Surface Decoration of ZnWO$_4$ Nanorods with Cu$_2$O Nanoparticles to Build Heterostructure with Enhanced Photocatalysis

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Received: 1 December 2017; Accepted: 28 December 2017; Published: 9 January 2018

**Abstract:** The surface of ZnWO$_4$ nanorods was decorated with Cu$_2$O nanoparticles (Cu$_2$O/ZnWO$_4$) prepared through a precipitation method. The Cu$_2$O nanoparticles were tightly deposited on the ZnWO$_4$ surface and had average diameters of 20 nm. The nanoparticles not only promoted the absorption and utilization of visible light but also facilitated the separation of photogenerated charge carriers. This brought an improvement of the photocatalytic activity. The 5 wt % Cu$_2$O/ZnWO$_4$ photocatalyst displayed the highest degrade efficiency for methylene blue (MB) degradation under visible light, which was 7.8 and 2 times higher than pure ZnWO$_4$ and Cu$_2$O, respectively. Meanwhile, the Cu$_2$O/ZnWO$_4$ composite photocatalyst was able to go through phenol degradation under visible light. The results of photoluminescence (PL), photocurrent, and electrochemical impedance spectra (EIS) measurements were consistent and prove the rapid separation of charge, which originated from the match level structure and the close contact with the interface. The radical and hole trapping experiments were carried out to detect the main active substances in the photodegradation process. The holes and ·O$_2$•$^-$ radicals were predicted to dominate the photocatalytic process. Based on the characterization analysis and experiment results, a possible photocatalytic mechanism for enhancing photocatalytic activity was proposed.

**Keywords:** nanoparticles; ZnWO$_4$; degradation; photocatalysis

1. Introduction

Photocatalytic technology can directly use solar energy to degrade organic pollutants using super oxidation capacity, mild reaction conditions, and no secondary pollution. The development of an efficient semiconductor photocatalyst plays an important role in the practical application of photocatalytic technology [1]. Recently, ZnWO$_4$ received widespread attention due to its excellent performance in degrading organic pollutants under ultraviolet light [2,3]. Meanwhile, the ZnWO$_4$ photocatalyst also has the advantages of stable chemical properties and is easy to develop. However, the pure ZnWO$_4$ photocatalyst suffers from a higher photogenerated charge recombination rate and a low utilization rate of sunlight, which severely limits its practical application ability [4,5]. Therefore, the key problem for improving the photocatalytic performance of ZnWO$_4$ is to boost the rapid separation of photo-generated electron-hole pairs on the basis of efficient utilization of solar energy.

Noble metal decorated ZnWO$_4$ can promote the rapid separation of photogenerated charge through the schottky barrier since the Fermi level of noble metal is more positive than ZnWO$_4$ [5,6]. Additionally, ion doping, such as seen in fluorine and chlorine [7–10], could greatly enhance photocatalytic performance since the doped atoms can act as electron traps and promote photogenerated charge separation. In addition, construction of heterojunction photocatalyst by combining ZnWO$_4$ with other semiconductors, such as Bi$_2$WO$_6$/ZnWO$_4$ [11], ZnWO$_4$/BiOI [12], and BiOBr/ZnWO$_4$ [13], provides...
a feasible route to facilitate the effective transmission of the charge through interfacial interfaces. Additionally, by combining ZnWO$_4$ with material that has a $\pi$–$\pi$ conjugated structure like C$_3$N$_4$ [14,15] and graphene [16] could effectively inhibit the combination of photo-generated carriers due to the special conductivity of the conjugate material. Recently, Niu [17] and Li [18] prepared Ag/AgCl and Ag@AgBr nanoparticles decorate ZnWO$_4$ nanorods, respectively, to obtain more visible light utilization efficiency for the surface plasmon resonance of Ag nanoparticles. In addition, surface modification of ZnWO$_4$ with narrow band-gap and matching energy level semiconductors not only improved the visible light response but promoted the separation of the photogenerated charges.

