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ARTICLE TYPE

Cu₂O NPs decorated BiPO₄ photo-catalyst for enhanced organic contaminant degradation under visible light irradiation

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The surface of BiPO₄ was decorated with Cu₂O nanoparticles (NPs) (hereafter designed as Cu₂O/BiPO₄) via an interfacial self-assembly method. The physical and photo-physical properties of the Cu₂O/BiPO₄ hybrid photo-catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray fluorescence spectrometry (XRF), UV-vis diffuse reflectance spectroscopy (DRS) and photo-electro-chemical (PEC). Compared with bare BiPO₄ and Cu₂O, the Cu₂O/BiPO₄ composites exhibited significantly enhanced photocatalytic activity for methylene blue (MB) degradation under visible light irradiation. The 5 wt. % Cu₂O/BiPO₄ showed the highest photocatalytic activity under visible light irradiation, which was about 12.25 times than BiPO₄. Significantly, the superior stability was also observed in the five cyclic runs. The Cu₂O/BiPO₄ hybrid photocatalysts exhibited dramatically enhanced photo-induced electron-hole separation efficiency, which was confirmed by the results of photocurrent measurements. On the basis of the experimental results and estimated energy band positions, the mechanism of enhanced photocatalytic activity was proposed.

1. Introduction

Photo-catalysis uses solar energy to produce hydrogen via water splitting^[1] and degradation of organic pollutants. It possesses the highly desired property of low-cost and environmental friendliness, and has been intensively studied as one of the ways to solve the current global energy and environmental pollution crisis^[2,3]. In the past decade, remarkable progress has been made in TiO₂-based photo-catalyst, and various approaches such as doping with metals^[4], coupling with other semiconductors^[5-7], and anchoring organic dyes^[8] were used to overcome its drawbacks of wide band gap and rapid recombination of photo-generated electrons and holes. However, TiO₂-based photo-catalyst still cannot fully meet the requirement of practical application in environmental cleaning driven by solar energy. Therefore, the development of new and more efficient visible-light-driven (VLD) photo-catalysts is still urgently needed for the efficient harvest of solar energy^[9].

BiPO₄ is a newly discovered photo-catalyst with more attractive UV light activity than TiO₂ (P25)^[10, 11] and it has attracted increasing interest in the past few years^[12-15]. It is not only efficient in de-coloration of dye, but also superior in mineralization of the difficult degradable phenol. Therefore, BiPO₄ is a promising photo-catalyst and has much potential in remediation of environment. However, similar to TiO₂, BiPO₄ is also a wide band gap (4.1 eV) photo-catalyst and the quantum efficiency is not high enough to meet the requirement of industrial application^[16]. Thus, it still needs to improve the photo-performances of BiPO₄ photo-catalyst. It is a key point to increase its quantum efficiency and extend its light absorption range. In the past few decades, several narrow band gap semiconductors such as AgI^[17], BiOCl^[18] and BiVO₄^[19] were

coupled with BiPO₄, and it was found that the photocatalytic activities of the composites were significantly improved under visible light. Actually, fabrication of heterostructured materials containing BiPO₄, such as AgBr/BiPO₄^[20], Ag₃PO₄/BiPO₄^[21,22], C₃N₄/BiPO₄^[23], and BiOI/BiPO₄^[24] could significantly accelerate the separation of the photogenerated carrier charges and enhance the photocatalytic performance of BiPO₄. However, the point contact caused by these bulk phase recombination could lead to low conjunction of BiPO₄ with semiconductors, which could limit the photo-induced charge separation.

In order to further meet the needs of practical applications of BiPO₄ in photo-catalysis, nanoparticles modified semiconductor composites had attracted more and more attention recently, because the recombination of electron and hole was greatly inhibited due to the small size of nanoparticle, thus the quantum efficiency of BiPO₄ was dramatically improved by CdS^[25,26] nanoparticles and BiPO₄ could suppress the agglomeration of nanoparticles^[27] have an excellent dispersion and larger specific surface area. Therefore, the obtained high semiconductor contact area separated the photo-generated charges and improved photocatalytic. However, the toxic Cd ion could be released in water to pollute the environment.

