Chinese Chemical Letters Vol. 13, No. 11, pp 1127 – 1130, 2002
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# A Novel Regeneration Method of Cu(0)-deposited $TiO_2$ Photocatalytic Film: Air-assisted Electrochemical Oxidation

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**Abstract:** A rapid deactivation of $TiO_2$ film was observed in the process of the photocatalytic degradation of formic acid in the presence of Cu(II) due to the deposition of Cu(0). A novel regeneration method, air-assisted electrooxidation, could efficiently retrieve the photocatalytic activity of the deactivated film. $HNO_3$ medium has a regeneration extent of 97.2% for first run, much higher than that of HCl and $H_2SO_4$ mediums.

**Keywords:** Photocatalysis, electrooxidation, regeneration, $TiO_2$, formic acid, copper.

Copper, a priority pollutant[1], is present in many industrial wastewater, moreover, a major fraction of the Cu(II) is coexistence with organics. For them, the destruction of the organic pollutants and the simultaneous removal or recovery of Cu by the $TiO_2$ photocatalysis is an attractive technique[2]. However, a critical problem associated with the application of the technique is the Cu(0) deposition. The deposited copper may occupy active sites on $TiO_2$ surface, eventually causing the catalysis to lose activity completely. Thus, an approach to regenerating periodically photocatalyst is strongly desired[3]. This situation arouses our interest in regenerating the Cu(0)-fouled $TiO_2$ film.

For the oxidation potential of Cu(0) is lower than that of oxygen evolution, it is possible to oxidize Cu(0) to dissoluble Cu(II) by applying an anodic potential lower than that of the oxygen evolution. On the other hand, sparging-air can speed up mass transfer, moreover, the reaction, $2Cu(0) + 4H^+ + O_2 = 2Cu^{2+} + 2H_2O$, is feasible from the view of thermodynamics. Based on above considerations, a novel regeneration method, air-assisted electrooxidation, was proposed, which is a combination of air and electrochemical oxidation of deposited Cu(0). The aim of this letter is to present an approach to the feasibility of the regeneration method using formic acid as a test solution.

## Experimental

Photocatalyst was Degussa P25. Formic acid was prepared to 10.0 $mmolL^{-1}$ (Chemical oxygen demand (COD): 157 mg $L^{-1}$) and adjusted to pH 4 with NaOH. ITO glass plates (Indium-tin oxide) were from Shenzhen Nanya Tech. CO., LTD. The $TiO_2$/ITO film

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(10.1 cm×4.0 cm) was prepared using a method similar to that reported in the literature[4]. The thickness of $TiO_2$ film was estimated from SEM to be 2-3 μm.

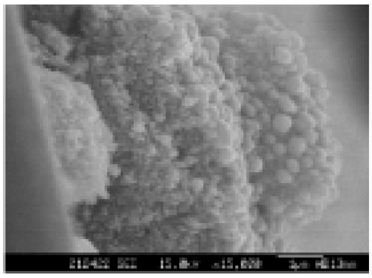
The photocatalytic apparatus consists of four parts, a 500 W high-pressure mercury lamp, a double-welled quartz cooling tube with a 5.0 mm thickness, a batch rectangular quartz reactor (11.6 cm×8.5 cm×0.7 cm) open to air and an ITO glass plate with $TiO_2$-immobilized film. The UV lamp was suspended vertically in the cooling tube. The ITO/$TiO_2$ plate was immersed in the reactor located 2.0 cm in front of the lamp.

Photocatalysis: A 35.0 mL solution of the formic acid containing 2.0 mmol$L^{-1}$ Cu(II) was fed into the photoreactor. Except as indicated, general reaction conditions were 0.1 $Lmin^{-1}$ airflow and 60 min for a batch run. Regeneration was conducted in common rectangular electrolyser. A Ti plate and the ITO glass with Cu(0)-deposited $TiO_2$ film, situated 5.0 cm apart from each other, were used as cathode and anode, respectively. A constant airflow of 0.1 L $min^{-1}$ was sparged into the electrolyser from its bottom by a micropore pipe. The reaction was conducted until no deposited Cu(0) on the $TiO_2$ film was observed and the reaction duration was defined as regeneration time.

## Results and Discussion

Photocatalytic reduction of Cu(II) is a controversial topic[5-6]. One of these controversial issues is the product of photoreduction of Cu(II) is Cu(0) or $Cu_2O$? [7-10]. In our experiment it was observed that a red product was deposited on the $TiO_2$ film, simultaneous to COD removal. The XRD spectrum of the mixed $TiO_2$ with the deposited substance showed three stronger diffraction peaks at 2θ angles of 37.8°, 50.36° and 74.04°, except for the diffraction peaks of $TiO_2$. These characterizations are consistent with that of XRD peaks of Cu(0), suggesting that the red deposited substance is Cu(0), not $Cu_2O$.