As commonly known, Cu$_2$O can absorb the most visible light for the band gap at about 2.2 eV [19] when using Cu$_2$O nanoparticles modified for the wide bandgap semiconductor. Modifications such as TiO$_2$ [20], BiVO$_4$ [21], and BiOBr [22] can greatly enhance the absorption of visible light on the composite. Moreover, based on the morphology, the grain size of the catalyst has an important influence on the activity. Various morphologies of Cu$_2$O can be prepared through multiple methods [23] and exhibit excellent photocatalytic performance. Some studies have pointed out that Cu$_2$O nanoparticles were recently modified on the TiO$_2$ nanosheets or multi-walled carbon nanotubes not to enhance the light absorption but to improve the separation of the photogenerated carriers. This generates a higher photocatalytic performance [24,25]. Considering the criteria, this action loaded the Cu$_2$O nanoparticles onto the surface of the ZnWO$_4$ nanorods to further improve the utilization rate of visible light and then stimulate production of more electron–holes. Meanwhile, the match between the level structure and the intimately contacted interface of ZnWO$_4$ and Cu$_2$O are beneficial for accelerating the separation of the photogenerated charge carriers, which improves the photocatalytic activity. In fact, there are no previous studies about using Cu$_2$O nanoparticles to decorate ZnWO$_4$ nanorods.

Herein, we modified Cu$_2$O nanoparticles onto the surface of ZnWO$_4$ nanorods. The Cu$_2$O nanoparticles were tightly deposited on the ZnWO$_4$ surface with average diameters of 20 nm. Our results proved that the Cu$_2$O nanoparticles greatly promoted the absorption and utilization of visible light. Meanwhile, the introduction of Cu$_2$O nanoparticles provides a new channel for charge transfer. This greatly inhibited photo-generated carrier recombination and accelerated the migration of interfacial charge carriers. The effects of different Cu$_2$O nanoparticles content on the visible light absorption and charge separation of the composites were investigated. The 5 wt % Cu$_2$O/ZnWO$_4$ photocatalyst displays the highest degrade efficiency for methylene blue (MB) degradation, which was 7.8 and 2 times more than seen in pure ZnWO$_4$ and Cu$_2$O. Based on the characterization analysis and experiment results, a possible photocatalytic mechanism on enhancement of photocatalytic activity was proposed.

2. Experimental

2.1. Synthesis of Photocatalysts

The catalyst is prepared with deionized water. The activity test process uses ultrapure water. All of the reagents are analytically graded. Initially, the synthesis of ZnWO$_4$ was carried out using the hydrothermal method based on previous work [26]. Typically, Na$_2$WO$_4$·2H$_2$O (3 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (3 mmol) were dispersed in 25 mL distilled water with magnetic stirring for 15 min. Then, the two above aqueous solutions were mixed together through magnetic stirring at room temperature for 30 min. Afterward, the mixture was transferred into a Teflon-lined steel autoclave and the autoclaves were heated in a convection oven at 180 °C for 12 h. The resulting precipitates were collected and washed with deionized water and absolute ethanol. The samples were then dried at 80 °C for 10 h.

Then, Cu$_2$O/ZnWO$_4$ composite was prepared using a simple reductive solution chemistry route based on a previous report [22]. First, measured amounts of cetyl trimethyl ammonium bromide (CTAB) and ethylene diamine tetra acetic acid (EDTA) were dissolved in 50 mL deionized water and stirred until a stable suspension was obtained. Then, 0.5 g ZnWO$_4$ was added into the uniform
suspension and stirred for 30 min, followed by the addition 0.06 g Cu(Ac)$_2$. Thirty minutes later, 25 mL NaOH solution (0.45 mol·L$^{-1}$) was added dropwise to the mixed solution. The color of the solution became blue, demonstrating the formation of Cu(OH)$_2$. After 30 min, the solution color slowly turned to orange by adding 25 mL of ascorbic acid (AA) (0.3 mol·L$^{-1}$) solution dropwise. Finally, composites were washed with ethanol and water and dried at 60 °C for 6 h to obtain Cu$_2$O/ZnWO$_4$.

2.2. Characterization

The crystal structure and phase analysis of the Cu$_2$O/ZnWO$_4$ composite was analyzed through X-ray diffraction (XRD) using a Rigaku D/MAX2500 PC diffractometer (D/MAX2500 PC, Rigaku Corporation, Tokyo, Japan) with Cu K$_\alpha$ radiation, with an operating voltage of 40 kV and an operating current of 100 mA. The morphology and particle size of the catalyst were observed through transmission electron microscopy (TEM, JEM-2010, JEOL Ltd., Akishima, Japan). The UV-visible light (UV-Vis) was used to determine the light absorption properties of the catalyst (Puxi, UV1901, Beijing, China). The surface chemical state was analyzed by an X-ray photoelectron spectrocope (XPS, Shimadzu Kratos, AXIS-Ultra DLD, Tokyo, Japan) with a monochromatized Al K$_\alpha$ radiation source (1486.6 eV). We performed electrochemical and photoelectrochemical measurements using a three-electrode quartz (CHI-660E, Chen Hua Instruments, Shanghai, China). Photoluminescence (PL, Hitachi F-7000, Tokyo, Japan) Spectra were collected to explore the recombination of photogenerated carriers.

