Photocatalytic degradation of dodecyl-benzenesulfonate over TiO_2–Cu_2O under visible irradiation

Chenghui Han [a,b], Zhiyu Li [b], Jianyi Shen [a,*]

[a] Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, PR China
[b] Jiangsu Radio & Television University, Nanjing 210036, PR China

ARTICLE INFO

ABSTRACT

A series of TiO_2–Cu_2O mixed oxides were prepared by the hydrolysis of titanium butoxide and reduction of copper acetate with hydrazine. These composite oxides were characterized by X-ray diffraction (XRD), inductively coupled plasma spectrometry (ICP), high-resolution transmission electron microscopy (HRTEM), N_2 adsorption and UV–vis techniques. Photocatalytic degradation of dodecyl-benzenesulfonate (DBS) under visible irradiation was performed, and effects of composition of catalysts and reaction conditions were studied. It was observed that TiO_2–Cu_2O composite oxides exhibited better photocatalytic activity than Cu_2O or TiO_2 alone. Among these composite oxides, the 5%TiO_2–Cu_2O displayed the highest activity, and the degradation percentage of DBS and COD reached 97.3% and 65%, respectively. In addition, it was found that the decomposition of DBS followed the first-order kinetics and the adsorption of DBS followed the Langmuir model. Oxygen in solution played a vital role in the elimination of COD.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Surfactants are widely used in domestic and industrial processes. After use, surfactants are usually discharged along with waste water, which cause serious ecological pollution since their biodegradation and bioelimination through bacteria are slow [1]. Although biological treatment is a facile route to decontaminate surfactants, there are such problems as enhanced foam formation, decreased activity of the active sludge and retarded biodegradation of the accompanying pollutants [2]. Photocatalytic oxidation is an advanced oxidation process (AOP) to solve these problems as mentioned above. This AOP process has received extensive attention in the field of organism containing waste water treatment, since this technique decomposes many toxic materials without reproducing pollutants. Dodecyl-benzenesulfonate (DBS) is an important surfactant frequently used in industry, and therefore it is an important polluting agent. The frequently used photocatalysts were TiO_2 [3–9] and TiO_2 containing composite oxides [10,11] since Hidaka firstly introduced TiO_2 to degrade DBS [3]. Due to the wide band gap, the application of TiO_2 might be limited only to the violet light range. Therefore, the effective use of solar energy is limited. In order to increase the effective use of solar energy, modified TiO_2 were usually adopted. Chatterjee and Mahata [12] observed that 60% DBS (0.04 mmol) could be degraded under irradiation of visible light for 5 h over the TiO_2 modified by a dye.

In 1998, Hara et al. [13] discovered that Cu_2O powder could catalyze the decomposition of water into H_2 and O_2 under solar light, in which Cu_2O exhibited good catalytic performance and stability. Since the band gap potential of Cu_2O is only 2.0 eV, electrons at band gap are easily excitated under visible light irradiation. However, it is disadvantageous that the easy recombination of electron and hole results in low catalytic activity of Cu_2O. In order to control the rate of recombination, the composites of semiconductor materials possessing different band gaps were prepared and found to be able to suppress the electron–hole recombination, resulting in the better catalytic performance. Senevirathna et al. [14] deposited quantum sized Cu_2O on the nano-particles of TiO_2 to produce the catalyst TiO_2–Cu_2O and found that this composite system photogenerated hydrogen from water and methanol under visible light. Since Cu_2O content in this composite system was low, the reaction was still faster under the irradiation of violet light than that of visible light. Bessekhouad et al. [15] also observed the Cu_2O–TiO_2 composite oxides via the mixture of Cu_2O (particle size < 5 μm) with commercial P25 TiO_2 exhibited a superior activity for the degradation of Orange II under visible irradiation than Cu_2O alone. These results seemed to suggest the following process: the electrons and holes generated on Cu_2O by visible irradiation were transferred to TiO_2 so that the recombination of electron–hole (e–h) pairs was suppressed and thus the quantum efficiency was enhanced.