Cu₂O photocatalysts have been widely studied for their excellent visible-light-driven photocatalytic activity for hydrogen evolution from water^[28], photocatalytic reduction of CO₂^[29] and organic pollutants, because of its direct band gap of 2.0 eV, low toxicity, abundance and low cost^[30]. Importantly, recent works have led to the development of Cu₂O-based composite photocatalysts with efficient visible light absorption and suppression of recombination of photogenerated charge carriers^[31,32]. For example, 10 nm Cu₂O nanoparticles^[33,34] had been loaded on TiO₂ Nano-sheets and multiwall carbon nanotubes to improve the photocatalytic activity, in which Cu₂O nanoparticles not only

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enhanced the light absorption but separated the photo-generated carriers, thus to improve the photocatalytic performance of TiO₂ and multiwall carbon nanotubes. Herein we report the synthesis of novel and stable Cu₂O/BiPO₄ photo-catalysts for improved visible-light responsive photo-catalysis, in which Cu₂O extended the visible light absorption. Compared with Cu₂O/Au/BiPO₄^[35], Cu₂O/BiPO₄ composites was the most studied photocatalysts for the low cost, the amazing and controllable morphology, and the higher photocatalytic activity. Additionally, the improved photocatalytic performance was due to the synergistic effect of large contact area, specific energy band structure and enhanced charge separation at the interface of Cu₂O and BiPO₄.

2. Experimental

2.1 Synthesis of BiPO₄

All reagents were analytical grade and used without further purification. Typically, Bi(NO₃)₃•5H₂O (3 mmol) was dispersed in distilled water with magnetic stirring at room temperature for 5 min. NaH₂PO₄•2H₂O (3 mmol) was added into the Bi(NO₃)₃ solution with vigorous stirring, leading to a white precipitate. After 30 min, the obtained slurry was then transferred into a 150 mL Teflon-lined autoclave and maintained at 160°C for 24 h. The reactor was then allowed to cool to room temperature naturally. The precipitate was collected and washed with distilled water, and the final products dried at 60°C for 12 h.

2.2 Fabrication of Cu₂O/BiPO₄ composite

0.5 g of BiPO₄ powder and ethylene diamine tetraacetic acid (EDTA) were dissolved into deionized water at room temperature. Cu(Ac)₂ (0.0705 g) was then added into the solution. After 30 min of continuous stirring, NaOH solution (20 mL, 0.45 mol/L) were dropped into the solution. Then, 20 mL hexadecyl trimethyl ammonium bromide (CTAB) and ascorbic acid (AA) solution were added to the obtained blue solution drop wise and the color slowly turned to red. The generated Cu₂O/BiPO₄ was washed with distilled water and absolute ethanol to remove the surfactant, and dried under vacuum. With nominal weight ratios of Cu₂O over BiPO₄ of 1, 3, 5, 7 and 9wt%, the final samples were denoted as 1wt% Cu₂O/BiPO₄, 3wt% Cu₂O/BiPO₄, 5wt% Cu₂O/BiPO₄, 7wt% Cu₂O/BiPO₄ and 9wt% Cu₂O/BiPO₄ respectively.

The sample named M-Cu₂O/ BiPO₄ was prepared by the direct mechanical mixing of Cu₂O and BiPO₄ in an agate mortar.

2.3 Photocatalyst characterization

Crystal structures of these prepared samples were characterized with X-ray diffraction (XRD) on a Rigaku D/MAX2500 PC diffractometer with Cu K α radiation, an operating voltage of 40 kV and an operating current of 100 mA. Morphologies of these samples were investigated with scanning electron microscope (SEM) (Hitachi, s-4800), energy dispersive X-ray spectroscopy (EDX) and transmission electron-microscopy (TEM) (JEOL Ltd., JEM-2010). UV-vis light (UV-vis) diffuse reflectance spectra were recorded on a UV-Vis spectrometer (Puxi, UV1901). Their chemical compositions were determined with an X-ray fluorescence spectrometer (XRF, Rigaku, and ZSX Promisll). Surface areas were determined with Brunauer-Emmett-Teller

(BET) method based on the N₂ adsorption and desorption isotherms on a Quantachrome Nova 4200e automatic analyzer (USA). Chemical states of these photocatalysts were analyzed with X-ray photoelectron spectroscopy (XPS) on a XSAM800 apparatus. The photocurrent measurements were conducted by using an electrochemical analyzer (CHI660E, Chen Hua Instruments, Shanghai, China) with a standard three-electrode configuration. A standard three-electrode cell with a working electrode (as-prepared photocatalyst), a platinum wire as counter electrode, and a standard calomel electrode (SCE) as reference electrode were used in the photoelectric studies. 0.1 M Na₂SO₄ was used as the electrolyte solution.

2.4 Photocatalytic activity

The photocatalytic activities of Cu₂O/BiPO₄ composites were evaluated with its catalytic degradation of MB under irradiation of visible light. A 250 W halide lamp (Philips) with a 420 nm cutoff filter was located at a distance of 10 cm from an unsealed beaker for the first test group. A glass reactor with 25±2 °C circulating water flowing outside was employed for the secondary test group. For each test, 0.1 g catalyst powder was added into 100 mL 10 mg/L MB solution. The test solutions were stirred in the dark for 30 min before irradiated under the visible light. During the irradiation, a 3 mL sample of the reaction suspension was taken every 5 minutes and centrifuged at 10000 rpm for 6min. The supernatant was collected and analyzed on the UV-vis spectrophotometer.