2.3. Photocurrent and Electrochemical Impedance Spectra Measurements

The photocurrent and electrochemical impedance spectra (EIS) measurements were conducted using an electrochemical analyzer (CHI660E, Chen Hua Instruments, Shanghai, China) with a standard three-electrode configuration. A standard three-electrode cell was used in the photoelectric studies including a working electrode (as-prepared photocatalyst), a platinum wire as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. An amount of 0.1 M Na$_2$SO$_4$ was used as the electrolyte solution. The visible light irradiation was obtained from a 500 W Xe lamp with a 420 nm cutoff filter.

2.4. Photocatalytic Activity

The photocatalytic gradation of organic pollutants was carried out in a tube photoreactor. In order to eliminate the effect of temperature on the rate of photocatalytic degradation, the photochemical reaction apparatus was connected to a circulating cooling device (Bilon, Xi’an, China) to control the temperature of the reaction solution in the test tube at 25 ± 2 °C. The irradiation light source was a 400 W metal halide lamp. Adding the filter glass sheets between the metal halide lamp and the reaction tube filtered wavelengths <420 nm. The catalyst activity was analyzed primarily by degrading 10 ppm MB by 0.1 g of catalyst. After stirring for 30 min under dark, 1 mL of sample was taken every 15 min. The collected supernatant solutions were analyzed by the spectrometer at the characteristic absorption peak of 664 nm. The samples obtained during the photocatalytic test were filtered through a filter. Additionally, the degradation of phenol solution was detected by using high performance liquid chromatography (HPLC).

3. Results and Discussion

The crystallographic structures of ZnWO$_4$ and Cu$_2$O/ZnWO$_4$ samples were confirmed by XRD measurements. As seen in Figure 1, the diffraction peaks were observed at 18.91°, 23.84°, 24.58°, 30.72°, 36.31°, 41.15°, and 53.63°, corresponding to the (110), (200), (210), (211), (220), (310), (222), (320), (321), (400) and (421) crystal surfaces of ZnWO$_4$, respectively. This aligns with the standard card (ICPDS 15-0774) [27]. The standard card and the characteristic diffraction peaks were narrow and sharp, indicating that the composites possessed of high crystallinity. Meanwhile, the composites showed high purity since there were no traces of other phases examined. Compared with pure ZnWO$_4$, the XRD patterns of the Cu$_2$O/ZnWO$_4$ composites did not vary in shapes or peaks and it was presumed that the
addition of Cu$_2$O did not change the crystal form of ZnWO$_4$. Additionally, no characteristic diffraction peaks attributed to Cu$_2$O were detected in the Cu$_2$O/ZnWO$_4$ composites (as seen the Cu$_2$O JCPDS 65-3288) [22], which was caused by the small amounts and the particle size of Cu$_2$O nanoparticles (max 7 wt %) as well as the high dispersion of Cu$_2$O nanoparticles.

![X-Ray Diffraction (XRD) patterns of ZnWO$_4$ and Cu$_2$O/ZnWO$_4$ photocatalysts.](image1)

Figure 1. X-Ray Diffraction (XRD) patterns of ZnWO$_4$ and Cu$_2$O/ZnWO$_4$ photocatalysts.

The TEM was performed on the ZnWO$_4$ and 5 wt % Cu$_2$O/ZnWO$_4$ composite to investigate the morphology and detail structural information of the Cu$_2$O/ZnWO$_4$ composite catalyst. As seen in Figure 2a, the pure ZnWO$_4$ nanorods have a smooth surface with a length of 200–500 nm and a width of 20–30 nm. In comparison, as seen in Figure 2b, the Cu$_2$O nanoparticles, with average diameters of 20 nm, were coated on the surface of ZnWO$_4$ nanorods uniformly. The Cu$_2$O nanoparticles did not significantly change its morphology or the size of ZnWO$_4$ photocatalysts, which was consistent with the XRD results. Meanwhile, the Cu$_2$O nanoparticles were beneficial for separating the photo-generated carriers and improving the degradation performance of composites.