In this work, we prepared the TiO_2–Cu_2O composite oxides by the hydrolysis of titanium butoxide and the reduction of copper acetate with hydrazine, in an attempt to catalyze the decomposition of DBS under solar energy. These composite oxides were characterized by X-ray diffraction (XRD), inductively coupled plasma

spectrometry (ICP), N_2 adsorption, high-resolution transmission electron microscopy (HRTEM) and UV–vis spectrum. Using tungsten lamp as a light source, photocatalytic degradation of DBS was performed over these composite oxides. The effects of catalysts composition and oxygen in solution on the degradation of DBS were investigated. In addition to these aspects, photocatalytic kinetics and adsorption of DBS on composite oxides were also studied and the corresponding reaction mechanisms were discussed.

2. Experimental

2.1. The preparation of TiO_2–Cu_2O

TiO_2–Cu_2O composite oxides were prepared by the following method. 12 g of cupric acetate (AR) was dissolved in 600 ml of distilled water, followed by the addition of 3.2 ml of PEG-400 (AR) under vigorous stirring. Afterward, 0.5374 g of tetrabutyl titanate (AR) digested with absolute ethanol was dropped into the solution of cupric acetate. A white precipitate was produced during the mixing. Then, 5 ml of 5 mol/L NaOH and 15 ml of 5 mol/L hydrazine were dropped sequentially into the above slurry under vigorous stirring, and the resulting mixture was kept standing at 12–14 °C for 15 min. A yellow precipitate was then formed. It was filtered, washed with distilled water to neutral and further washed with acetone. The sample was then degassed at 200 °C in vacuum for 3 h. A series of TiO_2–Cu_2O composite oxides were prepared in this way with different molar ratios of TiO_2/Cu_2O. The sample contained 5 mol% TiO_2 was labeled as 5%TiO_2–Cu_2O.

2.2. Characterizations

The surface areas (S_{BET}) of samples were determined by N_2 adsorption at the temperature of liquid N_2 employing the BET method using a Micromeritics ASAP 2020. Before each measurement, the sample (0.2–0.3 g) was degassed at 150 °C for 2 h.

XRD was performed on a Rigaku D/Max-RA X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15418 nm). The applied voltage and current were 40 kV and 40 mA, respectively. The scanning rate was 10°/min.

HRTEM images were obtained by a JEOL JEM 2100 electron microscope with an accelerating voltage of 200 kV.

UV–vis diffuse reflectance spectra were obtained by UV–vis spectrophotometer equipped with an integrated sphere (TU-1901, China). $BaSO_4$ was used as a reference for the measurements.

ICP was obtained by IRIS Intrepid Inductively Coupled Plasma spectrometer (Thermo Elemental Co., America).

2.3. Photocatalytic reaction

A dispersion consisting of the 100 mg/L DBS solution (200 ml) and 0.2 g of each catalyst was contained in a glass vessel at 25 °C and was illuminated with a 250 W tungsten lamp (visible irradiation). Magnetic stirring was kept all along with the reaction. In some cases, COD analyses were carried out according to the dichromate method. The concentration of DBS was monitored with a TU-1901 UV-Vis spectrophotometer at λ_{max} = 224 nm (UV absorption of the aromatic group) [9].

2.4. Adsorption of DBS on the TiO_2–Cu_2O

The suspensions of DBS (50 ml, at different initial concentrations) and TiO_2–Cu_2O (0.050 g) were contained in 100 ml conical flasks with plug and were allowed to equilibrate for 24 h in the

dark under constant stirring at 25 °C. The amounts of DBS adsorbed on TiO_2–Cu_2O were calculated according to the initial and final concentrations of DBS in the solutions:

$$\Gamma = \frac{(C_0 - C) \times 50}{1000 \times m} \tag{1}$$

where Γ (mg/g) is the adsorption capacity, C_0 and C (mg/L) are the initial and equilibrium concentrations of DBS, m (g) is the mass of TiO_2–Cu_2O used.

3. Results and discussion

3.1. Characterization of catalyst

XRD patterns of the samples Cu_2O, 5%TiO_2–Cu_2O and TiO_2 are presented in Fig. 1. It is seen that pure Cu_2O was prepared according to JCPDS-78-2076, and no peaks due to Cu and CuO were detected. The sample of TiO_2 exhibited pure anatase structure (JCPDS-21-1272). No diffraction peaks belonging to TiO_2 were observed for the sample 5%TiO_2–Cu_2O, indicating the high dispersion of TiO_2 on Cu_2O, since only diffraction peaks of Cu_2O were present for the sample.

