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Towards Understanding the TiO_2 -Mediated Photoredox Process of Cu(II) -Formic Acid Solution

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ABSTRACT

The performance of TiO_2 -film was investigated in the process of simultaneous photocatalytic Cu(II) reduction and COD (chemical oxygen demand) removal from Cu(II) -containing formic acid solution during successive batch runs. It was found that, during the first batch run, the Cu(II) ions could increase the COD removal efficiency, synchronous to the Cu(0) deposition, however, decrease the efficiency by a factor of 22.5% with the continuative proceeding of the deposition for the second batch run. Unexpectedly, after the second run the COD removal efficiency remained a constant, ca. 40%, and no longer continued decrease. The unexpected observation was attributed to the cycle of Cu(II) deposition and Cu(0) re-dissolution due to air oxidation at pH 2.73. The attribution was primarily confirmed by the scanning electron microscope image and several fluctuation phenomena in the reaction process, such as pH, Cu(II) concentration and photocurrent.

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Key Words: Photocatalysis; Wastewater; COD; TiO₂; Copper; Formic acid.

INTRODUCTION

TiO₂ heterogeneous photocatalysis has been widely considered to be a promising process for the elimination of toxic and hazardous organic substance from wastewater, drinking water and air.^[1-4] With the aim of commercializing this process, researches in this field have been diverse, such as fundamental aspects of photocatalysis,^[5,6] the designs and optimization of photocatalytic reactors,^[7,8] evaluation of process applicability for the treatment of a vast variety of organic contaminant^[1-3] and identification of intermediate products and reaction mechanisms etc. Recently our much attention has been paid to investigating the lifetime or photoactivity change of TiO₂ particular film during long-term use in view of practical application need.^[9]

It has been noticed that dissolved transition metals has been reported to influence profoundly the TiO₂-mediated photocatalytic degradation rate of organic pollutants^[10] and copper(II) as one of these metals seems to attract more attention since copper occurs in many industrial effluents originated from metal finishing, electroplating and modern microelectronic industries etc. and coexists frequently with organic pollutants in wastewater.^[10,11] Although there are some controversial results in the present literatures about the effect of Cu(II) on photocatalytic efficiency,^[10] it has been well known that copper(II) has negative and positive two-side effects. On the one hand, copper ions can trap photogenerated electrons and decrease the combination of electrons and holes by their reduction reaction, leading to an enhancement of photocatalytic degradation of organic pollutants;^[12] on the other hand, copper may be deposited on the TiO₂ particles, specially, on the TiO₂ film in the process of photocatalytic removal of organics simultaneously, probably resulting in photoactivity decrease or complete deactivation of the catalyst due to the blocking of the deposited Cu(0) from UV light.^[13] With respect to a TiO₂ particular film that may be repeatedly used in the Cu(II)-containing wastewater, it may be expected that the Cu photodeposition on the film would result in a decrease and finally complete deactivation of the film photoactivity. The expectation aroused our interests in orienting our research to investigating the deactivation and regeneration method of the TiO₂ film used to treat Cu(II)-containing organic wastewater repeatedly.^[9]

For Cu²⁺-formic acid solution at pH 4, the dependence of COD (chemical oxygen demand) removal efficiency on the number of repeated run was found to be as expected.^[9] With respect to Cu²⁺-formic acid solution at pH 2.73, unexpectedly, the COD removal efficiency was independent on the number of batch run after the second run. As a continuation of our work, this paper was devoted to approaching the unexpected observation and trying to understand the photocatalytic redox process of Cu(II)-formic acid solution at this pH value.



EXPERIMENTAL DETAILS

Material

The photocatalyst used was titanium dioxide (Degussa P25) with a surface area of $50 \text{ m}^2 \text{ g}^{-1}$ and an average particle diameter of ca. 30 nm. Formic acid was analytic grade reagent, and the solution was prepared with deionized water in the concentration of 10 mmol L^{-1} (COD: 157 ppm, pH 2.73) and no pH was adjusted unless otherwise stated. ITO (Indium-tin oxide) conductive glass plates (1.3 mm thick, $30.4 \text{ cm} \times 40.4 \text{ cm}$, $2 \Omega \text{ cm}^{-2}$), obtained from Shenzhen Nanya Technology Co., Ltd. P.R. China, were used as a support of TiO_2 films in order to conveniently measure photocurrent.

