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Enhanced Photocatalytic Efficiency of TiO_2 by Combining the Modification of Ag Nanoparticles with the Application of Anodic Bias

Chun HE[1, 2], Ya XIONG[1]*, Dong SHU[2], Xi Hai ZHU[1]

[1]School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275
[2]Department of Chemistry, Zhaoqing College, Zhaoqing 526061

Abstract: Ag-TiO_2/ITO film electrode was used as photoanode to investigate the feasibility of a hybrid technology of Ag nanoparticles combined with the application of anodic bias. The results showed that the deposited Ag and applied anodic bias have an apparent additive effect.

Keywords: Photoelectrochemistry, photocatalysis, Ag nanoparticles, TiO_2, formic acid.

Several attempts have been performed to improve the photocatalytic activity. One of them is noble metal deposition. The deposited metal, on the one hand, can suppress the electron-hole recombination, beneficial to the photocatalytic oxidation[1, 2]. On the other hand, some photogenerated positive holes will be attracted by negative-charged metal particles, if the accumulated negative charges are not consumed or not further transferred out of the metal particles, becoming recombination centers[3, 4]. Recently it has been reported that the anodic bias on the TiO_2 film can not only spatially separate conduction band electrons from the oxidation process[5], expectedly, but also drive away the accumulated photogenerated electrons on metal particles to another compartment of cell, reducing the electron-hole recombination and separating oxidation and reduction sites. Although electrochemically assisted photocatalytic degradation of organic pollutants was carried out on TiO_2 film[6, 7], the photoelectrocatalytic oxidation of organic pollutants on metal-loaded TiO_2 film has not still been reported to date. This situation encourages us to investigate a hybrid technology related to the combination of metal deposition with the applied electric field in order to improve photocatalytic degradation of organic pollutants. As a preliminary work, the present paper is devoted to approaching photoelectrochemical performance of Ag-TiO_2 film and the enhanced photocatalytic activity towards the oxidation of formic acid.

Experimental

The photocatalyst was Degussa P25. Formic acid was 10 mmolL^{-1} (COD: 157 ppm).

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*E-mail:cesxya@zsu.edu.cn

Film supporter was ITO (Indium-tin oxide) glass. Ag-TiO_2/ITO film was prepared first using a procedure in the literature[8] to prepare the TiO_2/ITO film and then depositing Ag on the film *via* photoreduction. Photoelectrocatalysis was conducted in a two-compartment reactor. The reported photocatalytic apparatus[9] was used as the photo-anodic compartment while the cathode compartment is with a Pt counter electrode.

Results and Discussion

This process of Ag photodeposition on TiO_2/ITO film was monitored using UV diffuse reflectance spectra. As shown in **Figure 1**, the peak of the TiO_2 film at 406.5 nm rapidly decreased with the reaction proceeding. Simultaneously, two new peaks appeared at 349.0 and 608.6 nm, respectively, and a well-defined iso-isosbestic point was observed at 325.3 nm. After 5 min, the diffuse reflectance peak of TiO_2 completely disappeared and the spectrum fully characterized the diffuse reflectance of deposited Ag. However, SEM (**Figure 2**) of the film indicates considerable uncovered-surface of TiO_2 film by Ag even after 20 min, suggesting that the film has still certain photocatalytic activity.

Figure 1 Diffuse reflectance of TiO_2 film in the process of Ag(0) deposition

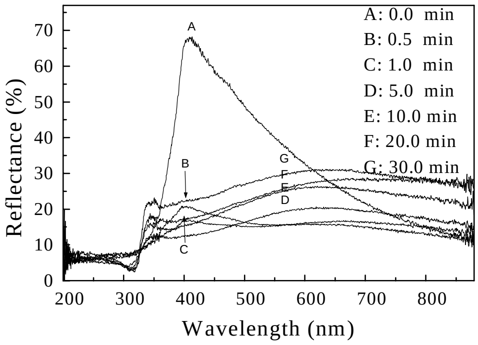
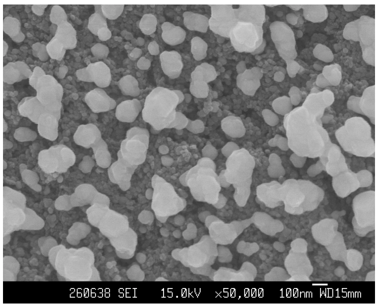


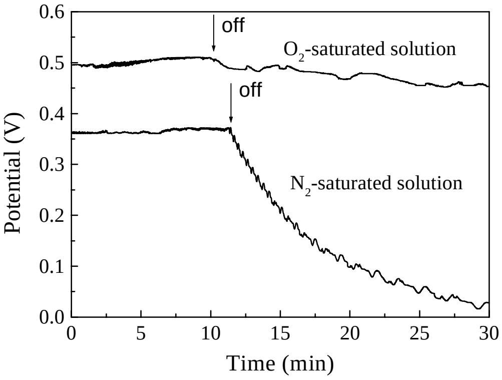
Figure 2 SEM image of the surface of Ag (0)-deposited TiO_2 film by a 20-min photoreduction



Although the photoelectrochemical performances of metal-loaded TiO_2/ITO film, such as Pt- and Au-TiO_2/ITO films *etc.*, have been investigated by several groups, very few studies concerned the Ag-TiO_2/ITO film[2]. Therefore, the Ag-TiO_2/ITO film was photoelectrochemically characterized in this context, prior to probing its catalytic activity.