Fig. 2 shows the TEM and HRTEM images for the 5%TiO_2–Cu_2O. Spherical particles could be clearly seen for the 5%TiO_2–Cu_2O, with the size of approximately 40 nm. The lattice distance was measured to be 0.246 nm according to the HRTEM image, which could be undoubtedly assigned to the lattice facet of Cu_2O (1 1 1). Some amorphous phases covered the Cu_2O lattice, which might be dispersed TiO_2 on Cu_2O.

The UV–vis diffuse reflectance spectra of Cu_2O, 5%TiO_2–Cu_2O and TiO_2 are displayed in Fig. 3. It is clear that the Cu_2O and TiO_2–Cu_2O could be excited by visible light with the wavelength around 610 nm, whereas TiO_2 exhibited the absorption at 388 nm, belonging to the ultraviolet light range.

Table 1 lists the compositions and surface areas of the samples. It is seen that the analyzed contents of TiO_2 in the samples were close to those desired. The surface area did not seem to change for
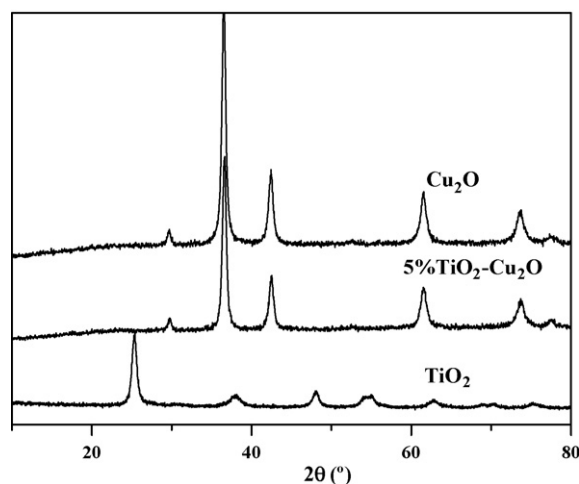

Fig. 1. XRD patterns of Cu_2O, 5%TiO_2–Cu_2O and TiO_2.

Table 1
Surface area and composition of TiO_2–Cu_2O.

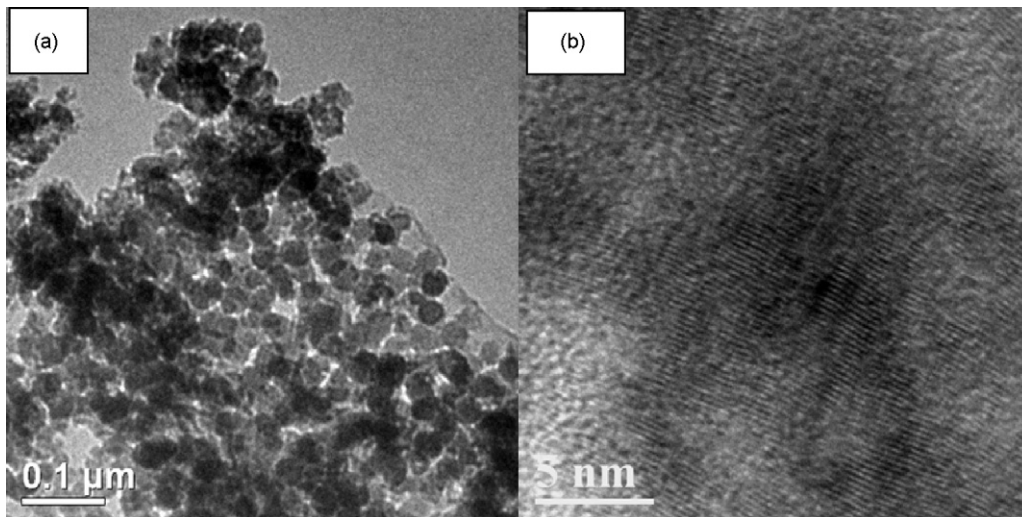| Sample	Cu_2O	Molar percentage of TiO_2 in TiO_2–Cu_2O					TiO_2
		2%	5%	10%	30%	50%	
S_{BET} (m²/g)	31	30	29	35	48	64	105
TiO_2 (ICP)		2.0	5.2	10.3	30.2	51.0	

Fig. 2. TEM (a) and HRTEM (b) images of the 5%TiO$_2$–Cu$_2$O.

the samples with the content of TiO$_2$ less than 5%. But addition of more TiO$_2$ increased the surface area apparently.