Preparation of TiO_2 Film on ITO Glass

The TiO_2 /ITO particular film was prepared according to the procedure in the reference.^[14] The suspension was prepared by addition of a 80-mg TiO_2 powder to 1.0 L distilled water, vigorous stirring of this suspension and then dispersing ultrasonically for 30 min resulted in a finely divided TiO_2 suspension. TiO_2 films were prepared by repeated dip coating of ITO glass slides with TiO_2 suspension, after dipping the coated films were dried at 100°C for 15 min and then calcined for 2 h at 400°C . The procedure was repeated 3 times. The resulted film had a thickness of ca. $3 \mu\text{m}$ from the scanning electron microscope (SEM) image.

Apparatus

A UV-PC3101PC spectrophotometer (SHIMASZU, Japan) was used to record the UV absorption spectra of solution. SEM images were obtained on a JSM-6330F-mode Field Emission Scanning Electron Microscope (JEOL, Japan). X-ray reflection diffraction (XRD) was performed using D/Max-III A Diffractometer (Rigaku Corporation, Japan) with Radiation of Cu target ($K\alpha 1$, $\lambda = 1.54056 \text{ nm}$).

Photocatalytic Set Up

The schematic diagram of the photocatalytic apparatus is presented in Fig. 1. The apparatus consists of four parts, a 500 W high-pressure mercury lamp, a double-welled quartz glass cooling tube with a 5.0 mm-thick cooling water, a batch quartz glass reactor ($11.6 \text{ cm} \times 8.5 \text{ cm} \times 0.7 \text{ cm}$) that was open to air and an ITO glass plate with TiO_2 -immobilized film ($10.1 \text{ cm} \times 4.0 \text{ cm}$). The UV lamp was suspended vertically in the cooling tube with a cooling water flow (650 mL min^{-1}) to maintain reaction isothermality. The circulating water also ensured infrared filtering of the incident ray. The cooling tube in which UV lamp was suspended was placed in front of the rectangular quartz reactor. The ITO glass

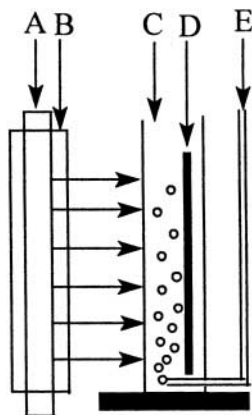


Figure 1. Schematic diagram of photocatalytic set-up. A: 500 W high-pressure mercury lamp; B: double-welled quartz glass cooling tube with a 5.0 mm-thick cooling water; C: batch quartz glass reactor (11.6 cm \times 8.5 cm \times 0.7 cm) that was open to air; D: ITO glass plate with TiO₂-immobilized film; E-compressed air.

plate with immobilized TiO₂ film was immersed in the reactor, located at 2.0 cm to the UV lamp.

Analysis

Chemical oxygen demand (COD) was measured with potassium dichromate after the sample was digested with a WMX COD microwave digestion system.^[15] All the TiO₂/ITOs were weighed prior to and after the deposition of copper to calculate the weight of the deposited copper. Photocurrent measurement was performed with a Model CH 650 potentiostat by using a Pt counter electrode placed in a compartment that was connected to the above-mentioned reactor via a salt bridge.

Experimental Procedure

A 35.0 mL solution of 10 mmol L⁻¹ formic acid containing 0.002 mol L⁻¹ Cu(II) ion was fed into the photoreactor, prior to starting photocatalytic reaction, and then a piece of the ITO glass with TiO₂ film was immersed in the solution. The reactor was timed starting when illumination and compressed air supply were switched on. General treating conditions were 0.1 L min⁻¹ airflow and 60 min for a batch run, except as indicated. The resulted solution was remained for optical absorption and COD analysis.