Additionally, in the degradation of BPA, HPLC was used to check the reaction procedure.

3. Result and discussion

3.1. Characterization of catalysts

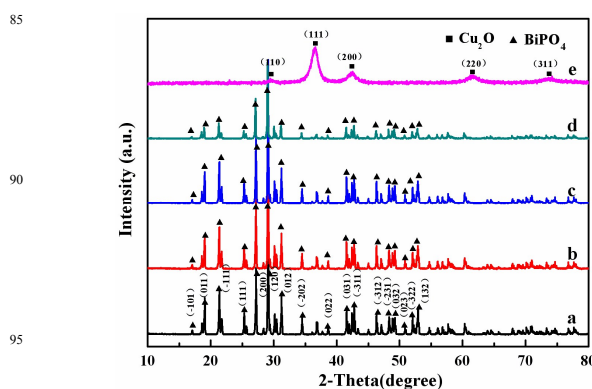


Fig. 1. XRD patterns of photo-catalysts: (a) BiPO₄, (b) Cu₂O (3 wt. %) / BiPO₄, (c) Cu₂O (5 wt. %) / BiPO₄, (d) Cu₂O (7 wt. %) / BiPO₄, (e) Cu₂O, respectively.

The crystal structure of the product was characterized by X-ray diffraction (XRD). The typical X-ray diffraction (XRD) spectrum of Cu₂O is presented in Fig 1. It shows five peaks, with 2 θ values of 29.6°, 36.5°, 42.4°, 61.5° and 73.7°, corresponding to the crystalline Cu₂O (JCPDS 65-3288), respectively^[30]. Diffraction characteristic peaks of BiPO₄ and the as-prepared Cu₂O/BiPO₄ at 2 θ values of 19.0°, 21.4°, 27.1°, 29.1° and 31.2° could be assigned to (011), (111), (200), (120) and (012) crystal planes of rhombic BiPO₄ (JCPDS15-0767)^[36]. Diffraction peaks

of $\text{Cu}_2\text{O}/\text{BiPO}_4$ composites were similar to those of BiPO_4 , indicating that the introduction of Cu_2O did not change the BiPO_4 crystal structure. However, no peaks of Cu_2O were detected because Cu_2O contents in the composites were too low with uniform dispersion in the petal structure of BiPO_4 [37].

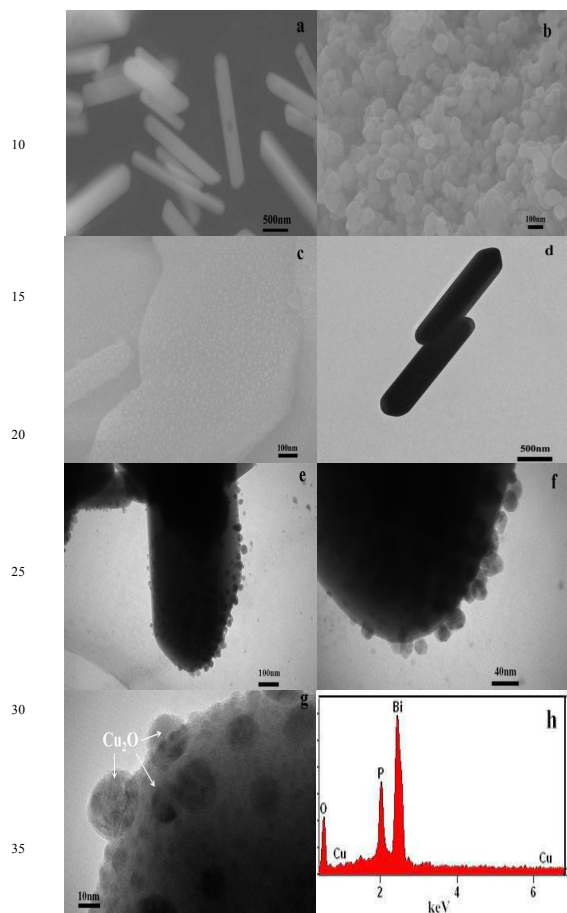


Fig. 2. SEM images of prepared photo-catalysts (a) BiPO_4 ; (b) Cu_2O ; (c) 5 wt.% $\text{Cu}_2\text{O}/\text{BiPO}_4$; (d, e) TEM of BiPO_4 and 5 wt.% $\text{Cu}_2\text{O}/\text{BiPO}_4$; (f) EDX images of 5wt% $\text{Cu}_2\text{O}/\text{BiPO}_4$

