Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Ag_3PO_4/CuO composites utilizing the synergistic effect of photocatalysis and Fenton-like catalysis to dispose organic pollutants

Peiyan Ma [a], Yong Yu [a], Jingjing Xie [b,*], Zhengyi Fu [b,*]

[a] School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, Wuhan, Hubei 430070, PR China
[b] State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei 430070, PR China

ARTICLE INFO

Article history:
Received 22 February 2017
Received in revised form 31 July 2017
Accepted 9 August 2017
Available online xxxx

Keywords:
Ag_3PO_4/CuO
Photo-Fenton
Visible light irradiation
Z-scheme photocatalytic mechanism
Water purification

ABSTRACT

Both photocatalysis and Fenton-like catalysis present promising and potential technologies for water purification. However, single photocatalysis or Fenton-like catalysis cannot meet the practical demand for complicated pollutes treatment in water. Herein, we report an environmentally benign Ag_3PO_4/CuO catalysts that combine the two catalysis. The synthesized Ag_3PO_4 acts as an efficient photocatalyst, and Fenton-like CuO catalysis decomposes organic pollutes in the presence of H_2O_2. A series of Ag_3PO_4/CuO composites were obtained by regulating the molar ratio of Ag_3PO_4 to CuO via hydrothermal and ion exchange reactions. The optimized composite shows a significant improvement in catalytic activity over pure Ag_3PO_4 under visible light or CuO with H_2O_2, owing to the synergistic effect of photocatalysis and Fenton-like catalysis. It is noticeable that the Ag_3PO_4/CuO composites retain efficient performance even after five cycling runs. The catalytic mechanism involves matched band structures, Z-scheme photocatalytic mechanism, and the generation of a large amount of hydroxyl radicals.

1. Introduction

Photocatalytic technologies utilizing solar energy and semiconductor photocatalysts are effective strategies for water purification. Until now, an enormous amount of research has been focused on the development of high-performance photocatalysts that exhibit high quantum yield over a wide range of the solar spectrum [1–3]. Several strategies have been designed to improve the activities of existing photocatalysts, including the doping of metallic or non-metallic ions. For example, doping Ti^{3+} to TiO_2 can narrow the band gap and extend absorption region in the visible light [4]. However, the defects induced by doping provide additional recombination centers, which decrease the performance. Another strategy is the heterogeneous photocatalytic system that involves the shift of photogenerated electrons and holes driven by thermodynamic energy [5,6]. Though the system effectively inhibits the recombination of photogenerated carriers, the redox ability of photogenerated electrons and holes is weakened after charge transfers. The third strategy is to decorate semiconductor particles with Cu(II) [7] and Fe(III) oxide amorphous nanoclusters [8] to produce visible- light activated materials. Therefore, an alternative approach of boosting the activity of the photocatalysts is still required in response to the complexity of environmental pollution.

Fenton oxidation has been generally regarded as one of the advanced oxidation processes for converting some organic macromolecules into small pollution-free molecules, CO_2, and H_2O [9]. Active oxidant-hydroxyl radicals can be produced via the serial reactions between the Fenton reagents (such as, $Fe^{2+}Cu^{2+}$) and H_2O_2. However, some shortcomings still limit the application of this homogeneous catalysis, including sensitivity to the pH change, metal ions pollutions and unrepeatable utilization. Recently, Fenton-like catalysis system composed of heterogeneous Fenton catalysts and H_2O_2 have gained extensive attention as the promising candidates such as BiOBr [10], Fe_3O_4 [11], CuO [12], CuS [13], CeO_2 [14], and carbon materials [15]. Although the synthesis of Fenton-like catalysis is feasible and economical, it shows weaker catalytic activity in comparison with photocatalysis. Accordingly, the essential issue is how to obtain Fenton-like catalysts with high activity.