RESULTS AND DISCUSSION

An Unexpected Observation: Phenomenon of Constant COD Removal

Theoretically, the metal ions with a standard reduction potential more positive than -0.2 V vs NHE can be reduced by the photoelectrons of TiO_2 since its conduction band edge ($\sim -0.2\text{ V}$ vs NHE at pH 0.0) represents the reducing power of the photogenerated electron. The standard reduction potentials for Cu^+/Cu , Cu^{2+}/Cu and $\text{Cu}^{2+}/\text{Cu}^+$ are 0.522, 0.345 and 0.167, respectively, therefore Cu^{2+} can be photoreduced to $\text{Cu}(0)$ and deposit or cover on the surface of TiO_2 film. It was expected that the deposition and covering would block the TiO_2 film from UV light, leading to the decrease and finally complete deactivation of the film photoactivity in the process of repeated batch run or long term use.

As expected, in the process of photocatalytic oxidation of formic acid containing copper ions a layer of red deposit on the surface of TiO_2 -film was observed. Considering that TiO_2 -mediated photoreduction product of copper(II) is a controversial issue,^[10] the red deposition with TiO_2 was analyzed by XRD. The XRD pattern shows three peaks appearing at 2θ angles of 43.280, 50.420, and 74.080, corresponding d -values of 2.0887, 1.8084, and 1.2787, respectively, in addition to the characteristic peaks of TiO_2 . The three peaks are of the XRD characteristics of $\text{Cu}(0)$, indicating that the Cu(II) was fully reduced to $\text{Cu}(0)$ rather than Cu_2O . The result is consistent with that reported by Wang et al.^[11] The mean diameter of the copper particles was estimated to be approximately 300–500 nm by SEM image.

In order to investigate the effect of $\text{Cu}(0)$ deposition on the TiO_2 film on the photocatalytic oxidation of organic pollutants, the dependence of COD removal efficiency from Cu(II) -containing formic acid solution with pH 2.73 on the batch run number was determined. It was found that the COD removal efficiency decreased 22.5% from the first to second run, however, from the second to the fifth run, the efficiency basically remained a constant, ca. 40%, instead of continuing to decrease, as shown in Fig. 2, which seems not to be different from the case at pH 4. The unexpected observation, referred to as the phenomenon of constant COD removal in the following discussion for the sake of convenience, aroused our more interests in probing the photocatalytic redox process of the Cu(II) -containing formic acid solution and further clarifying the reason for the constant COD removal in the view of consideration of fundamental research although it is unknown whether the observation is of some practical importance at this moment.

Potential Mechanism of the Constant COD Removal

Dependence of the deposited- $\text{Cu}(0)$ amount on the film on the batch run number was presented in the Fig. 3. Compared with Figs. 2 and 3, it can be seen that the above-observed change in COD removal efficiency seems to be proportional to the $\text{Cu}(0)$ deposition amount. For example, when COD removal efficiency decreased ca. 22.5% from the first to second run, then it did not change with increase in the batch run number, the $\text{Cu}(0)$ deposition amount correspondingly

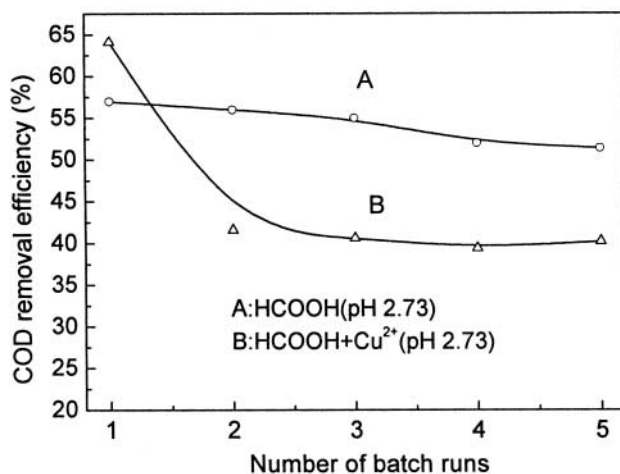


Figure 2. Dependence of COD removal efficiency on the number of batch runs.