3.2. Photocatalytic degradation of DBS as a function of composition of TiO$_2$–Cu$_2$O

Fig. 4 displays the photodegradation degree of DBS over the TiO$_2$–Cu$_2$O with different TiO$_2$ contents under visible light. It is clearly seen that the Cu$_2$O was much more effective than TiO$_2$ for the degradation of DBS under the visible irradiation owing to the narrower band gap of Cu$_2$O than that of TiO$_2$. More interestingly, the TiO$_2$–Cu$_2$O composite oxides exhibited higher activity than Cu$_2$O for the photocatalytic degradation of DBS. Among the TiO$_2$–Cu$_2$O photocatalysts studied, the one containing 5%TiO$_2$ showed the highest photocatalytic activity. About 66% of DBS were degraded over the Cu$_2$O while the degradation rate of DBS was as high as 97% over the 5%TiO$_2$–Cu$_2$O, although the two samples possessed similar surface areas. Therefore, the higher photocatalytic activity could be ascribed to the synergic effect between TiO$_2$ and Cu$_2$O. That is, the e–h pairs generated in Cu$_2$O upon the visible irradiation were quickly transferred to TiO$_2$, where the recombination of e–h pairs were slowed down owing to the wide band gap of TiO$_2$, leading to the higher quantum efficiency and hence the improved photocatalytic activity.
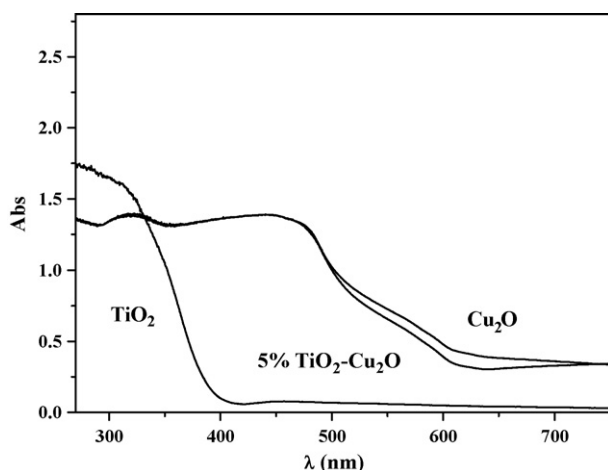
3.3. Photocatalytic kinetics

Fig. 5 shows the variation of DBS concentration versus time over the 5%TiO$_2$–Cu$_2$O. It is seen that no degradation of DBS occurred without the presence of a catalyst. On the other hand, the concentration of DBS decreased continuously with the reaction time when 1 g/L of the 5%TiO$_2$–Cu$_2$O was added. The linear relationship of $\ln(C/C_0)$ with respect to the irradiation time suggested the first-order kinetics. The rate constant was found to be 0.0371 min^{-1}.

It is generally accepted that the photocatalytic kinetics follows the Langmuir–Hinshelwood (L–H) model, as expressed below:

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{kK_b} \times \frac{1}{C} \tag{2}$$

where k denotes the apparent rate constant for the process, K_b is the adsorption coefficient of reactants, and C is the concentration of the substance to be degraded. When the initial concentration C_0 is used in Eq. (2), the reaction rate would be the initial rate r_0. Eq. (2) indicates a linear relationship between $1/r_0$ and $1/C_0$. Fig. 6 represents such linear correlation with different initial concentrations, indicating that the photocatalytic reaction did follow the L–H model.
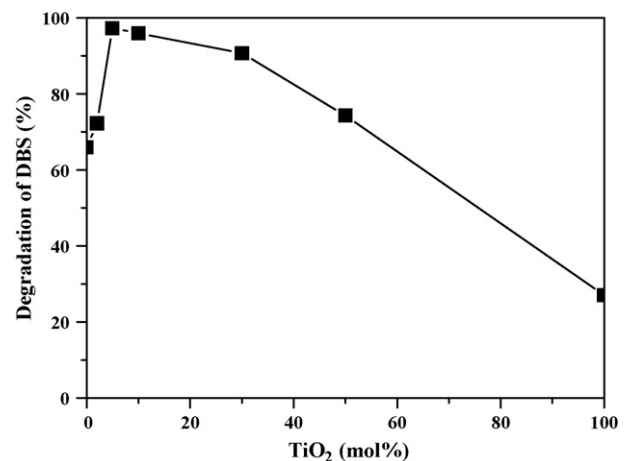

Fig. 3. UV–vis diffuse reflectance spectra of Cu$_2$O, 5%TiO$_2$–Cu$_2$O and TiO$_2$.