Ag_3PO_4, a high-performance photocatalyst, displays outstanding quantum efficiency [16,17], and thus can degrade organic dyes under visible light irradiation, which make it a promising candidate in the areas of material, chemistry, and environmental protection [18]. It is noticeable that the synthesis of Ag_3PO_4 can be controlled in solution at room temperature, and also coupled with other functional materials to decrease the price and to improve the

* Corresponding authors.
E-mail addresses: crystalplane413@163.com (J. Xie), fuzhengyi@whut.edu.cn (Z. Fu).

http://dx.doi.org/10.1016/j.apt.2017.08.004
0921-8831/

performance. Due to the enhanced electron-hole separation efficiency, various Ag_3PO_4-based composites [19–25] show enhanced photocatalytic activity compared to pure Ag_3PO_4. Nevertheless, as discussed above, keeping the redox ability of the carriers is important There are some reports about the assistance of the light for the Fenton-like catalysis, in which more active species generate [26–29]. Therefore, combining Ag_3PO_4 photocatalysts with Fenton-like catalysts not only maintain the redox ability of photogenerated electrons and holes, but also introduce ·OH· radicals to assist the decomposition of organic pollute.

Here we designed an efficient Ag_3PO_4/CuO composite system to decompose organic dyes in the presence of H_2O_2 under visible light irradiation. The formation of Ag_3PO_4/CuO composite not only improves the catalysis activity and stability of Ag_3PO_4, but reduces the cost of the catalyst. Firstly, CuO is a stable metal oxide. Therefore, the combining of CuO with Ag_3PO_4 would reduce the dissolution of Ag_3PO_4 in water. Secondly, the conductive band of Ag_3PO_4 is not negative enough, the adsorbed O_2 molecules on the surface of Ag_3PO_4 are difficult to be reduced to superoxide radicals $\cdot O_2^-$.CuO and Ag_3PO_4 have matched energy band structure. Therefore, the shortcoming of Ag_3PO_4 could be compensated. Thirdly, CuO as a Fenton-like catalyst could produce OH· after the addition of H_2O_2. Therefore, it could be concluded that the performance of Ag_3PO_4 could be significantly improved after the formation of Ag_3PO_4/CuO composites. To our best knowledge, this is the first report about the Ag_3PO_4/CuO photo-Fenton like catalyst. In the present work, we have focused on the exploration of appropriate catalysis systems, the development of matched synthesis techniques for mass production of catalysts, as well as an in-depth study of the synergistic effects of the two catalysts. Based on the comparative analysis of the degradation behavior, the corresponding catalysis mechanism was also proposed to extend this novel strategy.

2. Experimental

2.1. Materials

$Cu(Ac)_2{\cdot}H_2O$, $AgNO_3$, PVP, $NaH_2PO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}12H_2O$, H_2O_2(30%), $Na_3PO_4{\cdot}12H_2O$, ethanol and rhodamine B(RhB) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were used as received without further treatment.

2.2. Synthesis of CuO sample

CuO were synthesized via a one-step hydrothermal method [30].Typically, 3.5 mmol $Cu(Ac)_2{\cdot}H_2O$ and 150 mg polyvinylpyrrolidone (PVP) were dissolved in 35.0 mL distilled water, respectively. Then, the PVP solution was dropped into $Cu(Ac)_2{\cdot}H_2O$ solution . After stirring for 30 min, the mixture was poured into a Teflon-lined stainless steel autoclave and heated to 200 °C for 1 h. The obtained precipitates were washed with distilled water and then dried at 60 °C for 24 h.