The morphologies and microstructures of the as-synthesized samples were further investigated by SEM, TEM, HRTEM and EDX. As shown in Fig. 2a, pure BiPO_4 was of nanorod structure with smooth and clean surface [38]. The pure Cu_2O was observed as shown in Fig. 2b, and its morphology was comprised of irregular spherical particles of about 50-100 nm. As shown in Fig. 2c, Cu_2O with a size of 20 nm were uniformly dispersed on the surface of the BiPO_4 nanorod with an intimately contact, and did not affect the crystal structure of the BiPO_4 . Pure BiPO_4 (Fig. 2d) is made up of irregularly nanorods with a smooth surface. The TEM image of $\text{Cu}_2\text{O}/\text{BiPO}_4$ (Fig. 2e) clearly shows that some Cu_2O nanoparticles with diameter of less than 20nm were uniformly deposited on the smooth surface of BiPO_4 nanorods. With the further increase of the magnification, the Cu_2O nanoparticles can be clearly observed distributing on the surface of BiPO_4 , as shown in Fig. 2f. Fig. 2g shows the HRTEM microscopic morphology of the Cu_2O on the surface of BiPO_4 under high magnification. In the EDX spectrum of $\text{Cu}_2\text{O}/\text{BiPO}_4$ composite as shown in Fig. 2h, Bi, P, Cu and O peaks were observed. Additionally, elemental composition of the composite nameplates was further analyzed with XRF as listed in Table 1 with the $\text{Cu}_2\text{O}/\text{BiPO}_4$ ratio of 0.044:1, which was less than the

theoretical ratio of 0.05:1 of the 5 wt% $\text{Cu}_2\text{O}/\text{BiPO}_4$ composite, indicating the Cu_2O was deposited on the BiPO_4 with partial lose during the preparation.

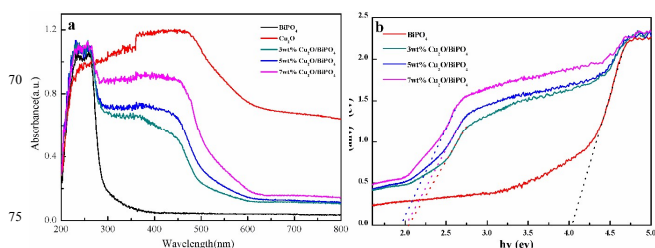


Fig. 3. (a) UV-vis diffuse reflection spectra of the samples and (b) the band gap energies of BiPO_4 and $\text{Cu}_2\text{O}/\text{BiPO}_4$.

Fig. 3 shows the UV-vis diffuse reflectance spectra of the as-prepared photo-catalysts. The absorption edge of pure BiPO_4 photo-catalysts was about 320 nm, with band gap (E_g) calculated to be 4.1 eV [39]. Compared with pure BiPO_4 , all $\text{Cu}_2\text{O}/\text{BiPO}_4$ samples exhibited a spectral response in the visible light region due to photosensitizing effect of the incorporated Cu_2O . Furthermore, the absorption intensity was gradually increased with the increase of Cu_2O content, which confirmed that the $\text{Cu}_2\text{O}/\text{BiPO}_4$ samples could be excited to produce more electron-hole pairs under the same visible light irradiation with higher photo-catalytic performance. In addition, the band gap energies were calculated from a plot $(\alpha hv)^{1/2}$ versus photoenergy (hv) using the Kubelka-Munk function which shows the relationship of band gap E_g and absorption coefficient α . The equation is as follows: $\alpha hv = A(hv - E_g)^{1/2}$, where α is the absorption coefficient, v is the frequency of the light, and h is Planck's constant. The Tauc plot, $(\alpha hv)^{1/2}$ versus hv is shown in Fig. 3. The estimated band gap of the single BiPO_4 and as-synthesized $\text{Cu}_2\text{O}/\text{BiPO}_4$ was about 4.1 eV, 2.1eV, 2.0 eV, 1.9 eV, respectively. Therefore, it can be inferred that the introduction of Cu_2O is beneficial to improve the light absorption of BiPO_4 .