Fig. 4. Photocatalytic degradation of DBS as a function of composition of TiO$_2$–Cu$_2$O under 250 W tungsten lamp (visible irradiation). Initial concentration of DBS: 100 mg/L; catalyst loading: 1.0 g/L; pH 7.0; t = 1 h.
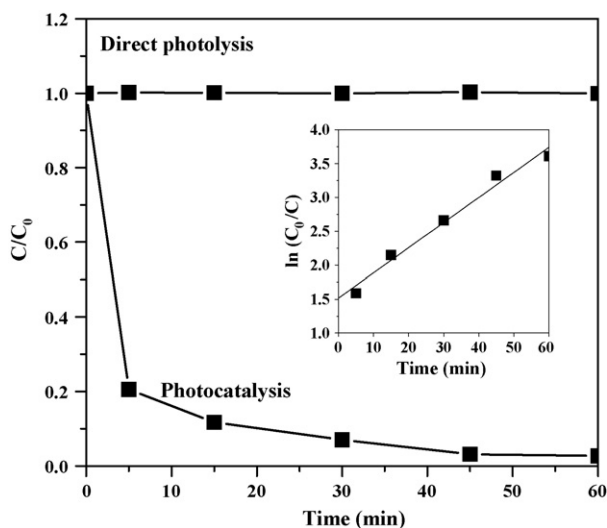
Fig. 5. Photocatalytic degradation of DBS over the 5%TiO$_2$–Cu$_2$O. The inset shows the apparent first-order kinetics for the corresponding photocatalytic reaction. Initial concentration of DBS: 100 mg/L; catalyst loading: 1.0 g/L; pH 7.0.

3.4. Adsorption of DBS on TiO$_2$–Cu$_2$O

Adsorption plays a key role in most photocatalytic reactions [16,17]. Fig. 7 depicts an adsorption isotherm of DBS on the 5%TiO$_2$–Cu$_2$O at 25 °C in dark. The isotherm follows the Langmuir model, and the saturation coverage was found to be 58 mg/g.

3.5. Effect of oxygen in solution

In order to see the effect of O$_2$ on the photocatalytic degradation of DBS, gases of N$_2$ or air was bubbled in the solution during the reaction over the 5%TiO$_2$–Cu$_2$O. Fig. 8 shows the degree of degradation of DBS and the reduction of COD with and without the presence of O$_2$. Since the degradation was measured according to the change of concentration of DBS with a light at 224 nm, which was actually the absorbance of benzyl ring in DBS, it reflected the degree of aromatic ring opening in DBS during the photocatalytic reaction. It was not the indication of complete mineralization of DBS. On the other hand, the reduction of COD represented the percentage of DBS that was completely mineralized.

Fig. 8 shows that the photocatalytic degradation of DBS over the 5%TiO$_2$–Cu$_2$O was much higher in air than in N$_2$. Although more than 80% of DBS could be photocatalytically degraded over the
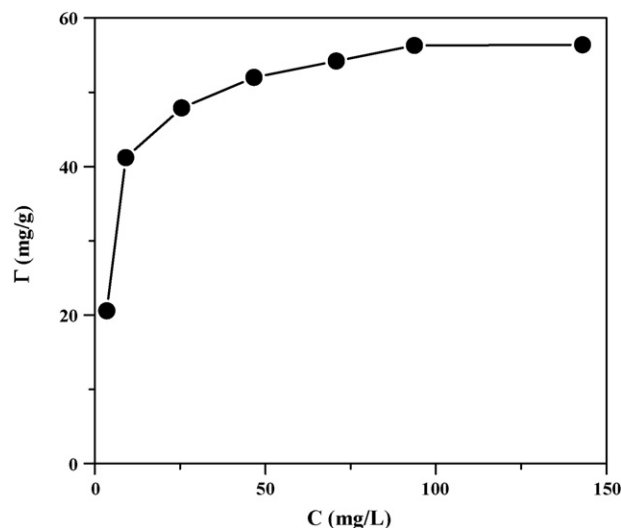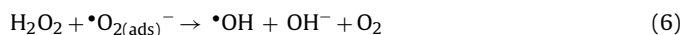

Fig. 7. Adsorption isotherm of DBS on the 5%TiO$_2$–Cu$_2$O at 25 °C in dark.

