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ARTICLE

Enhanced Photocatalytic Activity of Cu_2O/Cu Heterogeneous Nanoparticles Synthesized in Aqueous Colloidal Solutions on Degradation of Methyl Orange

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Abstract: Heterogeneous Cu_2O/Cu nanoparticles were synthesized by a colloidal chemistry approach using ascorbic acid as a reducing agent and polyvinylpyrrolidone as a surfactant. Morphology and structure of Cu_2O/Cu nanoparticles were analyzed by SEM, XRD and N_2 sorption techniques. The catalytic performances of Cu_2O/Cu nanoparticles for the degradation of methyl orange (MO) were investigated and reaction kinetics of MO degradation over the catalyst was also studied. The results show that the heterogeneous Cu_2O/Cu nanoparticles display cobblestone-like morphology with particle sizes ranging from 20 nm to 40 nm, which are slightly smaller in particle size and higher in BET surface areas than pure Cu_2O. The Cu_2O/Cu nanoparticles demonstrate good potential on degradation of MO because Cu nanoparticles in the Cu_2O/Cu heterostructures promote the interfacial charge-transfer kinetics between Cu and Cu_2O. High initial MO concentration produces low degree of MO degradation, and increases the reaction time to reach equilibrium, and the degradation reactions follow the pseudo-first-order kinetics model. The Cu_2O/Cu catalyst still exhibit good catalytic activity after 4 photodegradation cycles of MO solutions.

Key words: Cu_2O/Cu; heterogeneous photocatalysts; degradation; methyl orange

Dye wastewater discharge from textile, cosmetic, paper, leather, pharmaceutical and nutrition industries has posed a significant threat to the environment and public health owing to its non-biodegradability, toxicity and potential carcinogenic risk [1,2]. Methyl orange (MO) is a commonly employed water-soluble azo dye, which can enter the body through ingestion and metabolize into aromatic amines, leading to intestinal cancer[3]. To data, several techniques, such as adsorption, coagulation, biodegradation, membrane separation and advanced oxidation processes (AOPs) have been developed for the treatment of colored wastewater[4]. Of the above-mentioned treatment techniques, advanced oxidation processes (AOPs) have attracted much attention on the dye degradation based on the generation of reactive species in the presence of catalysts, which can degrade a broad range of organic pollutants quickly and non-selectively[5]. At present, many metal oxides, such as TiO_2, Mn_2O_3, ZnO, Fe_2O_3, CuO and Cu_2O, have been used as catalysts for the degradation of colored wastewater due to their unique physical and chemical properties[6,7].

Cuprous oxide (Cu_2O) is a p-type semiconductor with a direct band gap of 2.17 eV and demonstrates potential applications on degradation of organic contaminants because of its high catalytic activity, non-toxicity, good environmental acceptability and abundance [8]. In the past few years, much effort has been devoted to synthesize a variety of Cu_2O nanostructures, including nanowires, nanoboxes, nanocages, nanospheres, nanocubes and nanooctahedra [9,10], and they are mostly prepared by wet chemical reduction, a hydrothermal method, electrodeposition, and high-pressure sputtering etc. Among these methods, wet chemical reduction is a simple method for producing nanomaterials in large quantities and at

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low-cost.

As we know, the catalytic activity of Cu_2O depends strongly on electron-hole separation, and it is difficult to improve the catalytic activity of pure Cu_2O significantly due to the easy recombination between electrons and holes. However, heterogeneous photocatalysts by adding noble metal (Ag, Cu, Pt) or other semiconductors (TiO_2, ZnO) can show enhanced photocatalytic activity compared to pure Cu_2O due to the electron and hole transfer between the two phases [11]. Significant advances have been made in recent years to design various kinds of semiconductor-based heterogeneous photocatalysts. Metal/semiconductor is one of the most popular heterogeneous photocatalysts, and has been extensively studied because of its excellent catalytic activity [12]. However, to the best of our knowledge, most heterogeneous metal/semiconductor photocatalysts are obtained by introducing other metallic salt during their syntheses. In the present research, we developed a facile approach for the syntheses of heterogeneous Cu_2O/Cu photocatalysts only by adjusting the reaction temperature, and their catalytic degradation abilities were also investigated to evaluate their potential in removal of MO from wastewater.