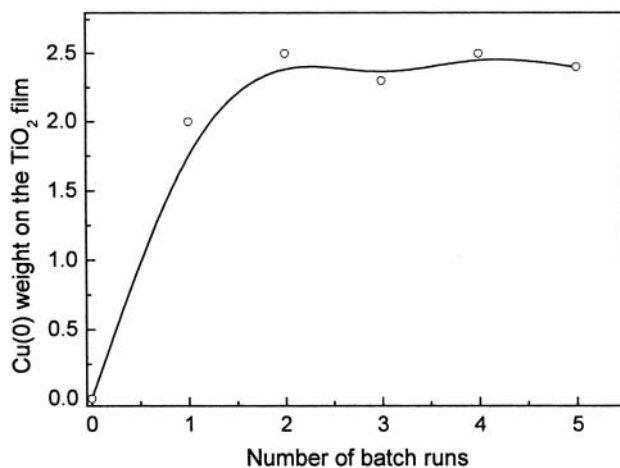


Figure 3. Dependence of Cu(0) weight on the TiO₂ film on the number of batch runs.

increase from 2.0 mg to 2.5 mg and then the Cu(0) weight on the film basically remained a constant, ca. 2.5 mg, no longer increased as the batch run number increased. As a sequence, it was reasonably believed that the decrease in the COD removal efficiency could be attributed to the blocking of UV light by the Cu(0)-deposited layer before the second run. Analogously, the phenomenon of the constant removal efficiency after the second may be also dependent on the nature of Cu(0) photodeposition.

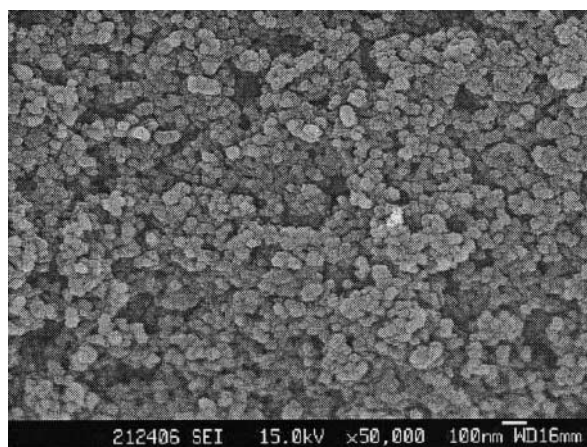
The SEM images of deposited Cu(0) on TiO₂ film in the process of the repeated runs are presented in the Fig. 4. Compared with Figs. 4a and b–d it was found that



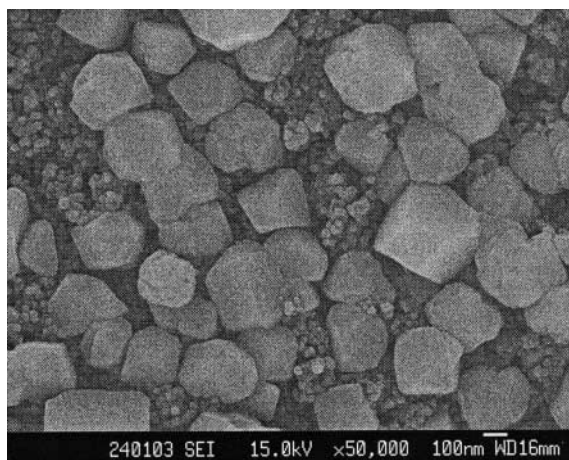
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the surface of TiO_2 film was mostly covered by the deposited $\text{Cu}(0)$ during the first run, but the covered content is not apparently increased and basically remained the similar naked-surface of TiO_2 film after the second run. As a result, it was primarily inferred that the similar naked-surface of the TiO_2 film might associate with the phenomenon of the constant COD removal efficiency. An issue further to be clarified is why the TiO_2 film could not be completely covered by the deposited $\text{Cu}(0)$ in



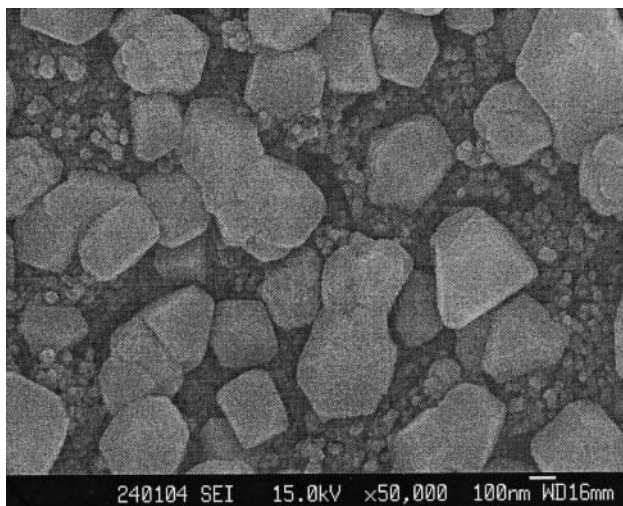
(a)