5%TiO$_2$–Cu$_2$O in N$_2$ (benzyl ring opened), the reduction of COD was only less than 15% (mineralization was far from completion). With the presence of O$_2$, the reduction of COD was greatly increased. The reduction of COD could reach 65% in 1 h in the photocatalytic reaction of DBS over the 5%TiO$_2$–Cu$_2$O in air. It has been reported that the following reactions hardly occur without the presence of oxygen [18,19]:

$$e_{cb}^- + O_{2(ads)} \rightarrow {}^\bullet O_{2(ads)}^- \tag{3}$$

$${}^\bullet O_{2(ads)}^- + H^+ \rightarrow HO_2{}^\bullet \tag{4}$$

$$2HO_2{}^\bullet \rightarrow O_2 + H_2O_2 \tag{5}$$

$$H_2O_2 + {}^\bullet O_{2(ads)}^- \rightarrow {}^\bullet OH + OH^- + O_2 \tag{6}$$

$$H_2O_2 + e^- \rightarrow OH^- + {}^\bullet OH \tag{7}$$

The electrode potential of cavity h$^+$ in Cu$_2$O is 0.46 eV at pH 7.0, and OH$^-$ cannot be directly oxidized to the free radical $^\bullet$OH [15]. Accordingly, little $^\bullet$OH were produced under N$_2$ atmosphere, and only the cavity h$^+$ acted as the oxidizing sites for adsorbed DBS, leading to the benzyl ring opening of DBS without the complete degradation. That might be the reason why the reduction of COD was low under N$_2$ atmosphere. On the other hand, the presence of oxygen ensured the process of steps (3)–(7), leading to the formation of strong oxidative sites $^\bullet$OH, which played the function of
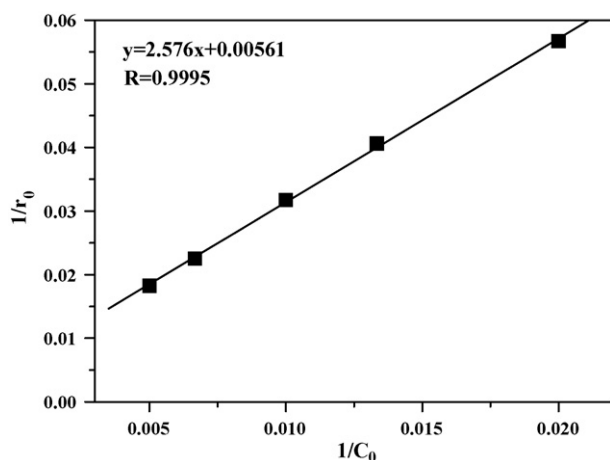

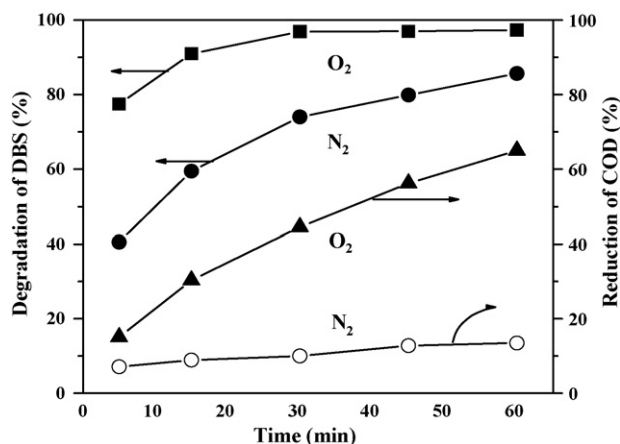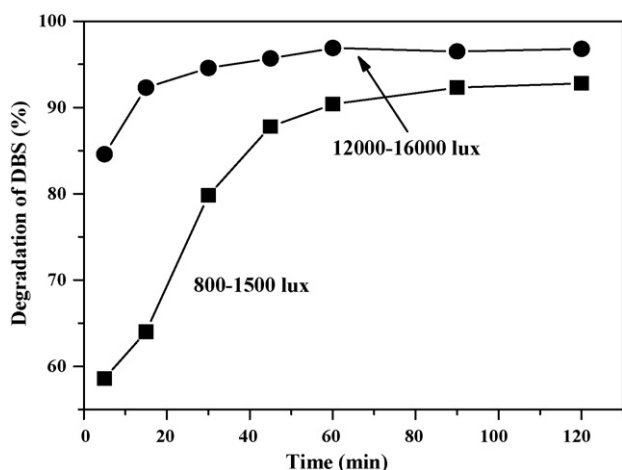**Fig. 6.** The linear correlation of 1/r_0 versus 1/C_0.