1 Experiment

0.50 g $CuSO_4$ and 0.36 g ascorbic acid ($C_6H_8O_6$) were added into 50 mL of polyvinylpyrrolidone (PVP) (0.13 mol/L) aqueous solution under stirring. Then, 10 mL of sodium hydroxide (NaOH) solution (0.10 mol/L) was added dropwise into the above mixture at 60 and 90 °C. After centrifugation, the solid precipitate was washed with distilled water, and dried at 60 ℃ for 4 h.

The morphology of Cu_2O nanocrystals was observed by SEM (Philips XL30 FEG) and TEM (FEI/Philips Techal 12 BioTWIN). The Brunauer-Emmett-Teller (BET) surface area of Cu_2O nanocrystals was characterized by a nitrogen sorption technique (Quantachrome Autosorb-iQ). X-ray diffraction (XRD) patterns of Cu_2O nanocrystals were recorded using a D/Max-2400 diffractometer (Cu Kα radiation, $\lambda = 0.154\,055$ nm) in a range of diffraction angle 2θ from 0° to 5° to analyze the diffraction peaks of Cu_2O nanocrystals. The mass fraction of Cu in the Cu_2O/Cu composites was calculated using the relative ratio:

$$\frac{I_{\mathrm{Cu(111)}}}{I_{\mathrm{Cu_2O(111)}} + I_{\mathrm{Cu(111)}}} \tag{1}$$

where, $I_{\mathrm{Cu(111)}}$ and $I_{\mathrm{Cu_2O(111)}}$ are the intensity of diffraction peaks in Cu (111) and Cu_2O (111) planes, respectively.

0.02 g of Cu_2O nanoparticles was dispersed in 50 mL of MO aqueous solution (5, 10, 15, 20 mg/L). Then, 0.5~5 mL of aqueous H_2O_2 (30 wt%) was added into the reaction mixture. The catalytic reaction was performed with a 40 W tungsten lamp as the visible-light source under magnetic stirring at 25 °C for 5 h. The mixture of catalyst and MO solution was centrifuged for a given time interval. Then, 2 mL of supernatant solution was analyzed immediately using an UV-visible spectrophotometer.

The degree of MO degradation (*D*) was estimated by the following equation:

$$D = \frac{C_0 - C_t}{C_0} \times 100\% \tag{2}$$

where C_0 (mg/L) is the initial concentration of MO and C_t (mg/L) is the concentration of MO at time *t* during the catalytic reaction.

The pseudo-first-order kinetics was expressed in terms of Langmuir-hinshelwood (*L-H*) model [13].

$$\ln(\frac{C}{C_0}) = kt \tag{3}$$

where *k* is the pseudo-first-order rate constant.

2 Results and Discussion

The crystallographic structure and phase purity of the product are examined by XRD. Fig.1a presents the typical XRD patterns of the sample synthesized at 60 °C. All of the diffraction peaks correspond to Cu_2O [JCPDS 05-0667][14]. No other diffraction peaks resulting from possible impurities such as Cu and CuO are detected, indicating pure Cu_2O is obtained under this experimental condition. The XRD patterns of the sample synthesized at 90 °C is also shown in Fig.1b. The sample is found to be composite materials, which are characterized by the two types of diffraction peaks, i.e., Cu_2O (JCPDS 05-0667) and Cu (JCPDS 04-0836), and the content of Cu is 19.7 wt% (Table 1).

Fig.2a and 2c is the typical SEM and TEM image of as-prepared Cu_2O samples, respectively. The Cu_2O products show the cobblestone-like morphology with particle sizes

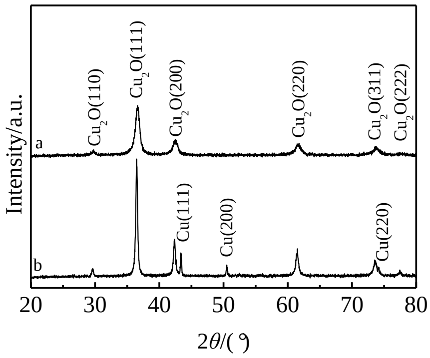

Fig.1 XRD patterns of Cu_2O/Cu (a) and Cu_2O (b)

