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Short Communication

Bi_2WO_6/Cu^0: A novel coupled system with enhanced photocatalytic activity by Fenton-like synergistic effect

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ABSTRACT

A novel coupled system of Bi_2WO_6/Cu^0 was successfully designed which combined two different advanced oxidation processes of photocatalysis and Fenton-like for degradation of organic contaminants. The degradation rate of phenol by nanosized Bi_2WO_6/Cu^0 was three times higher than that by bare Bi_2WO_6. The synergistic effect between Bi_2WO_6 and Cu^0 played a crucial role in the enhancement of photocatalytic activity. Moreover, this coupled system exhibited excellent photocatalytic stability and no derivative of Cu^0 was found. The effects of the amount of Cu^0 on improving the catalytic performance were also investigated and the possible mechanism of the synergistic system was proposed.

1. Introduction

Advanced oxidation processes (AOPs), which is defined as aqueous oxidation processes resulting in the destruction of target pollutants primarily based on the intermediacy of hydroxyl radicals, have been widely studied and applied in the degradation of organic compounds [1]. As one of the AOPs techniques with promising potential for environmental application, heterogeneous photocatalysis exhibits great advantages in utilizing solar energy and mineralizing organic pollutants into CO_2 and H_2O [2]. Instead of using a single photocatalysis technology, combination of heterogeneous photocatalysis with other AOPs to produce a synergistic effect has been found to be effective in enhancing the performance of photocatalysis process as well as to be cost-effective [3]. For instance, Fenton reaction was the fastest process among different AOPs techniques according to the comparison in early reports [4]. However, large volumes of iron sludge would be generated in the Fenton process which will prevent the Fenton reaction moving on. Moreover, the narrow range of pH values limits the wide application of Fenton reaction in waste water treatment.

Recently, great efforts have been devoted to overcome the above drawbacks. Among various approaches, it was reported that heterogeneous Fenton system containing iron supported catalysts can induce so-called Fenton-like reaction, such as zero valent iron (ZVI) [5], goethite (α-FeOOH) [6] and ferrihydrite [7]. The application of zero valent metals such as iron, copper, nickel or zinc, has played a significant role in mineralizing organic pollutants in waste water [5]. However, zero valent metals often suffer from decreased performance of degradation with time because of the formation of a surface layer of oxides.

In the present work, we designed a novel composite photocatalyst Bi_2WO_6/Cu^0 with synergistic effect of Fenton-like oxidation processes by immobilizing zero valent metal on the photocatalyst with the purpose of enhancing the degradation rate of the contaminants and eliminating the drawbacks of the conventional zero valent metals. Bismuth tungstate (Bi_2WO_6) has been reported to have potential in visible-light induced photocatalysis process [8]. Considering that the dissolution of iron ions from zero valent iron would depress the photocatalytic property of Bi_2WO_6 [9], herein we introduced zero valent copper (ZVC) instead of the most commonly used ZVI. Moreover, it was also reported that the production rate of hydroxyl radicals in solution by introducing Cu was higher than those by other transition metals such as Ni, Mn, Co *etc.* [10]. Bi_2WO_6 can provide photogenerated electrons for Cu^0 under irradiation, which will prevent the oxidation of Cu^0 and thus the Fenton-like reaction lasts longer. In other words, the photogenerated electrons can be trapped by Cu^0 thus preventing the electron–hole recombination and improving the photocatalysis performance. This coupled system with enhanced activity and excellent stability, not only offers a new idea to improve the activity of photocatalyst, but also inspires us to design new heterogeneous advanced oxidation systems for waste water treatment in practical application.

2. Experimental

The Bi_2WO_6/Cu^0 composite photocatalysts were synthesized in ethylene glycol (EG) by a solvothermal method. In a typical synthesis procedure, $Cu(OH)_2$ precipitation was firstly obtained by

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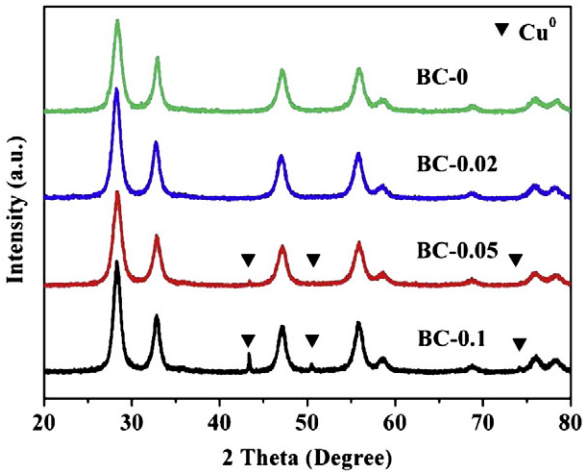

Fig. 1. XRD patterns of the Bi_2WO_6 and Bi_2WO_6/Cu^0 samples with different Cu^0 contents.

mixing $Cu(NO_3)_2$ and NaOH aqueous solutions. After being rinsed with de-ionized water, the fresh precipitate was dispersed in EG. Then $Bi(NO_3)_3 \cdot 5H_2O$ (0.49 g) and $Na_2WO_4 \cdot 2H_2O$ (0.17 g) were mixed together in EG so as to form a transparent solution. Different volume of the $Cu(OH)_2$ suspension was added in order to obtain different molar ratios of Cu^0:Bi_2WO_6 (0, 0.02, 0.05, and 0.1). The final volume of the suspension was adjusted to 40 mL by adding EG. After being stirred for 4 h, the solution was transferred to a 50 mL Teflon-lined autoclave with a stainless steel tank and heated at 160 °C for 18 h. Afterwards, the obtained samples (BC-0, BC-0.02, BC-0.05 and BC-0.1, denoted according to the molar ratio of Cu^0:Bi_2WO_6) were rinsed with de-ionized water and anhydrous ethanol, and then dried at 60 °C for 4 h.

