

Copper modified TiO₂ catalysts: application to nitrobenzenes degradation

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Abstract. Copper doped TiO₂ by the method of sol-gel preparation was conducted to stimulate the TiO₂ visible light response and enhance the performance of photocatalytic degradation. By XRD, SEM and EDS analysis, molar ratio of 1.0%, 1.5%, 2.0% and 1.0% Cu doped TiO₂ presented smaller grain sizes (20-50 nm) than German P25 TiO₂ (50-100 nm). Especially, 1.5% Cu doped TiO₂ presented the highest and finest degree of crystallinity from XRD peak. Its reunion phenomenon was the weakest among all Cu doped TiO₂. Combined with Cu doping structure, micro stress changes as well as the performance of the degradation of nitrobenzenes (NBs), the optimum mol ratio of Cu doped TiO₂ was 1.5%. With 1.5% Cu doped TiO₂ for 180 min UV light degradation of NBs, the removal efficiency was 60.02%, two times higher than that of Germany P25 TiO₂. The reaction of NBs photocatalytic degradation by Cu_xTi_(1-x)O₂ followed first order kinetics. Synthetically, SEM, ESD and performances of NBs degradation confirmed that the optimal formula of Cu_xTi_(1-x)O₂ for degradation of NBs was Cu_{0.0183}Ti_{0.9817}O₂.

1. Introduction

Metal ions such as Cu, Fe, Ag, etc., doped into the surface of TiO₂ catalyst is one of the most promising methods to produce important influence on the photochemical properties of the catalysts [1]. This method can narrow the band gap to stimulate the visible light catalytic response [2]. This phenomenon is due to that the light irradiation between metal nanoparticles and TiO₂ cause Fermi energy balance by the charge transfer [2,3].

Fermi level of the metal nanoparticles is lower than that of TiO₂ catalyst. Therefore, the electronics of excited states in TiO₂ can shift from its conduction band to metal nanoparticles. Thus the metal nanoparticles become the favourable electron trap, contributing to the electronic-hole separation and effectively promote the photocatalytic reaction [3].

Compared with precious metals, copper has obvious economic advantage. Therefore Cu modification of photocatalyst has been the hotspot in research and application in materials, chemical industry and environment improvement [1,3]. Nitrobenzene (NBs) is a typical

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refractory poisonous and harmful organic pollutants, wide occurrence in the environment [4]. Though researches on the Cu doped TiO₂ were conducted for years [5], yet the optimal amount of copper doped into TiO₂ and the performance of nitrobenzene degradation need to be further studied.

This study aims to investigate the Cu modification of TiO₂ to increase its visible light response, in order to enhance the performance of photocatalytic degradation of NBs. The optimal amount of Cu doped for TiO₂ was determined by characterization of the physical and chemical properties of Cu_xTi_(1-x)O₂.

2. Materials and Methods

Synthesis of Cu_xTi_(1-x)O₂. Cu modified TiO₂ catalysts were synthesized using the method of sol-gel preparation. Solution A was got by the preparation of 20.0 mL tetrabutyl titanate solved in 60.0 mL anhydrous ethanol, with blending on medium-high speed about 10 minutes. Cu(NO₃)₂ powders with 27.8 mg, 41.7 mg, 55.6 mg and 69.5 mg respectively, were dissolved in 40.0 mL distilled water (i.e., 1.0%, 1.5%, 2.0%, and 1.0% mol ratio of Cu to TiO₂). Then the solution was mixed with 40.0 mL anhydrous ethanol and 8 mL concentrated nitric acid with blending on medium-high speed about 15 min, producing the solution B. Moreover, the solution S was achieved by mixing the solution A with the solution B on rate of 3 mL/min for 30 min. Sol was formed after the solution S was heated in the water bath at 80 °C for 2 h and standing for 10 hours. The aged sol S was put in freeze drying machine (at 13.3 Pa and -52 °C) for 24 h. The informal Cu-TiO₂ was then grinded and weighed. Finally, the informal Cu-TiO₂ was put in muffle furnace for calcination with periodic heating way: at constant temperature for 0.15 hour, 300 °C for 0.15 h, 350 °C for 1 h and 400 °C for 1 h.

Characterization of the photocatalysts. Shapes, particle sizes and compositions of Cu-TiO₂ particles were determined by a scanning electron microscope (SEM) with energy disperse spectroscopy (EDS) at 15 kV (XGT-1000WR HORIBA, Japan). Phase identification of the structures were measured by X-ray diffraction (XRD) (Shimadzu XD-D1, Japan) at 40 kV and 300 mA, equipped with a graphite monochromator which produced Cu K_α radiation at wavelength 1.54 Å.