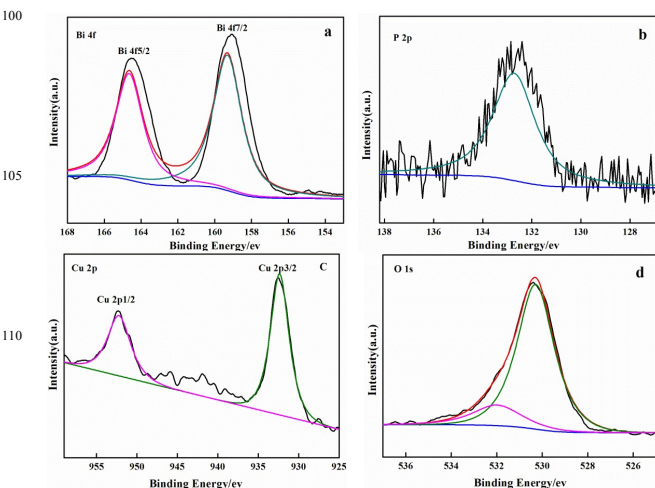


Fig.4 XPS spectra of (a) survey spectrum, (b) P, (c) Cu, (d) O of the sample 5 wt.% $\text{Cu}_2\text{O}/\text{BiPO}_4$.

Fig. 4 shows the XPS scan spectra of the $\text{Cu}_2\text{O}/\text{BiPO}_4$ (5 wt. %) composite. The results indicated the presence of Bi, P, Cu and O in the $\text{Cu}_2\text{O}/\text{BiPO}_4$ (5 wt. %) composite. except of the C element from the sample fabrication and/or the XPS instrument itself.

High resolution spectra of Bi 4f, P 2p, Cu 2p, and O 1s are shown in Fig. 4a-d. In Fig. 4a, the characteristic peak at 159.31 eV and 164.64 eV are ascribed to Bi 4f7/2 and Bi 4f5/2, which confirms that the chemical state of Bi in the samples is +3^[40]. In Fig. 4b, the peaks of P 2p at 132.8 eV were due to the PO₄³⁻ in BiPO₄^[17]. Fig. 4c displays the Cu 2p core level spectrum. The Cu 2p3/2 and Cu 2p1/2 spin-orbital photoelectrons were located at binding energies of 932.34 eV and 952.22 eV, respectively, which are in good agreement with the reported values of Cu₂O^[41]. XPS O1s peaks can be fitted into two peaks located at ca. 530.1 eV and 532.2 eV (Fig 4d), which are attributed to the lattice oxygen of Cu₂O, BiPO₄ and surface-adsorbed oxygen species (O₂ or H₂O), respectively^[42].

3.2 Photocatalytic activity

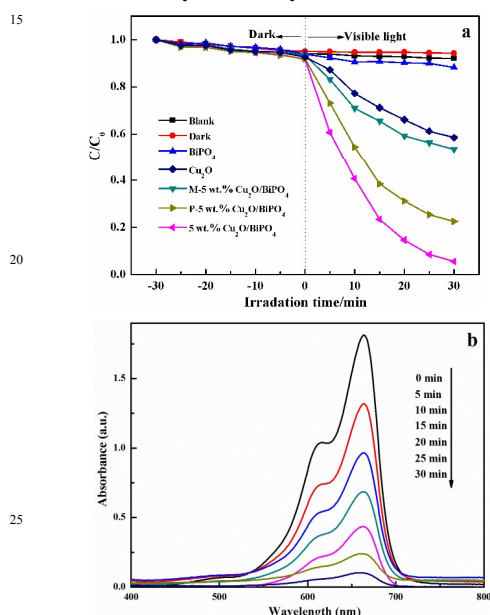


Fig.5. (a) Comparison of photocatalytic activities over different samples, (b) Degradation curves of MB solution over 5 wt. % Cu₂O/BiPO₄ under visible light

The photocatalytic degradation of MB molecules was used to evaluate the photocatalytic activity of samples under visible light irradiation. Prior to light illumination, the reaction mixture was stirred for 30 min in darkness in order to reach adsorption/desorption equilibrium between dye and catalyst. As can be seen from Fig. 5a, the concentration of MB was almost unchanged in the dark controls, indicating that the dye adsorbed capacity of photocatalyst composite can be ignored. As shown in Fig. 5a, only slightly degraded of MB by the pure BiPO₄, indicating that the photolytic degradation was negligible. In contrast, the Cu₂O/BiPO₄ exhibited good photocatalytic degradation activity under visible light irradiation, 5 wt. % Cu₂O/BiPO₄ degraded nearly 98% of MB after 30 min irradiation. However, the same material prepared by precipitation degraded only 77.4% of MB after irradiation 30 min. The difference observed was thought to be attributed to prepared via an interfacial self-assembly method, resulting in their relatively higher photocatalytic activity. The absorption changes for the MB solution in the presence of 5 wt.% Cu₂O/BiPO₄ catalyst during

the photocatalytic process is shown in Fig.5b. the absorption peak was significantly decreased after 30 min.