**Figure 1** SEM image of the section of ITO glass-supported $TiO_2$ film covered by a layer Cu(0)

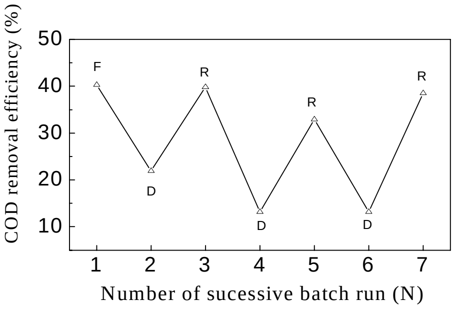


(Left-ITO glass plate; Middle-$TiO_2$ film; Right- Cu(0) layer)

The photocatalytic activity of the $TiO_2$ film was determined used formic acid as a test compound in the both presence and absence of Cu(II), respectively. The $TiO_2$ film could remove COD from the Cu(II)-free formic acid solution and keep basically constant COD removal efficiency (34.6±1.194) in the process of repeatedly batch runs, presenting a stable photocatalytic activity. However it presents a changeable COD removal efficiency for the Cu(II)-containing solution. When it was used first run, it showed a 51.3% COD removal efficiency, higher than that for the Cu(II)-free solution. However, the efficiency decreased rapidly with increasing in the number of batch run. When the film was used third time, the COD removal efficiency is only 6.7%, almost losing the photocatalytic activity of $TiO_2$. It can be seen from **Figure 1** that the surface of $TiO_2$ film was covered by a layer Cu(0) of about 2-3 μm after second batch run. Therefore, it was reasonable that the decrease in COD removal efficiency was attributed to the shielding of UV by the Cu(0)-deposited layer.

As expected, the air-assisted electrooxidation could remove the deposited Cu(0) from the deactivated film in 15 min that is much shorter than the regeneration time (24 h) reported by Ramanathan *et al.*[3] Interestedly, the different regeneration mediums, HCl, $H_2SO_4$ or $HNO_3$, had no effect on regeneration time, all in 15 min, but they presented apparent different regeneration extent[11], 67.5% for HCl, 76.1% for $H_2SO_4$ and 97.2% for $HNO_3$, indicating that $HNO_3$ was a preferred regeneration medium. It was reported that, under the illumination of UV light, the $NO_3^-$ could generate reactive OH radicals[12]. As a sequence, it was presumed that the remained $NO_3^-$ on or/and in the regenerated $TiO_2$ film could photogenerate reactive OH radicals by the same mechanism[12], and it was well known that the radicals could efficiently degrade organic pollutants. The desirable regeneration performance of $HNO_3$ medium might be attributed to the formation of these additional OH radicals. Due to the same reason, the following experiments will be performed in $HNO_3$ medium.

**Figure 2** Change of COD removal efficiency in the process of successive deactivation-regeneration cycles

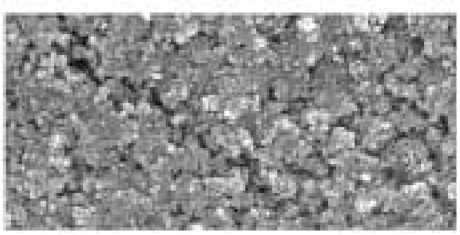


(F: fresh; D: deactivation and R: regeneration)

The above discussion is based on the first run. However, from the view of actual application, an important question to be answered is whether the repeated deactivation-regeneration affects the photocatalytic activity and the stability of the $TiO_2$ film. **Figure 2** presents the COD removal efficiencies in three deactivation-regeneration cycles. As shown in the figure, the regeneration-post COD removal efficiencies slightly decrease after third cycle, and their regeneration extents of third cycle are 97.6%. Comparing the SEM images of the fresh and third-regeneration films by air-assisted electrochemical oxidation at 1 V, no apparent difference was observed, suggesting that the repeated regeneration do not obviously destroy the surface structure of the $TiO_2$ film.

We have once attempted to further enhance the regeneration efficiency by increasing cell voltage. Although the regeneration time could be saved, when a cell voltage of 30 V was applied, the regeneration extent of third cycle was much decreased. And **Figure 3** shows some apparent crackles, revealing that the $TiO_2$ film has been destroyed. One of possible reasons for the destruction may be that oxygen evolution at higher applied cell voltage results in the falling off of the part film. Accordingly, the applied anodic potential of regeneration had better been controlled below the potential of oxygen evolution.

**Figure 3**. SEM image (1000 folds) of successive deactivation-regeneration cycles after three times at 30 V and in $HNO_3$



## Acknowledgments

Financial support by NNSF of China (29977030), NSF (990274) and EPA Project of Guangdong (1999-14), Foundation of the Education Ministry for the Returned Scholar from Abroad and Sci. and Techn. Proj. of Guangdong (A3030502), The Key Lab of Environ.l Sci. and Technol. of High Education of Hennan Province

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Received 22 February, 2002