V_{oc} represents the energy difference between the Fermi level of semiconductor and the reduction potential of the redox couple in the solution. Therefore, any accumulation of electrons in the film will present a negative shift in V_{oc}. The scenario has been observed in our experiments. On the one hand, with respect to O_2-saturation solution, V_{oc} (O_2) of TiO_2/ITO film is 356 mV, lower than that for N_2-saturated solution (496 mV). This is because the surface-adsorbed O_2 scavenges the photogenerated electrons in the O_2-saturated solution, resulting in less accumulation of the electrons on the film. This effect is readily seen in **Figure 3**, the open circuit photovoltage decays move rapidly with time in O_2-saturated solution, after light was turned off, while it decreases rather slowly in the absence of air. On the other hand, in the N_2-saturated solution, V_{oc} first increased with increasing Ag nanoparticle deposition, then decreased with the highest V_{oc} of 0.52 mV at about 0.36% (Wt./Wt.). The increase is consistent with the fact that Ag nanoparticle is highly electronegative as the Fermi level can be shifted to negative potentials with chemical modification or charging effect[10] while the decrease can be attributed to the block of incident light by Ag nanoparticles on the film, as shown in **Figure 1**. The highest V_{oc} represents a balance of the two effects. However, with respect to the O_2-saturated solution, no highest V_{oc}, different from the case for N_2-saturated solution, was observed and the V_{oc} (O_2) decreased more rapidly with increasing Ag-deposited amount. Obviously, this result suggests that the deposited-Ag has an effect of enhancing O_2 scavenging the photogenerated electrons.

Figure 3 Decay curves of open circuit voltage after light was turned off



Noticeably, because V_{oc} (N_2) represents the maximum accumulation of the electrons, V_{oc} (O_2)/V_{oc} (N_2) is the fraction of the remained photogenerated electrons after the electrons are partly scavenged by O_2. The experiment showed that there are still remained accumulation electrons on Ag-TiO_2/ITO film although Ag deposition can increase the efficiency of O_2 scavenging the electrons. For example, for TiO_2/ITO film with 0.36% deposited Ag, the fraction of the remained electrons is 67%. Therefore, it is reasonable to employ an anodic bias to drive away the remained accumulation electrons in order to increase photocatalytic efficiency, as mentioned previously.

The photocatalytic activity is strongly dependent on the amount of deposited silver. For the photocatalytic processes, the COD removal efficiencies increased rapidly with increasing amount of deposited Ag from 0.0 to 1.7%. However, overcoated Ag will form a continuous Ag layer to mask TiO_2 film, consequently causing a decrease or even ineffectiveness in photocatalytic activity. For photoelectrocatalytic process, a similar change tendency was observe. However, the COD removal efficiency for photoelectrocatalytic process is apparently higher than that of pure photocatalytic process on neat TiO_2 film or Ag-loaded TiO_2 film. This more obvious enhancement effect denotes that deposited Ag can not only trap the photogenerated electrons but also assist the external electric field to migrate them from the TiO_2 film anode to counter electrode in another compartment of the cell. The rate constant for the COD removal was determined from the pseduo-first-order kinetic analysis of these data. These rate constant is in order: photoelectrocatalysis on Ag-TiO_2/ITO film (0.05 min^{-1}) > photocatalysis on Ag-TiO_2/ITO film (0.028 min^{-1}) ≈ photoelectrocatalysis on TiO_2/ITO film (0.023 min^{-1}) > photocatalysis on TiO_2/ITO film (0.013 min^{-1}), (applied anodic bias: 0.8 V*vs*. SCE). It is evident that the combination of the Ag-deposition and the application of anodic bias has a beneficial effect in enhancing the rate of the photocatalytic oxidation of formic acid. Upon close examination of these values it was found that the former is a simple sum of the latter two basically. As a result, one can infer that the enhancement observed in the combined methods is an additive effect, consistent with the photoelectrochemical performance observed previously. However, the additive effect will be more important when one considers the need for degradation of some organic pollutants that are usually recalcitrant to electrochemical or heterogeneous photocatalytic treatments. Further investigation on this technology is proceeding.

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