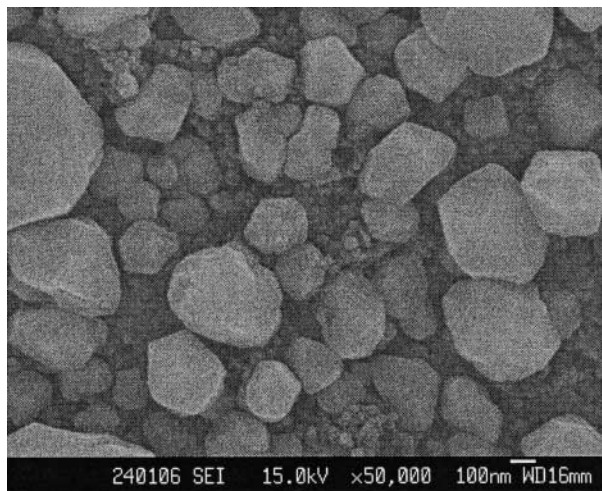
(b)

Figure 4. SEM images of the surface of $\text{Cu}(0)$ -deposited TiO_2 film in the presence of air (a: TiO_2 film prior to reaction; b: after the first run; c: after the second run and d: after the fifth run).

(continued)



(c)



(d)

Figure 4. Continued

the process of the repeated batch runs for the Cu(II)-containing formic acid solution at pH 2.73 in the presence of air.

In the studied photocatalytic reaction system, there are several possible reactions relative to Cu(II) ion. In addition to the photoreduction of Cu(II)



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the deposited Cu(0) may be re-oxidized to dissolvable Cu(II) ions by the following two possible routes. One is the hole-mediated oxidation



the other is air oxidation in some acidic medium



Obviously, the competition between the reactions (1) with (2) or (3) can be regarded, in a sense, to be the competition between the photodeposition and dissolution of the Cu(0). If the photodeposition rate is comparable to the re-dissolution one when the photodeposition proceeds in some extent, the TiO₂ particular film will not be completely covered by the Cu(0).

To clarify which reaction, (2) or (3), is responsible for the re-oxidation dissolution of the photodeposited Cu(II). The TiO₂ film-mediated photocatalytic experiments at another pH value, 4.0, for Cu(II)-containing formic acid solution were also carried out. In these experiments the COD removal efficiency rapidly decreased and finally approached to zero with increasing in the run number in the process of repeated batch runs.^[9] In other words, the phenomenon of constant COD removal efficiency was not observed at this pH value. The fact denotes that the existence of the constant COD removal efficiency is highly dependent on the pH value of reaction medium. However, reaction (2) is not affected by the pH value of reaction medium, as a result, the dissolution of the Cu(0) is possibly contributed to the reaction (3), i.e., air oxidation, not to the reaction (2).

Evidences for the Potential Mechanism**Comparison of the Photocatalytic Process in the Presences of Air or Nitrogen Gas**

Although it was reported that Cu₂O, another possible deposit of Cu(II) photoreduction, is likely to be dissolved in acidic medium via reaction (4)^[16]



the application of the reaction (3), i.e., air oxidation of Cu(0) at acidic condition, to interpreting observations in photocatalytic experiments has not been reported. Although the air oxidation of Cu(0) at acidic condition is thermodynamically feasible, it was unknown whether the reaction is kinetically favorable, in other words, whether the reaction really occurred in the process of the photocatalysis. Accordingly, it is necessary to further confirm the mechanism of the constant COD removal efficiency.