Fig. 8. Photocatalytic degradation of DBS over the 5%TiO$_2$–Cu$_2$O with the presence of O$_2$ or N$_2$. Initial concentration of DBS: 100 mg/L; catalyst loading: 1.0 g/L; pH 7.0.

Fig. 9. Photocatalytic degradation of DBS over the 5%TiO$_2$–Cu$_2$O under solar light irradiation. Initial concentration of DBS: 100 mg/L; catalyst loading: 1.0 g/L; pH 7.0.

complete degradation of DBS, resulting in the remarkable reduction of COD.

3.6. Degradation of DBS under solar light

The 5%TiO$_2$–Cu$_2$O catalyst was tested for the photocatalytic degradation of DBS under natural solar light. The results are shown in Fig. 9. It is seen that DBS could be effectively degraded over the 5%TiO$_2$–Cu$_2$O under natural solar light. In addition, the rate of degradation of DBS was increased with the increase of intensity of the solar light. At the intensities of 12,000–16,000 lx of natural light, more than 95% of DBS could be degraded in 1 h.

4. Conclusions

A series of TiO$_2$–Cu$_2$O were prepared by the hydrolysis of titanium butoxide and reduction of copper acetate with hydrazine. The formation of composite oxides TiO$_2$–Cu$_2$O significantly enhanced the photocatalytic activity for the degradation of DBS under visible lights, especially with the one containing 5 mol% of TiO$_2$. The synergetic effect between Cu$_2$O and TiO$_2$ could be explained by the conventional principle, i.e., the e–h pairs generated by visible lights in Cu$_2$O (with narrow band gap) could be rapidly transferred into TiO$_2$ (with wide band gap) so that the direct recombination of e–h pairs could be slowed down. As a result, the increase of life time of e–h pairs improved the photocatalytic activity for the degradation of DBS under visible lights.

Oxygen was found to play an important role for the degradation of DBS over the 5%TiO$_2$–Cu$_2$O under visible irradiation. Without the presence of O$_2$, photo-holes produced in Cu$_2$O did not seem to oxidize OH$^-$ to the free radical $^\bullet$OH. In this case, the degradation of DBS mainly involved the benzyl ring opening without the significant reduction of COD. In contrast, the presence of O$_2$ promoted the formation of $^\bullet$OH free radicals and thus the complete oxidation of DBS with a significant reduction of COD.

The photocatalytic degradation of DBS over the 5%TiO$_2$–Cu$_2$O under visible irradiation was found to follow the Langmuir–Hinshelwood model, in which the adsorption of DBS was an important step in the photocatalytic kinetics. A Langmuir isotherm was obtained for the adsorption of DBS over the 5%TiO$_2$–Cu$_2$O in dark, with the saturation uptake of 58 mg/g. Such high adsorption uptake of DBS on the catalyst might be an important factor in determining the photocatalytic activity.