![Transmission Electron Microscopy (TEM) images of ZnWO$_4$ and Cu$_2$O/ZnWO$_4$.](image2)

Figure 2. Transmission Electron Microscopy (TEM) images of (a) ZnWO$_4$; (b) Cu$_2$O/ZnWO$_4$.

Figure 3a shows the UV-visible diffuse reflectance pattern of ZnWO$_4$, Cu$_2$O and Cu$_2$O/ZnWO$_4$ samples. As seen in Figure 3a, the pure ZnWO$_4$ shows its fundamental absorption edge at 320 nm due to its large band-gap energy while the Cu$_2$O exhibited strong absorption in the $\lambda < 600$ nm region. When Cu$_2$O nanoparticles were modified on the ZnWO$_4$ surface, it brought more visible light absorption for all of the Cu$_2$O/ZnWO$_4$ composites, and red shifted into the visible light region because of the photosensitizing effect of the incorporated Cu$_2$O nanoparticles. Additionally, the visible light absorption edge increased with rising Cu$_2$O content. The forbidden band width of a semiconductor
catalyst can be calculated using the Kubelka-Munk equation [28]. The result is shown in Figure 4b. According to the literature [21,29], the Cu2O was a direct transition semiconductor and the ZnWO4 was an indirect transition. As such, the band gap of pure Cu2O and ZnWO4 was calculated to be 1.9 and 3.7 eV (as seen in Figure 3b), respectively.

![Figure 3](image)

**Figure 3.** (a) UV-visible light (UV-vis) diffuses reflection spectra of pure ZnWO4, Cu2O and Cu2O/ZnWO4 samples; (b) the band gap energies of ZnWO4 and Cu2O.

![Figure 4](image)

**Figure 4.** X-Ray Photoelectron Spectroscopy (XPS) spectra of Cu2O/ZnWO4 sample: (a) Survey of the sample; (b) Zn 2p; (c) Cu 2p and (d) W 4f.

So as to demonstrate the interaction between Cu2O and ZnWO4 in Cu2O/ZnWO4 composites, the valence state and the binding energy in Cu2O/ZnWO4 were determined by using XPS. The results show that the element of Cu, O, Zn, W and C all appear in the full XPS spectrum of Cu2O/ZnWO4 and the corresponding high resolution spectra, which are noted in Figure 4b–d. Zn 2p binding energy position was shown in Figure 4b. In Figure 4b, we can observe that the characteristic peaks appear at 1022.1 and 1044.5 eV, respectively, which corresponds to the peak position of Zn 2p3/2 and
Zn 2p\textsubscript{1/2} [14]. Figure 4c is the spectrum result of Cu 2p. There are two peaks shown at 931.9 and 951.9 eV, which corresponds to Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2}, respectively. The experimental results are consistent with reports in the literature [22]. The XPS spectrum of W 4f (as seen in Figure 4d) shows that two binding energy peaks appear at 35.0 eV and at 37.4 eV, respectively for W 4f\textsubscript{7/2} and W 4f\textsubscript{5/2}, which determines the existence of W [30]. After the analysis of XRD and XPS, it can be concluded that Cu\textsubscript{2}O and ZnWO\textsubscript{4} coexist in the Cu\textsubscript{2}O/ZnWO\textsubscript{4} sample.

The photoluminescence (PL) spectra can evaluate the transfer and recombination processes of photogenerated e\textsuperscript{−}/h\textsuperscript{+} pairs in semiconductors. It is widely accepted that the lower PL intensity, the lower photo-carrier recombination rate and the higher photocatalytic performance [31]. The excitation wavelength ZnWO\textsubscript{4} and Cu\textsubscript{2}O in the Cu\textsubscript{2}O/ZnWO\textsubscript{4} architectures was 315 nm. The comparison of PL spectra is shown in Figure 5. The main emission peak is centered at 465 nm for the ZnWO\textsubscript{4} sample due to the recombination of photogenerated carriers in the ZnWO\textsubscript{4}. Once Cu\textsubscript{2}O nanoparticles were added, the photoluminescence dropped markedly and the 5 wt % Cu\textsubscript{2}O/ZnWO\textsubscript{4} composites displayed the lowest PL intensity, which indicates that the photogenerated carriers were effectively separated in the composite semiconductors. This shows that the process was conducive to promoting the photocatalytic properties of the composite material.