It was expected from the reaction (3) that the phenomenon of the constant COD removal efficiency is heavily dependent on O₂ in air in addition to previously

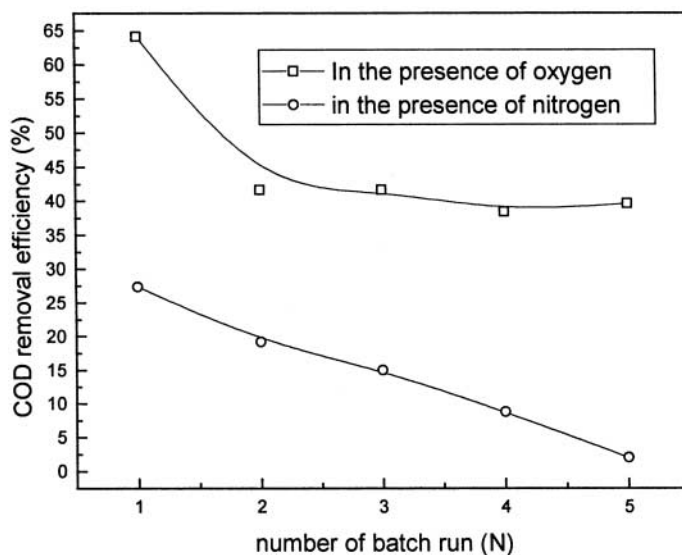


Figure 5. Comparison of the dependences of COD removal efficiency or Cu(0)-deposited amount on reaction time in the presence of nitrogen gas and air.

mentioned pH value of reaction medium. In order to clarify the role of O_2 , a same photocatalytic experiment in the presence of nitrogen gas was carried out. It can be seen from Fig. 5 that the COD removal efficiency in the presence of N_2 decreased linearly with the run number and the phenomenon of the constant COD removal efficiency did not occur. Moreover, the surface of TiO_2 film was basically covered by grand Cu(0) particles and no naked surface of TiO_2 film was observed after 5 time runs, as shown in Fig. 6. Obviously, the fact indicates that the constant COD removal efficiency is considerably associated with the existence of O_2 .

Change of UV-vis Spectra of the Cu^{2+} Solution with the Number of Batch Runs

Dependence of the UV spectra of the Cu (II)-containing formic acid on the number of the batch runs was presented in Fig. 7. It can be seen from the figure that the absorbance of Cu(II) ions, approximately proportional to Cu(0) concentration, has an apparent drop for the first batch run, however, it seems to fluctuate irregularly near the absorbance of the original solution instead of continuing to drop after the second batch run. The irregular fluctuation of Cu(II) concentration may be believed to be a result of the competition between the photodeposition of the Cu(II) ions and the air re-oxidation dissolution of the deposited Cu(0) on the TiO_2 film. In other words, the fluctuation may imply the occurrence of the reaction (3), simultaneous to the proceeding of the reaction (1).

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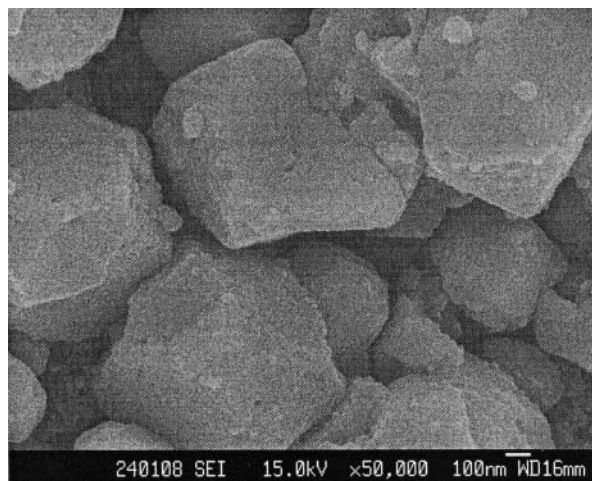


Figure 6. SEM images of the surface of Cu(0)-deposited TiO₂ film after the fifth run in the presence of nitrogen gas.