Photoreactor and photocatalytic reaction. The initial NBs concentration was 120 mg/L in all experiments. NBs degradation experiments were conducted using a 500 mL inner glass carried in a box. The photoreactor was composed of a light reaction device, the box body and a controller. Wavelength light with 365 nm source was adopted from a 250 W high pressure mercury lamp (Jinyuan, China). The cooling temperature was controlled by a cold trap with water circulation. German Degussa P25 TiO₂ was used for a contrast test. All catalysts experiments were conducted using the same catalyst dosage of 1 g/L addition into 400 mL NBs solution. All samples were filled with 0.22 μm membranes (Millex GS, Millipore). Performance liquid chromatography (Agilent 1200 HPLC, USA) was used to detect the concentration of the NBs.

3. Results and Discussion

XRD and SEM for Cu_xTi_(1-x)O₂. Fig. 1 (a-f) showed the XRD and SEM images for the 1.0%, 2.0%, 1.5% and 2.5% Cu doped TiO₂. Significance of peak shape of the preparation of Cu doped TiO₂ appeared in positions of 101 (0.352), 004 (0.2382), 200 (0.1896), 105/211 (0.1698), 204, 166/220 and 215 from the XRD. Obviously, the prepared catalytic crystals are the sharp titanium type TiO₂ [6].

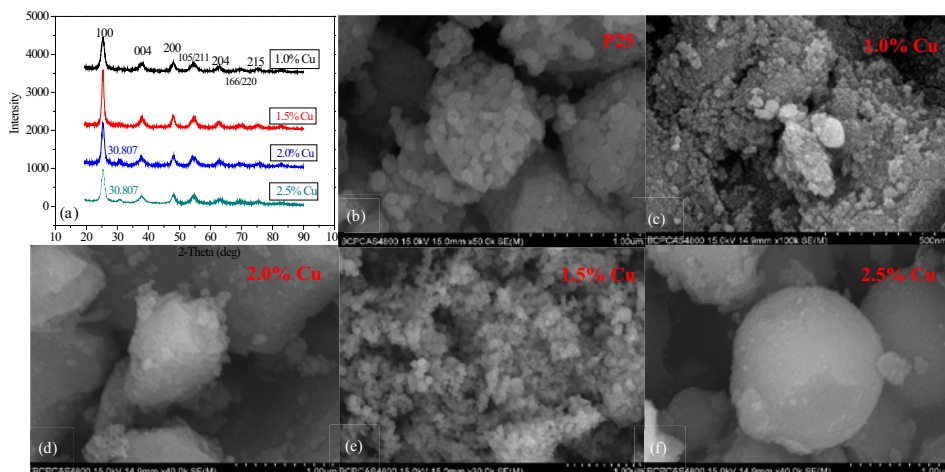


Fig. 1 XRD and SEM for 1.0%, 2.0%, 1.5% and 2.5% Cu doped TiO₂

P25 TiO₂ presents highly photocatalytic activity, gradually becoming a standard of photocatalytic materials [6]. Fig. 1 (a) revealed that the peak height of P25 TiO₂ was sharper and higher than that of the prepared Cu-TiO₂. From Fig. 1 (b-f), the grain sizes of 1.0% Cu-TiO₂ and 2.5% Cu-TiO₂ with 20-50 nm were smaller than that of P25 TiO₂ with 50-100 nm, whereas the grain structures both presented spherical. Combined with Cu doping structure, micro stress would be changed [7]. Reunion phenomenon was also observed, which was mainly caused by the nanoscale Brownian motion and van der Waals force [8].

EDS for Cu_xTi_(1-x)O₂. Fig. 2 and Table 1 showed that actual doped Cu weight percentage was 0.9%, 1.44%, 1.44% and 0.9%, and the corresponding molar percentage was 1.14%, 1.83%, 2.03% and 3.72% respectively, for the 1.0% (A1), 2.0% (A2), 1.5% (A3) and 2.5% (A4) Cu doped TiO₂. Molar ratio of 1.83% for Cu-TiO₂ presented larger overflow than the design molar. Its possible reasons concluded: (1) the uneven mixing in sample analysis pretreatment, resulting in Cu ions concentration in the EDS scanning area; (2) experimental deviation during the process of weighing tetrabutyl titanate solvent, etc. Overall, Cu doping mol ratio met the experiment expectation.