2.3. Synthesis of Ag_3PO_4/CuO composite catalyst

The preparation of Ag_3PO_4/CuO composites was carried out by an in- situ precipitation method (Fig. 1). Typically, 2.49 mmol $AgNO_3$ was dissolved in 50 mL of distilled water followed by the addition of as-prepared CuO. After the solution was stirred for 30 min, 50 mL of a neutral buffer solution containing NaH_2PO_4 (0.000835 mol) and NaH_2PO_4 (0.000835 mol) was added. After that, the mixed solution was stirred for 5 h. The obtained precipitates were washed 3 times with distilled water and dried at 60 °C for 24 h. Three Ag_3PO_4/CuO composites were synthesized using the same method with Ag_3PO_4 to CuO molar ratios of 1:1, 0.5:1, and 0.33:1. Therefore, the corresponding samples were denoted AC 1.0, AC 0.5, and AC 0.33. For comparison, pure Ag_3PO_4 particles were prepared by mixing 40 mL of $AgNO_3$ (0.075 mol L^{-1}) with 10 mL of Na_3PO_4 (0.1 mol·L^{-1}) solution directly. In the preparation process of Ag_3PO_4/CuO composites, as shown in Fig. 1, PVP-regulated CuO microspheres were destroyed after the addition of Ag^+, and the obtained CuO nanoparticles were decorated on the surface of the later-generated Ag_3PO_4 particles.

2.4. Catalyst characterization

The crystal structures of the composite catalysts were analyzed using X-ray diffraction (XRD) patterns on a Rigaku D/max-III. The morphologies of Ag_3PO_4/CuO composites were observed using a Zeiss Ultra Plus field emission scanning electron microscope (FESEM) and Hitachi H-800 transmission electron microscope (TEM). UV–Vis absorption spectra were obtained on a UV2550 spectrophotometer. X-ray photoelectron spectra were obtained in order to analyze the composition of the composites on an ESCALABMK II X-ray photoelectron spectrometer (XPS).

2.5. Catalytic activity test

Catalytic activity tests were conducted under visible light irradiation from a 300 W Xe lamp with a UV filter. In each experiment, 0.01 g of as-prepared Ag_3PO_4/CuO sample was dispersed in 10 mL RhB solution (1×10^{-5} mol·l^{-1}) at room temperature. The solution was magnetically stirred in the dark for 0.5 h to ensure the establishment of adsorption-desorption equilibrium between the catalyst and RhB dye. Then, H_2O_2 was added to the solution and continuously stirred under visible light irradiation. 3.0 mL of the solution was suctioned at a regular time interval and centrifuged to remove precipitates, and then the supernatant was analyzed by measuring its UV–Vis absorption spectrum. The catalytic degradation behavior of RhB dye was obtained by recording the variation of its absorption spectrum as a function of irradiation time. The detection experiments concerning oxidizing species in the catalytic processes were also completed by adding a quencher and scavenger of ·OH, $\cdot O_2^-$, and h^+ into the RhB solution prior to the photocatalyst.

3. Results and discussion

3.1. Characteristics of the microstructure of Ag_3PO_4/CuO composites

Fig. 2A presents the XRD patterns of pure Ag_3PO_4 and CuO particles. In reference to standard patterns, the diffraction peaks are assigned to body-centered Ag_3PO_4 (JCPDS No.06-0505) and monoclinic CuO (JCPDS No. 48-1548). As seen in Fig. 2B, Ag_3PO_4 crystals were obtained by the reaction of $AgNO_3$ and Na_3PO_4 solution. The pure Ag_3PO_4 powder did not show uniform surface morphology due to the fast reaction in solution at room temperature, the performance is affected. The catalysis reaction occurs on the surface of the catalyst. The smaller- sized particles expose more active sites. Therefore, the smaller the size of the particles is, the higher the catalysis activity displays. We repeated the preparation experiments of pure Ag_3PO_4 and control the experiment conditions accurately. Consequently, the performance of pure Ag_3PO_4 is repeatable. Micro-spherical CuO particles are formed (Fig. 2C) via a one-step hydrothermal method with PVP as the structure-modulated reagent. It is clear that the CuO microsphere is constructed of nanocrystal building units.

For the three composites with varied molar ratio of CuO to Ag_3PO_4 (Fig. 3A), the XRD results indicate the presence of body-

Please cite this article in press as: P. Ma et al., Ag_3PO_4/CuO composites utilizing the synergistic effect of photocatalysis and Fenton-like catalysis to dispose organic pollutants, Advanced Powder Technology (2017), http://dx.doi.org/10.1016/j.apt.2017.08.004