Table 1 Phase composition and BET surface areas at 60 and 90 °C

Temperature/ °C	W_{Cu}/ %	W_{Cu_2O}/ %	BET surface areas/ $m^2\ g^{-1}$
60	0	100	10.7
90	19.7	80.3	12.6

ranging from 40 nm to 60 nm. Cu_2O/Cu composite materials show similar morphology, and the size range of nanoparticles is between 20~40 nm (Fig.2b and 2d), which is slightly smaller than that of pure Cu_2O. The Brunauer-Emmett-Teller (BET) surface areas of Cu_2O/Cu composite materials is calculated to be 12.6 m^2 g^{-1}, which is larger than that of pure Cu_2O, suggesting a facilitation effect toward catalytic degradation of MO.

Fig.3a shows the effect of catalysts on degradation efficiency of MO. The degree of MO degradation is also very low using H_2O_2 in the absence of catalyst (only reaches 9.2% for 270 min), which indicates using H_2O_2 alone is not effective in degrading the stable MO. When both catalyst (Cu_2O/Cu or Cu_2O) and H_2O_2 are used to treat the MO solution, the synergistic effect on enhancing degradation capability of MO is remarkable. However, it is worth noting that Cu_2O/Cu demonstrates better photocatalytic performance for MO degradation (high degradation degree and short reaction time to equilibrium). Fig.3b displays the plots of $\ln(C_0/C)$ versus t for degradation of MO under above experiment conditions. It is obvious that they follow a linear relationship, suggesting that the degradation reaction obeys the pseudo-first-order kinetics model. The rate constants are found to be in the following order: 0.019 min^{-1} (Cu_2O/Cu) > 0.014 min^{-1} (Cu_2O) > 0.0005 min^{-1} (H_2O_2), indicating that Cu_2O/Cu has a high photocatalytic activity, which may be attributed to that Cu nanoparticles in the Cu_2O/Cu hererostructures promote the interfacial charge-transfer kinetics between Cu and Cu_2O [15].

Fig.4a shows the effect of H_2O_2 amount on degradation efficiency of MO. When no H_2O_2 is added into the solution, only 7.3% of the MO is degraded in 270 min, which suggests using Cu_2O/Cu alone is also not effective in degrading the stable MO. The presence of 0.5 mL H_2O_2 in the solution increases the degree of MO degradation to 78.3%. Further increasing the amount of H_2O_2 to 2 mL, the MO degradation degree increases to 93.2%. With more addition of H_2O_2 than 2 mL, the degree of MO degradation slightly improves to 93.9%. The kinetics of MO degradation by the Cu_2O/Cu particles containing different amounts of H_2O_2 is shown in Fig.4b. The rate constants are found to be in the following order: 0.020 min^{-1} (5 mL) > 0.019 min^{-1} (2 mL) > 0.006 min^{-1} (0.5 mL) > 0.0003 min^{-1} (0 mL). All those suggest that the continuous increase in the amount of H_2O_2 is not effective to enhance the MO degradation degree, so the optimum amount of H_2O_2 is 2 mL for the degradation of 50 mL of 10 mg/L MO.

Fig.5a shows the effect of initial MO concentration on the degree of MO degradation. The degree of MO degradation increases sharply in the initial stage and then gradually remains steady with the increase of reaction time. High initial MO concentration not only produces low degree of MO degradation, but also increases the reaction time to reach equilibrium. Fig.5b displays the plots of $\ln(C_0/C)$ versus t for degradation of MO with concentrations of 5, 10, 15 and 20 mg/L. It is obvious that they follow a linear relationship, suggesting that the degradation reaction obeys the pseudo-first-order kinetics model. The rate constants are found to be in the following order of 0.027 min^{-1} (5 mg/L) > 0.019 min^{-1} (10 mg/L) > 0.012 min^{-1} (15 mg/L) > 0.008 min^{-1} (20 mg/L), which is inversely proportional to the concentration of MO. This is attributed to more active sites covered by MO molecules at high concentration [16].