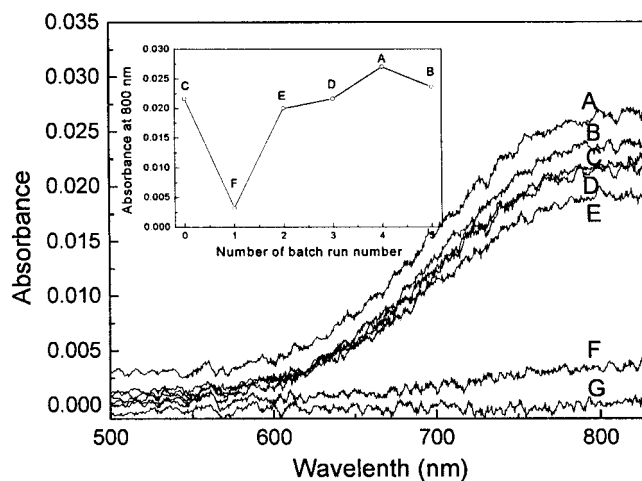


Figure 7. Dependence of UV-vis spectra of Cu²⁺ in the treated solution on the run the number of batch runs (A: after the 4th run; B: after the 5th run; C: initial solution; D: after the 3rd run; E: after 2nd run; F: after 1st; G: after 5th run in the presence of nitrogen gas).

Change of pH Value of Solution with Reaction Time

A similar fluctuation, with respect to pH value of the solution, was also observed in the photocatalytic process. As shown in Fig. 8, although the pH value has a considerable decrease, from 2.73 to 2.52, during the first batch run, it seems to

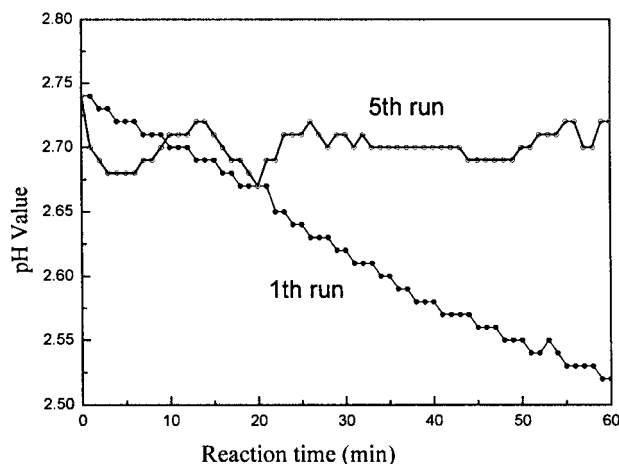
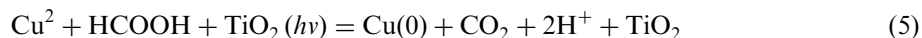


Figure 8. Change of pH value in the process of the photocatalytic reaction.

fluctuate about 2.69 during the fifth batch run. The pH fluctuation may be interpreted in the term of the competition between the reaction (3) and the following photocatalytic redox process:



The two reactions were believed to be the principle processes related to H^+ ions during the photocatalytic reaction, of course, they are not merely the two reactions due to the complexity of the photocatalytic process. Because the reaction (3) and (5) is a process of consuming and generating H^+ , respectively, if the rate of the two reactions is not changeable during the photocatalytic reaction, the pH value of the solution will appear rising at one moment and dropping at another moment, i.e., fluctuation. Accordingly, the result in Fig. 8 is regarded as another evidence for the occurrence of the reaction (3) during the photocatalytic reaction.

Change of Photocurrent with Reaction Time at Various Conditions

The photocurrent-time profiles under various experimental conditions are presented in Figs. 9a and b. Compared with curve A and B in Fig. 9a, it was found that the photocurrent enhancement effect of formic acid was apparently decreased for the first run in the presence of Cu(II), in particular, after the second batch run the photocurrent dropped to about 10^{-8} A, about 100 times less than that for the first run, as shown in the curve B of Fig. 9a and curve A of Fig. 9b. In the above studied range, it is believed that there are two factors that lead to the decrease of the photocurrent. One is the blocking of UV light by the deposited Cu(0) on the TiO_2 film; another is the trapping of the photogenerated electron by Cu(II) due to the occurrence of reaction (1). The former will result in a negative effect on the COD removal efficiency if most of the TiO_2 film was covered while the latter, in general,



