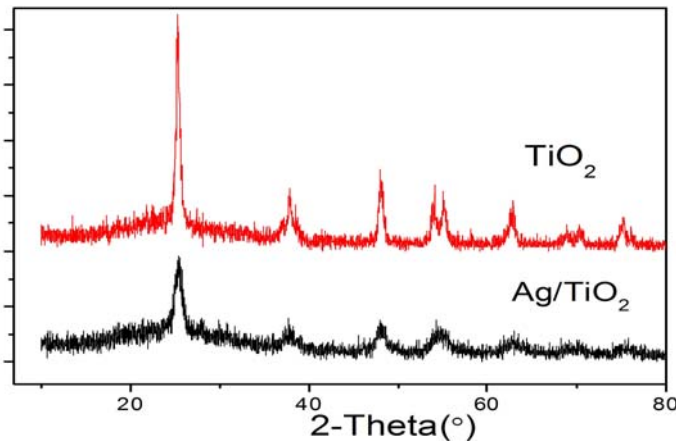


Fig. 3 XRD patterns of TiO_2 and Ag-deposited TiO_2 film electrodes

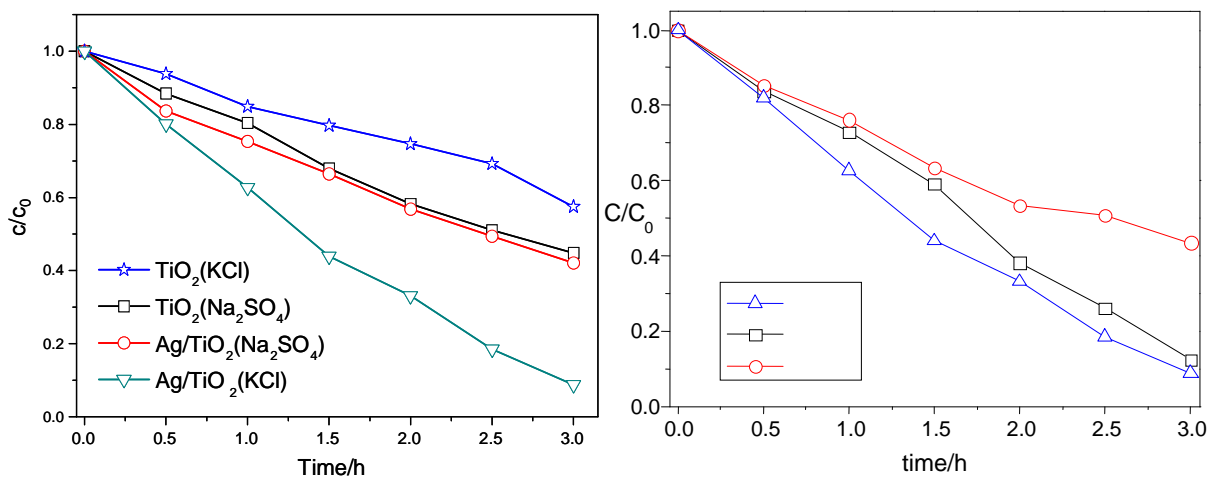


Fig. 4 Effect of electrolyte (a) and initial pH (a) on the MB PEC degradation rate

PEC degradation of MB. As shown in Fig.4, Ag/ TiO_2 presented higher degradation efficiency compared with pure TiO_2 . The degradation efficiency was lower on pure TiO_2 film electrode in KCl solutions, which may be due to the competed absorption between MB and Cl^- ions. However, the PEC rate accelerated remarkably on the surface of Ag/ TiO_2 in KCl solutions. Obviously, the PEC mechanism have changed in the Ag/ TiO_2 -KCl system. Usually, the PEC degradation of pollutant was carried through OH radicals, however, as reported, active chlorine radicals which are in-situ

generated during PEC progress can also take part in the oxidation reaction of pollutants. Thus, we proposed the enhanced PEC activity observed can be attributed to the function of photogenerated active chlorine carriers under the cooperation effect between the Ag particles and Cl⁻ ions. The effect of initial pH value was carried out in solution containing Cl⁻ ions. It can be seen that the PEC degradation rate increased when the initial pH increased and reached a maximum at pH 2.9, which is in accordance with the reported results that low pH value is favor for the generation of active chlorine.

Conclusions

The surface Ag-deposited TiO₂ film electrodes were prepared using photoreduction method. An enhancement of PEC activity of Ag-deposited TiO₂ catalyst has been achieved, especially in solution containing Cl⁻ ions. MB can be effectively oxidized using Ag-deposited TiO₂ under illumination of visible light at a potential above 0.8 V. The enhanced PEC activity observed can be attributed to the produce of photogenerated active chlorine carriers under the cooperation effect between the Ag particles and Cl⁻ ions in the solution.

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