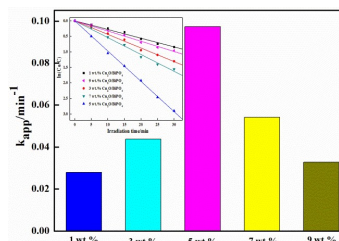


Fig. 6. Comparison of degradation of MB over Cu₂O/BiPO₄ composite with various Cu₂O contents of 1.0 wt.%, 3.0 wt.%, 5.0 wt.%, 7.0 wt.% and 9.0 wt.%.

The photocatalytic degradation rate constants (k) of Cu₂O/BiPO₄ composites are shown in Fig. 6. As shown in Fig. 6, the reaction rate constant k for the photocatalytic degradation of MB with Cu₂O/BiPO₄ composites containing 1 wt.%, 3 wt.%, 5 wt.%, 7 wt.% and 9 wt.% Cu₂O was 0.02798, 0.04374, 0.09739, 0.05416, 0.03289 min⁻¹, respectively. The sample prepared using a loading of 5 wt. % exhibited the highest photodegraded efficiency (0.09739 min⁻¹), and was thought to represent an optimal loading contributing to good particle dispersion and high photocatalytic activity. Once the loading of Cu₂O increased beyond a critical value, the nano-clusters of Cu₂O species were thought to agglomerate and shade the active sites on the surface of BiPO₄, resulting in a lower degradation rates. Therefore, an optimal Cu₂O loading amount on BiPO₄ existed, and was found to be 5 wt. % in this study. The specific surface area is an important factor to determine the adsorptive capability of the photo-catalysts toward organic contaminant (Table2). From the results of the nitrogen sorption tests, the specific surface area of pure BiPO₄, 3 wt. % Cu₂O/BiPO₄, 5 wt. % Cu₂O/BiPO₄, 7 wt. % Cu₂O/BiPO₄, and M-5 wt. % Cu₂O/BiPO₄ was calculated to be 2.79, 4.73, 6.37, 5.31, and 6.92 m²/g⁻¹, respectively. It is widely accepted that the larger specific surface areas could provide more reactive center sites and absorb more reactants, resulting in an improved photocatalytic activity. However, there was no significant difference between the samples in this system, which could be assumed that BET is not the main influence factor for the photocatalytic activity.

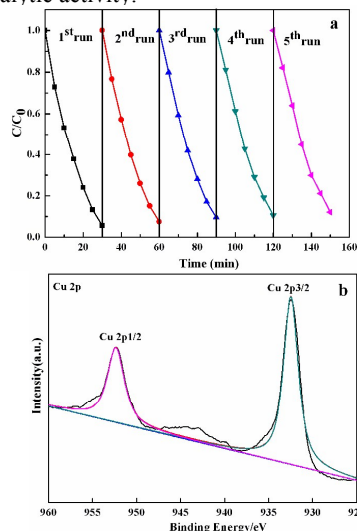


Fig.7. Recycling runs (a) of the degradation of MB over 5 wt. % $\text{Cu}_2\text{O}/\text{BiPO}_4$ composite under visible-light irradiation ($\lambda > 420$ nm). (b) and Cu 2p XPS spectra after photocatalytic reaction. The stability and reusability of $\text{Cu}_2\text{O}/\text{BiPO}_4$ hybrid photocatalysts were evaluated by the cycling photocatalytic degradation experiment, and the results are shown in Fig. 7. The results show that after five cycles, only slightly diminished degradation efficiency was observed, 5 wt.% $\text{Cu}_2\text{O}/\text{BiPO}_4$ retained over 89% of its original photocatalytic activity after five successive runs under the same experimental conditions, indicating the high stability of the catalyst during photocatalytic reaction. This decrease was thought to be due to some catalyst washout during the recovery steps, which could be minimized through the use of centrifugation between runs. Therefore, the results obtained illustrate that the incorporation of Cu_2O into the BiPO_4 matrix not only enhance the visible light photocatalytic performance of BiPO_4 , but also promote the stable-durability of the composites. To evaluate the structural stability, the crystalline structures of $\text{Cu}_2\text{O}/\text{BiPO}_4$ nanocomposite after experiments were studied (as shown in Fig. 7). In Fig. 7b, the two peaks in the spectra of Cu_2O appearing at 932.34 and 952.2 eV could be ascribed to the binding energies of Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. After the photocatalytic reaction, the Cu 2p_{3/2} and Cu 2p_{1/2} peaks of Cu_2O showed no obvious decrease and shift. The result imply no obvious of metallic Cu was found in the process of photocatalytic reaction.