References

[1] H. Hidaka, H. Kubota, M. Grätzel, E. Pelizzetti, N. Serpone, Photodegradation of surfactants. II. Degradation of sodium dodecylbenzene sulphonate catalysed by titanium dioxide particles, J. Photochem. 35 (1986) 219–230.
[2] A.M. Amat, A. Arques, M.A. Miranda, S. Seguí, Photo-Fenton reaction for the abatement of commercial surfactants in a solar pilot plant, Solar Energy 77 (2004) 559–566.
[3] H. Hidaka, H. Kubota, M. Gratzel, N. Serpone, E. Pelizzetti, Photodegradation of surfactants. I. Degradation of sodium dodecylbenzenesulfonate in aqueous semiconductor dispersions, Nouveau J. Chim. 9 (1985) 67–69.
[4] J. Zhang, H. Hidaka, Photodegradation of surfactants. 11. ζ-potential measurements in the photocatalytic oxidation of surfactants in aqueous TiO$_2$ dispersions, Langmuir 9 (1993) 1646–1650.
[5] N.N. Rao, S. Dube, Photocatalytic degradation of mixed surfactants and some commercial soap/detergent products using suspended TiO$_2$ catalysts, J. Mol. Catal. A: Chem. 104 (1996) 197–199.
[6] H. Hidaka, K. Ajisaka, S. Horikoshi, T. Oyamab, K. Takeuchi, J. Zhao, N. Serpone, Comparative assessment of the efficiency of TiO$_2$/OTE thin film electrodes fabricated by three deposition methods photoelectrochemical degradation of the DBS anionic surfactant, J. Photochem. Photobiol. A: Chem. 138 (2001) 185–192.
[7] R. Zhang, L. Gao, Q. Zhang, Photodegradation of surfactants on the nanosized TiO$_2$ prepared by hydrolysis of the alkoxide titanium, Chemosphere 54 (2004) 405–411.
[8] A.E. Jiménez, C.A. Estrada, A.D. Cota, A. Romaán, Photocatalytic degradation of DBSNa using solar energy, Solar Energy Mater. Solar Cells 60 (2000) 85–95.
[9] T. Zhang, T. Oyama, S. Horikoshi, J. Zhao, N. Serpone, H. Hidaka, Photocatalytic decomposition of the sodium dodecylbenzene sulfonate surfactant in aqueous titania suspensions exposed to highly concentrated solar radiation and effects of additives, Appl. Catal. B: Environ. 42 (2003) 13–24.
[10] S. Dube, N.N. Rao, Rate parameter independence on the organic reactant: a study of adsorption and photocatalytic oxidation of surfactants using MO$_3$-TiO$_2$ (M = Mo or W) catalysts, J. Photochem. Photobiol. A: Chem. 93 (1996) 71–77.
[11] H. Zhang, X. Quan, S. Chen, H. Zhao, Y. Zhao, The removal of sodium dodecylbenzene sulfonate surfactant from water using silica/titania nanorods/nanotubes composite membrane with photocatalytic capability, Appl. Surf. Sci. 252 (2006) 8598–8604.
[12] D. Chatterjee, A. Mahata, Visible light induced photodegradation of organic pollutants on dye adsorbed TiO$_2$ surface, J. Photochem. Photobiol. A: Chem. 153 (2002) 199–204.
[13] M. Hara, T. Kondo, M. Komoda, S. Ikeda, K. Shinohara, A. Tanaka, J.N. Kondo, K. Domen, Cu$_2$O as a photocatalyst for overall water splitting under visible light irradiation, Chem. Commun. 3 (1998) 357–358.
[14] M.K.I. Senevirathna, P.K.D.D.P. Pitigala, K. Tennakone, Water photoreduction with Cu$_2$O quantum dots on TiO$_2$ nano-particles, J. Photochem. Photobiol. A: Chem. 171 (2005) 257–259.
[15] Y. Bessekhouad, D. Robert, J.V. Weber, Photocatalytic activity of Cu$_2$O/TiO$_2$, Bi$_2$O$_3$/TiO$_2$ and ZnMn$_2$O$_4$/TiO$_2$ heterojunctions, Catal. Today 101 (2005) 315–321.
[16] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, TiO$_2$-assisted photodegradation of dye pollutants. II. Adsorption and degradation kinetics of eosin in TiO$_2$ dispersions under visible light irradiation, Appl. Catal. B: Environ. 15 (1998) 147–156.
[17] S. Kutsuna, M. Toma, K. Takeuchi, A. Ibusuki, Photocatalytic degradation of some methyl perfluoroalkyl ethers on TiO$_2$ particles in air: the dependence on the dark-adsorption, the products, and the implication for a possible tropospheric sink, Environ. Sci. Technol. 33 (1999) 1071–1076.
[18] Y. Chen, Z. Sun, Y. Yang, Q. Ke, Heterogeneous photocatalytic oxidation of polyvinyl alcohol in water, J. Photochem. Photobiol. A 142 (2001) 85–89.
[19] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, Appl. Catal. B: Environ. 31 (2001) 145–157.