3. Results and discussion

The compositions of the photocatalysts were investigated using XRD measurements. As shown in Fig. 1, Bi_2WO_6 presented orthorhombic phase (JCPDS card No. 39-0256), and Cu^0 as marked presented cubic phase (JCPDS card No. 65-9026). Moreover, neither possible impurities nor changes of the lattice parameters of Bi_2WO_6 in all samples are found, which implies that Cu was on the surface Bi_2WO_6.

The morphology of the Bi_2WO_6/Cu^0 (BC-0.05) sample was investigated by TEM. The panoramic view shown in Fig. 2a indicates that the as-prepared sample is composed of nanoparticles with size of 10–20 nm. A HRTEM image of the same sample is shown in Fig. 2b. The distance between two planes in Bi_2WO_6 particle is about 0.315 nm, which is in good agreement with the *d*-spacing of (131) plane of orthorhombic Bi_2WO_6. The result is well consistent with that of XRD pattern in Fig. 1, where the peak of (131) plane is much stronger compared with those in standard patterns. And the lattice fringes with interplanar spacing of 0.208 nm are also observed, corresponding to the (111) plane of Cu nanoparticles. The copper nanoparticles are in close contact with the Bi_2WO_6 nanoparticles, which is believed to facilitate the electron transfer between the metal and semiconductor [11].

To evaluate the effect of zero valent copper on the photocatalysis performance of the as-prepared Bi_2WO_6/Cu^0 photocatalyst, the degradation of phenol as target pollutant was carried out. The photo-degradation efficiencies of phenol as a function of irradiation time with different molar ratios of Bi_2WO_6/Cu^0 and H_2O_2 with 0.2% volume ratio under visible-light illumination (λ>420 nm) are presented in Fig. 3. The removal of phenol was not observed either by adsorption in dark or by visible-light illumination with H_2O_2, which revealed that all the degradation behavior was attributed to photocatalysis and Fenton-like process. Without the combination of Cu^0 (the BC-0 sample), the photo-degradation rate of phenol by Bi_2WO_6 was quite slow. With the introduction of Cu^0, the removal rate increased significantly. Especially in the first half hour when the catalytic process was dominated by Fenton effect, nearly 60% of phenol was quickly decomposed in the presence of the Bi_2WO_6/Cu^0 photocatalyst. Comparatively the degradation rate is less than 20% in the case of bare Bi_2WO_6 sample.

For different Bi_2WO_6/Cu^0 system, the degradation rate of phenol did not increase linearly with the content of Cu^0. The BC-0.05 sample exhibited the highest photo-degradation activity among all the samples. Photogenerated holes and electrons may be well separated since the electrons generated on the Bi_2WO_6 by light irradiation can be trapped by the reductive reaction of Cu^{2+} formed on the Cu^0 surface. This prevented the formation of surface passivation layer and the reduction of Cu^0 activity, thus extended the lifetime of Cu^0. But it was a contrary case when too much Cu^0 was introduced. There are two accounting reasons for this. For one thing, Cu^0 might transfer into larger crystal/clusters and disperse poorly on the Bi_2WO_6 surface when too much Cu^0 was introduced, which will decrease effective surface sites and lead to light shielding effect. Moreover, core–shell

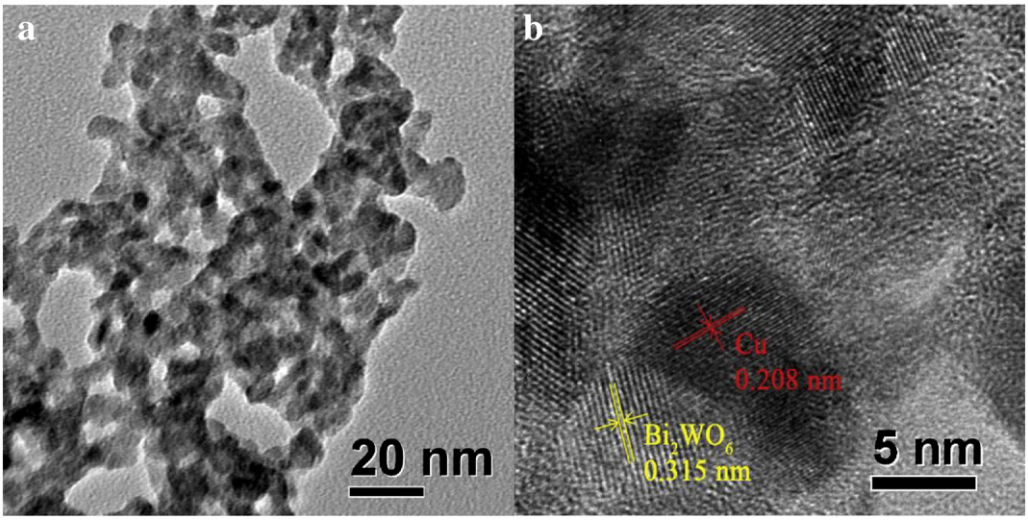

Fig. 2. TEM (a) and HRTEM (b) images of Bi_2WO_6/Cu^0 (BC-0.05) sample.