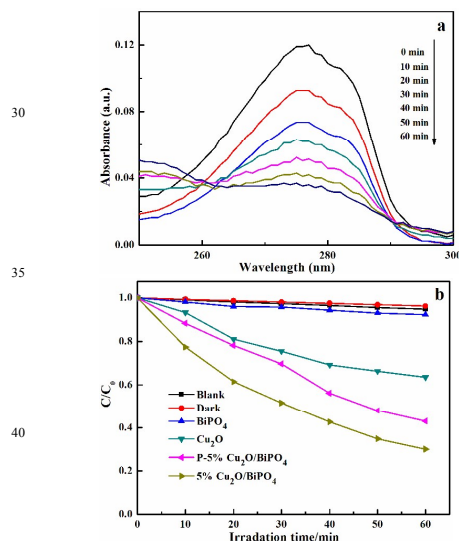


Fig.8 (a) Degradation curves of BPA solution over 5 wt. % $\text{Cu}_2\text{O}/\text{BiPO}_4$ irradiated under visible light; (b) Comparison of photocatalytic activities over different samples. BPA is a colorless organic compound and used as another model contaminant to investigate the photocatalytic activity for eliminating the photosensitization during the photocatalytic reactions. In order to evaluate the photocatalytic activity of $\text{Cu}_2\text{O}/\text{BiPO}_4$, the degradation of BPA was studied under various conditions, to assess the effect of photo-catalysis on the overall degradation rate for an initial concentration of 10mg/L with 50 mL. As displayed in Fig. 8a, the absorption of BPA in the visible light significantly decreases with the increase of irradiation time

and nearly disappears after 1h. The characteristic absorption peak at 278 nm was employed to determine the degradation degree of BPA, and the C/C_0 versus irradiation time was plotted in Fig. 8b. The experimental results indicated that the concentration of BPA was almost unchanged in the dark control for 30 min, which confirmed that BPA could not be degraded under irradiation. The BPA degradation rates were 70% and 58% over 5 wt. % $\text{Cu}_2\text{O}/\text{BiPO}_4$ and P-5 wt. % $\text{Cu}_2\text{O}/\text{BiPO}_4$ under visible light, respectively. By comparison of the BPA degradation rates, the photo-catalytic activity of 5wt. % $\text{Cu}_2\text{O}/\text{BiPO}_4$ was confirmed for the degradation of BPA, and affirmed that the disappearance of BPA molecules was due to photocatalytic degradation instead of only to adsorption.

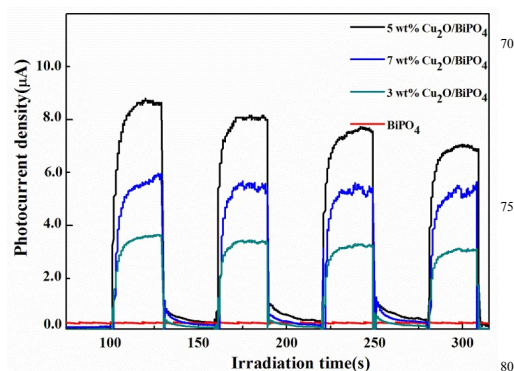
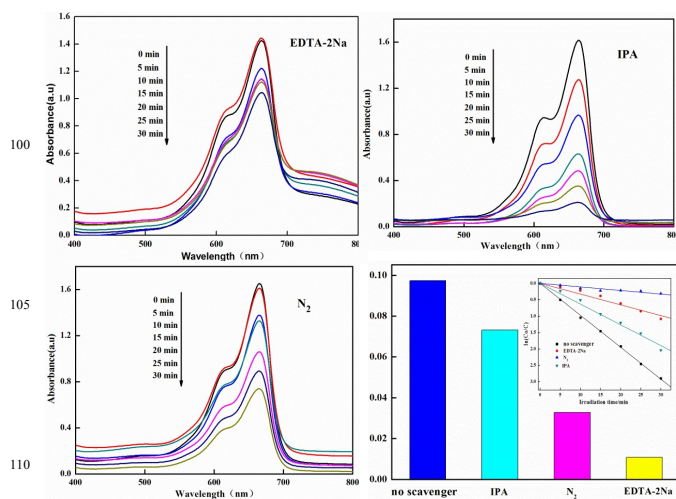


Fig. 9 Transient photocurrent of BiPO_4 and $\text{Cu}_2\text{O}/\text{BiPO}_4$ under visible light irradiation.