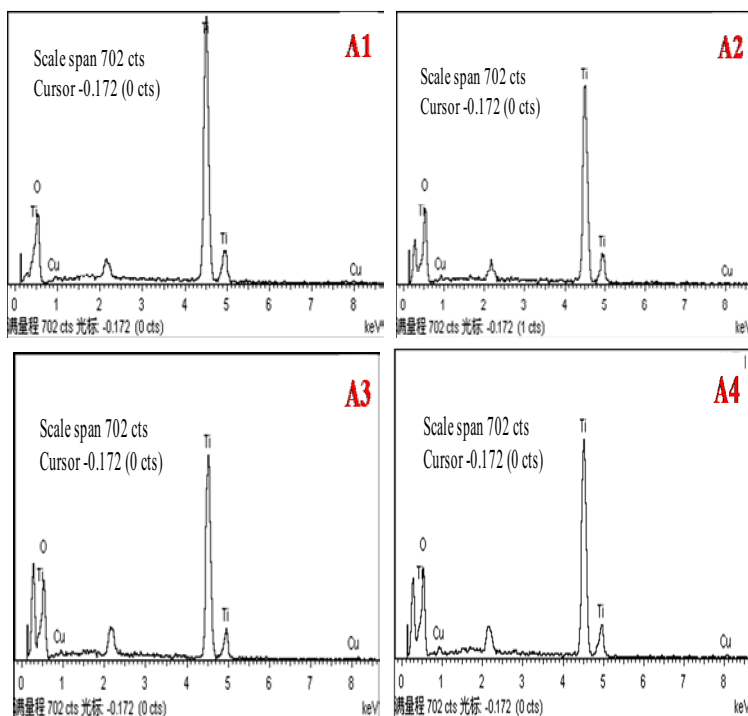


Fig. 2 EDS for 1.0% (A1), 2.0% (A2), 1.5% (A3) and 2.5% (A4) Cu doped TiO₂

Table 1 Spectrum scan parameters for the ratio of Cu to TiO₂

| Cu doped TiO ₂ | weight (%) | Atomic (%) | Molar (%) | Design molar (%) |
|---------------------------|------------|------------|-----------|------------------|
| 1.0% Cu-TiO ₂ | 0.90 | 0.38 | 1.14 | 1.0 |
| 1.5% Cu-TiO ₂ | 1.44 | 0.57 | 1.83 | 1.5 |
| 2.0% Cu-TiO ₂ | 1.60 | 0.65 | 2.03 | 2.0 |
| 2.5% Cu-TiO ₂ | 2.89 | 1.16 | 3.72 | 2.5 |

Performances of NBs degradation and dynamics analysis. With the preparation of different molar ratio of Cu-TiO₂ and P25 TiO₂, comparative studies on the photocatalytic degradation of NBs (see Fig. 3 (A)) were conducted.

Fig. 3 (A) showed that for 180 min degradation reaction with UV light, P25 TiO₂ degradation rate was also 26.97%. While the degradation rates of Cu-TiO₂ with 2.5%, 1.5%, 2.0% and 1.0% were 48.54%, 60.02%, 43.23% and 48.54% respectively, 1-2 times higher than that of P25 TiO₂ degradation performance. Therefore, the Cu modified TiO₂ could effectively improve the photocatalytic degradation of NBs.

Dynamic analysis was showed in Fig. 3 (B) and Table 2. Table 2 showed the dynamic equations for the different mixing amount of Cu and its parameters. It is generally believed that the heterogeneous catalytic degradation reaction rate equation can follow the Langmuir - Hinshelwood dynamic equation [9] which is suitable for the total reaction rate of NBs, seen Eq. (1):

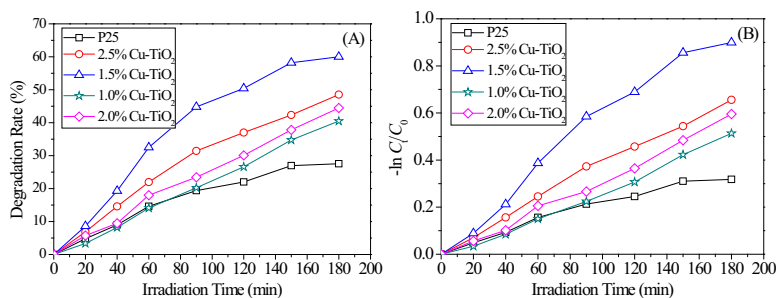


Fig. 3 (A) Nitrobenzene degradation performance by P25, 1.0%, 2.0%, 1.5% and 2.5% Cu doped TiO₂ and (B) kinetics

$$r = -\frac{dC}{dt} = \frac{k_1 k_2 C}{(1 + k_2 C)} \quad (1)$$

where, r is the total reaction rate for NBs degradation, C is the NBs concentration, k is the apparent reaction rate constant, k_1 is the reaction rate constant, and k_2 is the apparent adsorption constant.

Above photocatalytic experiment results showed that the NBs photocatalytic reaction can be fitted well by the following pseudo-first-order rate equation, as following Eq. (2):

$$r = -\frac{dC}{dt} = kC \approx k_1 k_2 C \quad (2)$$

Eq. (3) can be obtained from integration of Eq. (2), as following Eq. (3):

$$-\ln \frac{C_t}{C_0} = kt \approx k_1 k_2 t \quad (3)$$

where, C_t is the NBs concentration at time of t , and C_0 is the initial NBs concentration.

Table 2 Dynamics equations and parameters of P25, 1.0%, 2.0%, 1.5% and 2.5% Cu doped TiO₂

| Catalysts | Kinetics equation | k (min) | R ² | $t^{1/2}$ (min) |
|--------------------------|------------------------|-----------|----------------|-----------------|
| P25 | $y = 0.0018x + 0.0221$ | 0.0018 | 0.9673 | 372.8 |
| 2.5% Cu-TiO ₂ | $y = 0.0036x + 0.0122$ | 0.0036 | 0.9945 | 189.2 |
| 1.5% Cu-TiO ₂ | $y = 0.0053x + 0.0242$ | 0.0053 | 0.9758 | 126.2 |
| 1.0% Cu-TiO ₂ | $y = 0.0029x - 0.0218$ | 0.0029 | 0.9940 | 246.5 |
| 2.0% Cu-TiO ₂ | $y = 0.0023x + 0.0104$ | 0.0023 | 0.9784 | 225.2 |

Obviously, $\ln(C_t/C_0)$ was linear relationship with t . From Table 2, the linear coefficients of all the dynamics equations were all more than 0.96, presenting well linear relationship. It was observed that when TiO₂ with 1.5% Cu, the maximum value of k and the minimum value of $t^{1/2}$ were obtained for 126.2 min and 0.0053 min⁻¹ respectively. With Cu modification of TiO₂ with greater than or less than 1.5% molar, the reaction rate of r would be reduced, and its $t^{1/2}$ would increase. The reason might be that as an effective acceptor, the probability of recombination between light-excitation e^- and h^+ could be reduce by the doped Cu²⁺. And much more ·OH ions would be generated in TiO₂ surface. Thus the values of r in experiments would be enhanced. Results showed that the value of modification Cu²⁺ in TiO₂ surface had a optimal value, namely 1.83% molar Cu doped (1.5% design molar). When Cu²⁺ concentration was low than 1.83%, it could not effectively accept electronic, and less ·OH produced in the catalyst surface. Thus photocatalytic efficiency would be poor. When Cu²⁺

concentration was too high ($> 1.83\%$), excess Cu^{2+} would become the recombination center of the e^{-1} and h^{+} . This would increase the chances of the recombination of e^{-1} and h^{+} , resulting in a decline of catalytic activity [9]. Synthetically, SEM, EDS and performances of NBs degradation confirmed that the optimal formula of $\text{Cu}_x\text{Ti}_{(1-x)}\text{O}_2$ for degradation of NBs was $\text{Cu}_{0.0183}\text{Ti}_{0.9817}\text{O}_2$.

4. Summary

Sol-gel method was used for Cu doped TiO_2 . Characterization and analysis by SEM and EDS showed that, the grain sizes of Cu- TiO_2 with 20-50 nm were smaller than that of P25 TiO_2 with 50-100 nm, and the grain structures both presented spherical. Cu doped TiO_2 presented better performances for nitrobenzenes degradation. The efficiency of photocatalytic degradation of nitrobenzenes for 180 min by $\text{Cu}_{0.0183}\text{Ti}_{0.9817}\text{O}_2$ presented optimal, even 2 times more than German P25. Cu doping amount with lower or higher would lead to a decrease for the catalytic activity of TiO_2 . Further studies application of $\text{Cu}_{0.0183}\text{Ti}_{0.9817}\text{O}_2$ should be conducted to the of salinity and denitration of nitrobenzenes.

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