![Photoluminescence (PL) spectra of ZnWO\textsubscript{4} and Cu\textsubscript{2}O/ZnWO\textsubscript{4} composites.](image)

In order to better explain the photogenerated spectra, the Cu\textsubscript{2}O/ZnWO\textsubscript{4} composites should be effectively separated. The transient photocurrent responses of the ZnWO\textsubscript{4} and Cu\textsubscript{2}O/ZnWO\textsubscript{4} composites were recorded for several on/off cycles of irradiation. It was generally considered that the higher the peak intensity, the higher the separation efficiency of the photogenerated carriers [32]. As shown in Figure 6, when visible light is irradiated, the photocurrent increases sharply. In contrast, in the dark environment, the photocurrent was immediately reduced to zero. A significant photoelectric response was observed from the on/off photoperiod. In addition, ZnWO\textsubscript{4} showed almost no photocurrent response due to its lack of visible light response while the Cu\textsubscript{2}O/ZnWO\textsubscript{4} composites displayed much higher photocurrent intensity, where the 5 wt % Cu\textsubscript{2}O/ZnWO\textsubscript{4} composites exhibited the highest photocurrent density. This shows that the introduction of Cu\textsubscript{2}O nanoparticles will greatly improve the photocurrent response. The Cu\textsubscript{2}O/ZnWO\textsubscript{4} composites exhibit faster charge separation efficiency, which originates from the ZnWO\textsubscript{4} and Cu\textsubscript{2}O matching energy level structure that rapidly separates photogenerated hole pairs.
were consistent and illustrated that the introduction of Cu$_2$O could greatly accelerate the separation and transfer of photoelectron-hole pairs and improve the degradation performance of composites.

To further test the transport rate of the electrons more intuitively, the electrochemical impedance spectra (EIS) of the prepared materials was carried out. The size of the Nyquist curve reflects the reaction rate and resistance between grain and grain, grain boundaries, and after polarization. The electrode reaction rate decreases due to a larger radius. Small arc radii imply a faster interface electron transfer for better photocatalytic ability [33]. The EIS response of ZnWO$_4$ and Cu$_2$O/ZnWO$_4$ composites in visible light irradiation is shown in Figure 7. Obviously, the semicircular diameter of the composite was smaller than pure ZnWO$_4$, which demonstrates that the photo-generated charge can be effectively separated due to the strong interaction between ZnWO$_4$ and Cu$_2$O. The radius is the smallest when the composite ratio of Cu$_2$O is 5 wt %. All these results of EIS, photocurrent, and PL were consistent and illustrated that the introduction of Cu$_2$O could greatly accelerate the separation and transfer of photoelectron-hole pairs and improve the degradation performance of composites.

Figure 6. Photocurrent-time curves of bulk ZnWO$_4$ and Cu$_2$O/ZnWO$_4$ composites under visible light (>420 nm) irradiation with 30 s light on/off cycles.

To determine the photocatalytic performance of the catalyst, the activity of degradation MB by ZnWO$_4$, Cu$_2$O, and Cu$_2$O/ZnWO$_4$ were compared under the same experimental conditions. As seen in Figure 8a, the characteristic absorption peak of MB was 664 nm, and the intensity decreased gradually in the absence of 5 wt % Cu$_2$O/ZnWO$_4$ composite under visible light irradiation, and finally disappears at 90 min. Figure 8b displays the change of MB concentration (C/C$_0$) against photodegradation time for the prepared catalyst samples. The experimental results show that MB was not degraded in the absence of a photocatalyst or light irradiation. The MB degradation is a photocatalytic process, in which the photocatalysts generate photo-generated electron-hole pairs under illumination and further act on
the target degradation product. Pure ZnWO₄ has almost no photocatalytic activity because it does not respond to visible light. At the same time, the degradation rate of Cu₂O to MB was only 47%, which was due to the high recombination rate of excited electron-hole pairs [34]. As a comparison, the 5 wt % Cu₂O/ZnWO₄ composites could be degraded at about 90% MB solution, which was derived from the synergic effect of the Cu₂O/ZnWO₄ composites, and achieved the rapid separation of photogenerated carriers at the heterojunction. Meanwhile, it was observed that a higher amount of Cu₂O would decrease the photocatalytic activities. At higher content, the Cu₂O nanoparticles may agglomerate and reduce the specific surface area of the composites. Additionally, extra Cu₂O particles may become the new photogenerated recombination centers and, thereby, reduce the effective photogenerated pairs. Then the particles may inhibit the composite photocatalytic performance. All these results were consistent with the PL, photocurrent, and EIS test results of the composites. Therefore, the 5 wt % Cu₂O/ZnWO₄ composite exhibited better photocatalytic activity.