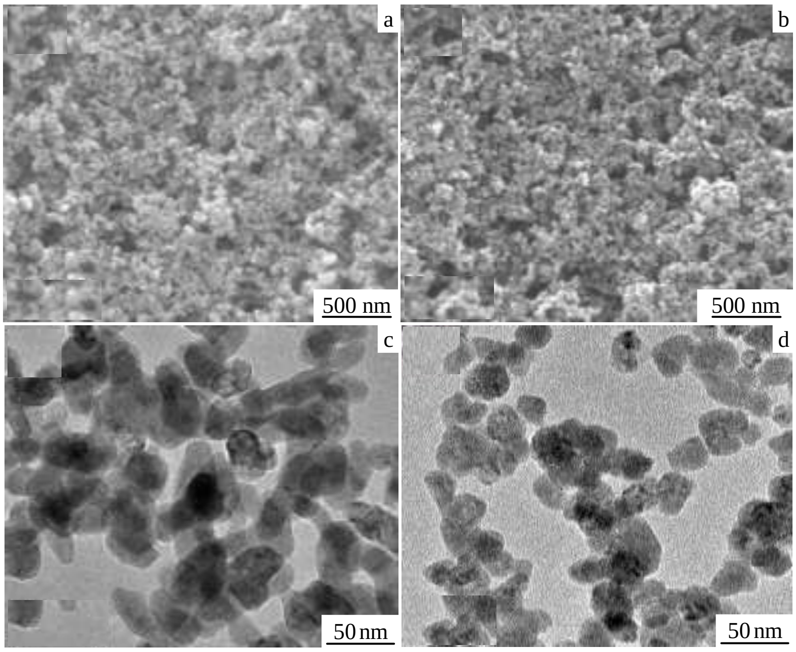

Fig.2 SEM images of Cu_2O (a), and Cu_2O/Cu (b); TEM images of Cu_2O (c) and Cu_2O/Cu (d)

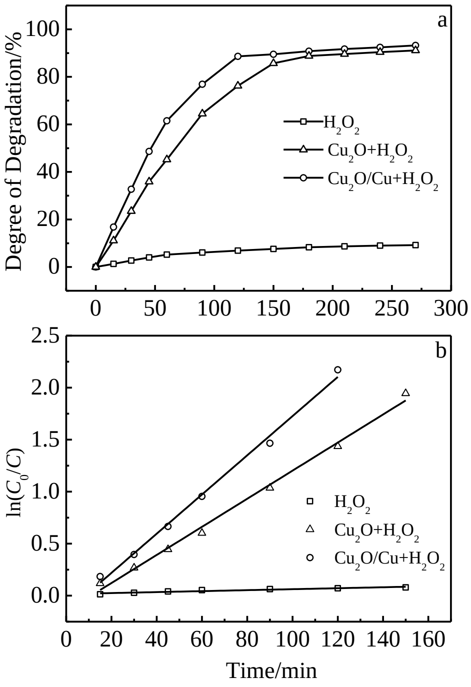

Fig.3 Degree of degradation (a) and pseudo-first-order kinetics model of MO degradation (b) by Cu_2O/Cu and Cu_2O

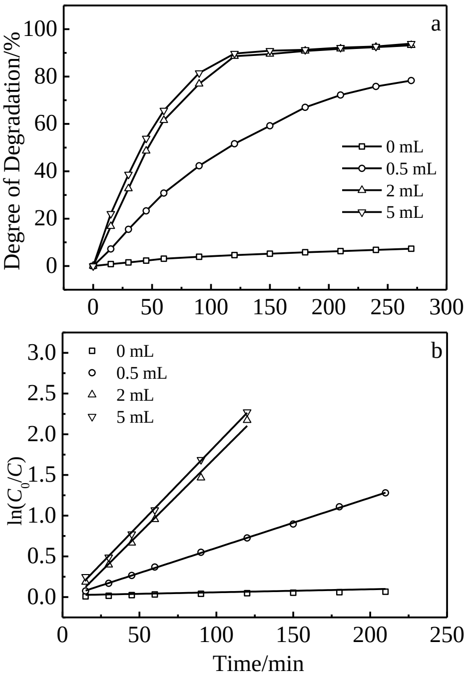

Fig.4 Degree of degradation (a) and pseudo-first-order kinetics model of MO degradation (b) by Cu_2O/Cu with different H_2O_2 amounts

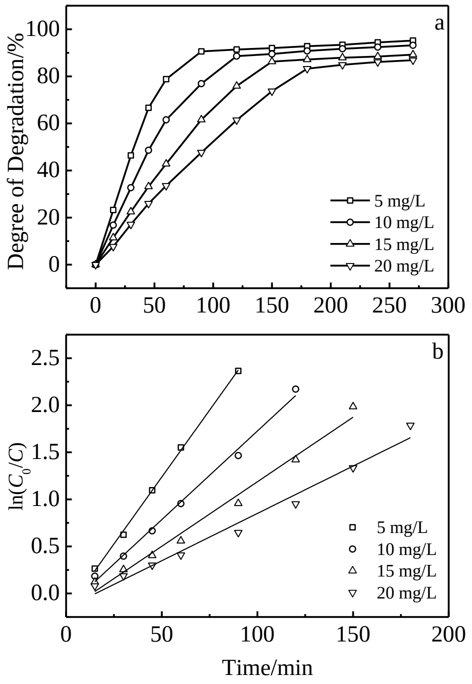

Fig.5 Degree of degradation (a) and pseudo-first-order kinetics model of MO degradation (b) by Cu_2O/Cu at different initial MO concentrations

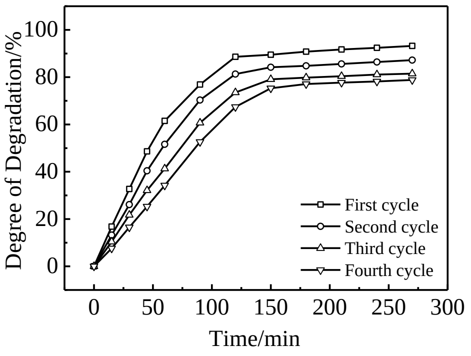

Fig.6 Degree of MO degradation by Cu_2O/Cu for 1~4 cycles

4 consecutive cycles were performed to check the stability and reusability of the Cu_2O/Cu catalyst. As shown in Fig.6, the catalyst does not exhibit a significant loss of activity after 4 photodegradation cycles of MO, and the degree of MO degradation can still reach 78.8% for 50 mL of 10 mg/L MO solutions, which indicates that Cu_2O/Cu nanoparticles are promising candidates for treatment of dye wastewater.

3 Conclusions

1) Cobblestone-like Cu_2O/Cu nanoparticles are synthesized and used as a catalyst to degrade MO solution. Higher degradation degree for MO can be obtained using Cu_2O/Cu than that using pure Cu_2O.

2) The degradation rate constant decreases as the initial MO concentration increases, and the degradation reaction can be represented by pseudo-first-order kinetics model.

3) The catalyst does not exhibit a significant loss of activity

after 4 photodegradation cycles of MO.

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杂化 Cu_2O/Cu 纳米粒子的水相合成及强化光降解甲基橙的催化活性研究

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摘　要：为了优化 Cu_2O 纳米粒子的光催化性能，以抗坏血酸作为还原剂、聚乙烯吡咯烷酮为表面活性剂，采用水相合成的方法通过调控反应温度制备出杂化 Cu_2O/Cu 纳米粒子。利用 SEM、XRD 和 N_2 吸附技术对 Cu_2O/Cu 纳米粒子的形貌特征和结构性能进行表征。同时，也研究 Cu_2O/Cu 纳米粒子催化降解甲基橙(MO)的效果和降解反应动力学。结果表明，制备的杂化 Cu_2O/Cu 纳米粒子为“鹅卵石”形状，粒径尺寸范围在 20~40 nm 之间，与纯 Cu_2O 粒子相比，杂化 Cu_2O/Cu 粒子具有尺寸小、比表面积大的特点。由于杂化材料中引入了 Cu 纳米粒子，促进了 Cu 和 Cu_2O 之间的界面电荷转移，使得 Cu_2O/Cu 纳米粒子展现更优异的催化性能。Cu_2O/Cu 催化降解 MO 的反应符合一级动力学反应模型。经过 4 次循环使用后，杂化 Cu_2O/Cu 仍然能表现出良好的催化活性。

关键词：氧化亚铜/铜；杂化光催化剂；降解；甲基橙

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