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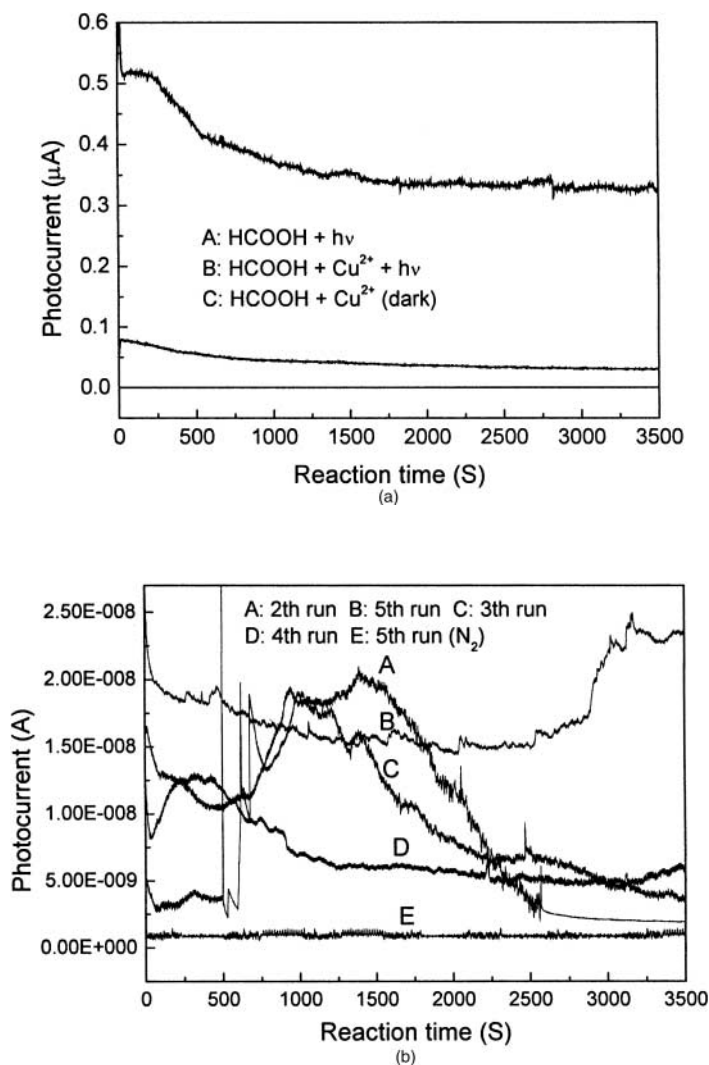


Figure 9. Change of photocurrent with reaction time in various conditions.

partly prevents the recombination of photogenerated electron and hole, followed by an increase COD removal efficiency. In the view of the two facts, it was not certain whether the decrease in photocurrent for the first batch run was mainly attributed to the former or the latter but the blocking of deposited Cu(0) from UV light should be responsible for such a low photocurrent after the second batch run.

It was worth noting that the photocurrent did not continue to drop to zero as the situation without radiation, but fluctuating at ca. 10^{-8} A in the process of the repeated batch runs, as shown in Fig. 9b. Although the fluctuation is not rather regular like wave, it is apparently different from the situation in the presence of nitrogen (curve E in Fig. 9b), in which the photocurrent is close to zero for



the fifth run. The above photocurrent fluctuation in the presence of air is consistent with the previously mentioned mechanism of the constant COD removal efficiency, that is, the Cu(0) deposition layer is in the competition of the Cu(II) photodeposition with re-dissolution via air oxidation, leading to the uncertainty of the covered area, followed by the photocurrent fluctuant. In other words, the photocurrent fluctuation can be regarded as another evidence for the proposed mechanism to explain the phenomenon of the constant COD removal efficiency.

CONCLUSIONS

Despite several numbers of studies were carried out on these TiO₂-Cu(II)-formic acid photocatalytic systems, many aspects with regards to the role of the metal ions in the photocatalytic reactions remain unclear still.^[16] In this work, the unexpected observation, i.e., the phenomenon of the constant COD removal efficiency in the process of successive batch runs can be regarded as an example in these unclear issues. Although several facts support our assumption that the phenomenon of the constant COD removal efficiency is associated with the competition between the photodeposition of Cu(II) and the Cu(0) re-dissolution due to air oxidation at various conditions, the complete confirmation of the assumption needs to wait for further investigations. Interestingly, another issue relative to the unexpected observation has attracted our attention, that is, how to employ the cycle of Cu(II) photodeposition and Cu(0) re-dissolution to trap the photogenerated electron and increase the photocatalytic efficiency.

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