Photocurrent is an effective method to reflect the generation, separation and migration efficiency of photo-generated carriers. It can be seen from Fig. 9 that pure BiPO_4 almost shows no photocurrent response under visible light because of the large band gap (4.1 eV), as the content of Cu_2O increased, the photocurrent increased then decreased, which had a positive correlation with the photocatalytic activity on the whole. The 5wt% $\text{Cu}_2\text{O}/\text{BiPO}_4$ composite sample shows the highest photocurrent density, indicating the efficient photo-generated charge transfer between Cu_2O and BiPO_4 . Thus, the sample 5wt% $\text{Cu}_2\text{O}/\text{BiPO}_4$ may achieve the most effective charge separation, which is consistent with the photocatalytic-activity measurements and our above discussions.



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Fig. 10. Photocatalytic degradation of MB over 5 wt. % $\text{Cu}_2\text{O}/\text{BiPO}_4$ in the presence of IPA, EDTA-2Na, N_2 and in the absence scavengers.

As shown in Fig. 10, EDTA-2Na, IPA and N_2 were added as an h^+ , $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ scavenger to the reaction liquid^[43-45], respectively. Results indicated that $\bullet\text{OH}$ were not the dominant active species in this process. In contrast, the introduction of EDTA-2Na had a significant effect on the k_{app} compared to that without scavenger, suggesting that h^+ was a dominant reactive species. The degradation efficiency of MB was also reduced significantly upon the introduction of N_2 , indicating that $\bullet\text{O}_2^-$ also played a large role in the photocatalytic degradation. Therefore, the photocatalytic process might be mainly governed by direct holes and $\bullet\text{O}_2^-$ oxidation reaction.

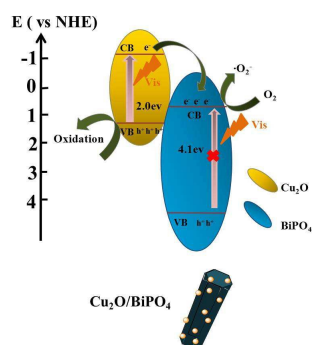


Fig.11 Schematic diagram of charge separation in a visible light irradiated $\text{Cu}_2\text{O}/\text{BiPO}_4$ composite (MB, 10 mg/L, $\lambda > 420$ nm, PH=6).

The energy match between two semiconductors is responsible for the efficient generation and separation process of the electron-hole pairs. A schematic for electron-hole separation and transportation at the $\text{Cu}_2\text{O}/\text{BiPO}_4$ photo-catalyst interface is shown in Fig. 11. The band gap of BiPO_4 and Cu_2O is 4.1 eV^[46] and 2.0 eV^[47], respectively. Therefore, BiPO_4 cannot be excited under visible light. Cu_2O absorbs the visible light and produces the photo-generated electron-hole pairs. Because the CB edge potential of Cu_2O (-1.16 eV) is more negative than that of BiPO_4 (0.5 eV), and the VB of BiPO_4 (4.6 eV) is more positive than that of Cu_2O (0.84 eV), the photo-generated electron on the CB of Cu_2O can transfer easily to CB of BiPO_4 , leaving the holes on the Cu_2O valence band. The photo-induced electrons transferring from the CB of Cu_2O to that of BiPO_4 are trapped by the adsorbed O_2 on the surface of the photo-catalyst, and then produce $\bullet\text{O}_2^-$. The $\bullet\text{O}_2^-$ are active species, which can easily decompose the MB dye. Through the above process, the photo-generated carriers can be separated efficiently and the photocatalytic activities of $\text{Cu}_2\text{O}/\text{BiPO}_4$ photo-catalyst can improve greatly. So, the enhancement of the visible light photocatalytic activity involves two major factors. One is due to the absorption improvement from the Cu_2O . The other is due to the separation efficiency improvement of the photo-generated carriers coming from the well-matched band gap between Cu_2O and BiPO_4 .

4. Conclusions

We have successfully synthesized $\text{Cu}_2\text{O}/\text{BiPO}_4$ hybrid photocatalysts by an interfacial self-assembly method. Enhanced visible-light photo-catalysis was achieved due to the synergistic effect between BiPO_4 and Cu_2O and high utilization of visible light. The 5wt% $\text{Cu}_2\text{O}/\text{BiPO}_4$ composites exhibited excellent visible-light-driven catalytic activity which degraded nearly 98% of MB after 30 min irradiation with good stability in photocatalysis recycling. The enhanced photocatalytic activity and increased photostability are likely due to the synergic effect of BiPO_4 and Cu_2O . Their matched band structures can effectively accelerate the charge separation and electron transfer from Cu_2O to BiPO_4 . Furthermore, the proposed mechanisms for the photocatalytic process may also provide some ideas for the future design of new photo-catalysts.

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Notes and references

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Cu₂O NPs decorated BiPO₄ photo-catalyst for enhanced organic contaminant degradation under visible light irradiation

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Graphical abstract:

