Study on preparation and photocatalytic properties of Cu_2O/TiO_2 composites by precipitation method

Chunhua Yuan

College of Chemistry and Chemical Engineering, Inner Mongolia University of Science & Technology, Baotou 014010 china

E-mail:yuanchunhua79@126.com

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Abstract. Cu2O/ TiO2 composite photocatalyst was prepared by precipitation method using Titany l sulfate, cupric nitrate and ethylenediamine as raw materials. The photocatalytic performance of photocatalyst was investigated by degradation of Methylene blue solution.The results showed that composite photocatalyst Cu2O/TiO2 was successfully prepared by precipitation method. The Cu2O/TiO2 composite photocatalys with Cuprous oxide content of 70% performed best photocatalytic activity, the degradation efficiency of Methylene blue under visible light irradation can reach 97 % within 40 min

1 Introduction

As one of the most widely used semiconductor, TiO_2 has the advantages of no toxicity, stability, low cost, no two pollution and so on.But it also has its own limitations[1]: as a wide band gap semiconductor[2], TiO_2 can only absorb sunlight in the ultraviolet part, so, its sunlight utilization rate is only about 5%[3], photogenerated electron hole is easy to composite, the quantum efficiency and low defects limit the effective utilization of solar energy[4]. Cu_2O is a typical narrow bandgap p-type semiconductor with band gap energy of 2.0～2.2 eV, and it can be completely stimulated luminescence catalytic reaction by $400 \leq \lambda \leq 600$ nm visible light. So it can make full use of solar energy, but the quantum efficiency of the photocatalytic reaction is lower, and the electron hole pair is more complex[5].

In this paper, the narrow band gap semiconductor Cu_2O is used to sensitized TiO_2, and the Cu_2O/TiO_2 composite material is formed. The composite materials can quickly transfer photogenerated electrons in the photocatalytic reaction, effectively prevent the recombination of electron hole pairs, so as to improve the quantum efficiency of semiconductor and the effective use of solar light catalytic reaction.

2. Materials and methods

2.1 Materials

Instruments: electronic analytical balance (FA1004 Shanghai Hengping Scientific Instrument Co., Ltd), digital display thermostatic water bath (HH-6 Shanghai Pudong physical optics instrument factory), electric thermostatic drying oven (101 Beijing ever-bright medical instrument factory), X ray diffraction (Rigaku-12KW Japan), tungsten (40W Lianhua Lighting Co., Ltd.) 722s visible spectrophotometer (Shanghai precision scientific instrument Co., Ltd.).

Reagent: Cupric nitrate, sodium hydroxide, ethylenediamine, glucose, titanyl sulfate, ammonia, urea, hydrogen peroxide (30%), anhydrous ethanol were of analytical reagent.

2.2Preparation of nanometer TiO_2

A certain amount of $TiOSO_4 \cdot 2H_2O$ was dissolved in distilled water in a certain temperature, then under magnetic stirring, a certain concentration of precipitant was slowly dropped. when the solution pH was 6～7, dropping was stopped , then filtering, and using deionized water and absolute ethanol wash several times. The filter object is arranged on the 110℃ blast drying oven after 3h, then under a certain temperature of the muffle furnace calcination 4H. Then, nano TiO_2

was spared by grinding with agate mortar.

2.3Preparation of composite materials Cu_2O/TiO_2

The amount of self-made titanium dioxide was dissolved in 200ml 0.07mol/l copper nitrate solution, in glass rod continuous stirring, ultrasonic 5min, adding ethylenediamine 2.8ml, weigh 1.12 g NaOH dissolved in the copper nitrate solution, fully dissolved, add glucose 1.4981g. Under magnetic stirring, the solution was taken in a constant temperature bath of 75℃ for 30min, then filtered, and washed several times with deionized water and absolute ethanol. The sediment was placed in the drying box of 60℃ for 3h, and then the Cu_2O/TiO_2 composite materials was prepared by the agate mortar grinding.

2.4 Characterization of composite materials Cu_2O/TiO_2

The matter phase is analyzed by D/Max-3cX of X-ray powder diffraction (XRD).Its test conditions: Cu Target k_a line, the Ni filter, the 40kV, 40mA, scanning range 20°～80°（2θ）, scanning speed 2°/min using X-ray diffraction.

2.5 Photocatalytic properties of composite materials Cu_2O/TiO_2

40W tungsten lamp was used as a visible light source, and the light distance was 10 cm.The photocatalytic reaction process was: (1) a certain amount of Cu_2O/TiO_2 composite powder was added to the methylene blue solution of 10mg/L;(2) firstly, in the absence of light, the solution was ultrasonic dispersed for 3min and magnetic stirred for 10 min, so that the organic molecular reached adsorption / desorption equilibrium on the catalyst surface; (3) with the light source opening, the photocatalytic reaction was carried out at room temperature, and the suspension system was kept magnetic stirring during the whole process of the photocatalytic reaction; (4) every 20 min beginning the light open, 5 mL suspension sample was removed and centrifuged 10 min, then the upper liquid was absorbed, the solution absorbance of light catalytic was measured with 722S visible spectrophotometer in 665nm. The degradation rate（η）=（A0-A1）/A0×100%

Type: The A_0 and A_1 was respectively absorbance value of before and after the degradation of methylene blue solution at the maximum absorption wavelength.

3 Results and discussion

3.1 XRD analysis of Composite catalyst Cu_2O/TiO_2

The XRD spectra of the composite samples were compared with that of pure Cu_2O and pure TiO_2 products in Figure 1. Peaks in the map can be referred to as the Cu_2O (space group is Pn3m; a0=0.4252 nm. JCPDS 05-0667) and cubic phase Cu_2O (JCPDS 34-1354) of the five corresponding peaks. No peak of CuO or Cu was produced. Which indicated that Cu_2O prepared by the chemical precipitation method was comparatively pure.

Average grain size is calculated by the Scherrer formula（Scherrer）：$d=K\lambda/(\beta\cos\theta)$ according to the sample crystal plane diffraction peak FWHM , and the mean grain size is 20.00nm.

Compared with the XRD diagram of the pure component, the Cu_2O/TiO_2(111）peak intensity is significantly lower, and the half peak width become larger, which shows that the crystallization degree of the catalyst decreased, and which is the general characteristic of the nano composite particles.

The formula of $S=6\times10^3/(\rho d)$ is applied to calculate their specific surface area s, type: P is the theory density of grain , and its specific surface area reaches 133.55m2/g.

3.2 Photocatalytic degradation of composite materials Cu_2O/TiO_2

3.2.1Effect of Cu_2O composite on degradation rate

$X_{Cu2O/TiO2}$（X=30%、50%、70%）composites 0.8g/L and 1ml30% were individually added to the methylene blue solution of 30mg/L. And the absorbance value is converted to degradation rate and the degradation rate is shown in Figure 2.

We can see from figure 2, the photocatalytic effect of composite materials is better than that of the cuprous oxide. When the deposition of doped cuprous oxide in the composite in quantity is 70%, light catalyst has the best catalytic effect. This is because when the cuprous oxide deposition incorporation is 70%, the light catalyst is the most suitable band gap width, the absorption spectral range with tungsten filament lamps for the visible spectral range overlap.

3.2.2 Relationship between degradation rate and catalyst dosage

The 0g (without), 0.01g, 0.02g, 0.04 g, 0.06g Cu_2O/TiO_2 composites were added respectively to five methylene blue(50ml). Another methylene blue water solution was taken, neither the addition of photocatalyst nor hydrogen peroxide.

And Figure 3 shows that under the conditions of pure light, the methylene blue is almost not decomposed. After adding the catalyst, the light 60min can degrade more than 70%. With the increase of the amount of photocatalyst, the degradation effect was better. Because the vegetation of the composite material is more trouble, the best effect is achieved with the least photocatalyst, so the best adding amount of photocatalyst is 0.8g/L.

3.2.3 Effect of hydrogen peroxide addition on the degradation of methylene blue

Under the condition of no stirring, the catalyst 0.4 g/L was added to methylene blue solution with 50ml concentration of 10mg/L. After ultrasonic dispersion 3min, 0mL, 0.2mL, 0.6mL, 1.0mL, 1.4mL and 1.8ml 30% hydrogen peroxide were added respectively, and the degradation experiment was carried out. After 20 min sampling 5mL, the supernatant was taken to measure its absorbance value. And the degradation rate was calculatedAs shown in Figure 4.

Figure 4 shows that under the conditions of no hydrogen peroxide, the Cu_2O/TiO_2 composite photocatalyst almost does not degrade methylene blue solution. When the amount of hydrogen peroxide is increased, the degradation effect is better. When the amount of hydrogen peroxide is 1ml, the effect is the best. However, if further increase in the amount of added, the degradation effect will be weakened.This may be H_2O_2 is also the agent of •OH, High concentration will produce a sharp increase of •OH, the degradation rate of ［s］ was reduced by the interaction of •OH with the reaction of methylene blue molecules. Therefore, the optimal addition amount of H_2O_2 was 1 mL. Therefore, the optimal adding amount of 30% hydrogen peroxide is 1.0mL.

4 Conclusions

(1)With using precipitation method, ammonia and urea as precipitation agent, $TiOSO_4$ as raw material, by controlling the concentration of precipitation agent and reaction temperature, a better dispersion of TiO_2 particles with average particle size of about 14.62nm was prepared.

(2)With using low-temperature chemical synthesis method, using copper nitrate and self-made nano TiO_2 as raw material, using glucose as reducing agent, by controlling the temperature and time, the Cu_2O/TiO_2 particles with good dispersion and average particle size in 20.00nm were synthesized.

(3)This experiment uses tungsten as light source, uses methylene blue as a probe on the photocatalytic properties of composite materials. The best catalytic conditions: ultrasonic 3 minutes, 30% of the amount of hydrogen peroxide 1.0mL, the catalyst dosage of 0.8g/L, the concentration of 10mg/L methylene blue degradation rate in 40min reached more than 97%.

To sum up, the excellent performance and great potential of Cu_2O/TiO_2 composite nano photocatalyst can not be ignored. In the decomposition and degradation of organic pollutants, especially in the aspect of treating Chinese Medicine Wastewater with complex components, Cu_2O/TiO_2 photocatalyst will have broad application prospects.

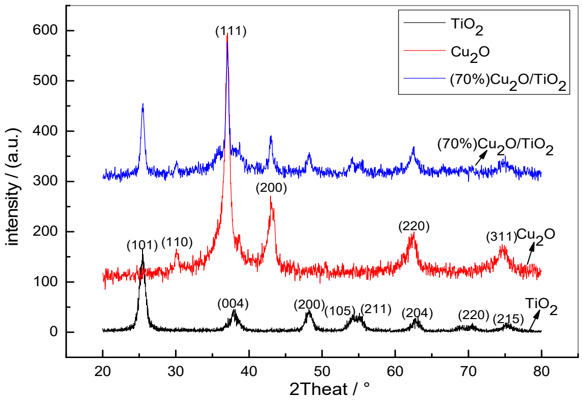

Fig1. XRD result of nano-70%）Cu_2O/ TiO_2

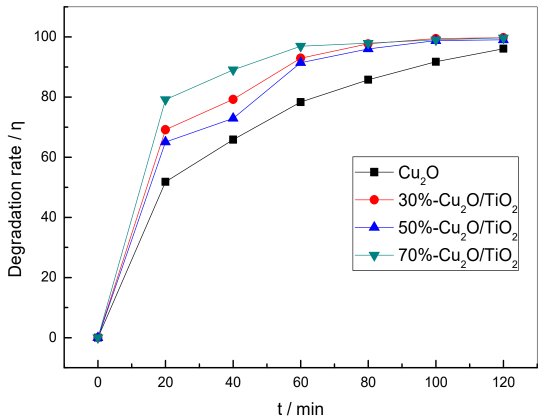

Fig2. Cu_2O content which have influence on the degradation rate

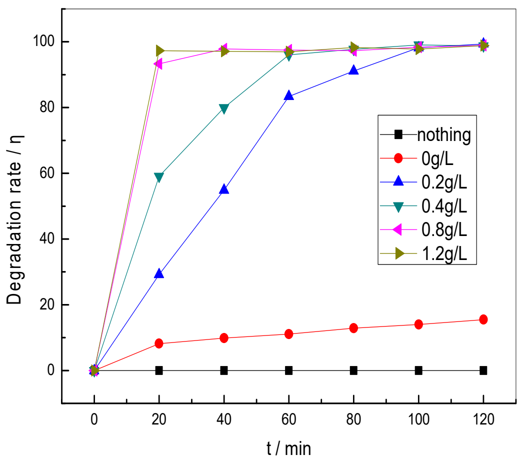

Fig3. Impact of different Cu_2O/TiO_2 concentrations on degradation rate

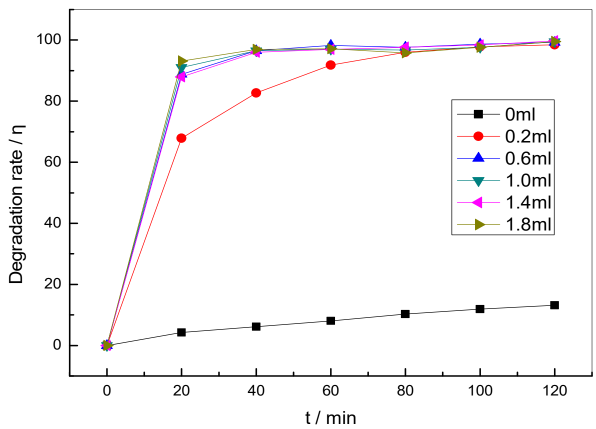

Fig4. Impact of different H_2O_2 concentrations on degradation rate

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