Figure 8. (a) UV-Vis spectral changes of methylene blue (MB) aqueous solution in the presence of 5 wt % Cu₂O/ZnWO₄ photocatalyst; (b) the activity of different catalysts to degrade MB in visible light.

Catalyst stability and reusability are also very important from the viewpoint of the catalyst’s practical applications. The photocatalytic activity of the 5 wt % Cu₂O/ZnWO₄ composites in the degradation of MB was studied in consecutive cycles under the same conditions (as seen in Figure 9). The degradation efficiency was slightly decreased after five cycles and the final degrade rate was approximately 83%, which indicates that the Cu₂O nanoparticles modified in ZnWO₄ surface preparation of composite photocatalyst could improve the recycling performance of the catalyst and the practical application value. It could act as a potential photocatalyst for water pollution.

Figure 9. Stability investigation of MB photocatalytic degradation over Cu₂O/ZnWO₄.
In order to further study the photocatalytic degradation performance of the composites, phenol was used as the degradation object, and the same conditions were tested. It can be seen from Figure 10 that the photolysis of the phenol solution in the blank condition is negligible, and the adsorption capacity of the composite material to the phenol in the dark environment is also very limited. In contrast, the CuSO/ZnWO4 photocatalysts exhibit higher catalytic degradation properties for phenol solution. The 5 wt % CuSO/ZnWO4 composite photocatalyst exhibits better photocatalytic performance, which was much higher than pure CuSO and ZnWO4. This is due to the composite having a bigger advantage than CuSO and ZnWO4. More visible light responses can be excited to produce more photogenerated pairs and the photogenerated pairs can be effectively separated between the two composite interfaces, which ultimately promote the photocatalytic performance.

![Figure 10. Linear relationship between ln(C/C0) and light time of phenol degradation.](image)

Quenching experiments explain the photodegradation process. In the free radical capture experiments of photodegradation, tert-butanol (TBA) and EDTA-2Na were used as capture agents for ·OH and h+, respectively [30]. Meanwhile, during the course of the experiment, nitrogen was used to remove oxygen to test whether the superoxide free radicals were active species during the degradation process. As seen in Figure 11, the photodegradation efficiency was significantly suppressed when the EDTA-2Na and in the N2-saturated experiment condition was added, which indicates that the h+ and O2− were likely the dominant active species in this process. In contrast, the dissolved ·OH was not the main active species due to the degradation rate constant showing only a slight decline when added to the TBA solution. Therefore, the photodegradation of MB over CuSO/ZnWO4 photocatalyst can be mainly associated with direct holes and O2− radicals for the photocatalytic degradation.

![Figure 11. First-order rate constant values of photogenerated active species trapped in the system of photocatalytic degradation of MB by CuSO/ZnWO4 under visible light.](image)
The photocatalytic degradation kinetic curve was investigated by the first-order simplification of Langmuir-Hinshelwood (L-H) kinetics, which is well established for photocatalysis at low initial pollutant concentrations [31]. The relevant equation is as follows:

$$\ln \frac{C_0}{C} = kt$$

where $C_0$ and $C$ are the concentrations of dye in solution at times 0 and $t$, respectively, and $k_{app}$ is the apparent first-order rate constant (min$^{-1}$). The $k$ value is obtained from the gradient of the graph of $\ln(C/C_0)$ versus time ($t$). Based on the characterization analysis and the experimental data, the mechanism of the high photocatalytic activities of Cu$_2$O/ZnWO$_4$ composites is discussed. Since the light absorption extends from ultraviolet light to visible light, there is no doubt that more visible light absorption can stimulate the generation of more photo-generated carriers, which could be effectively separated between the two composite interfaces because of the match level structure and ultimately promote the photocatalytic performance. According to the conduction band (CB) and valence band (VB) potentials of Cu$_2$O ($−1.2$ and $0.7$ eV, respectively [22]) and those of ZnWO$_4$ ($−0.8$ and $2.9$ eV, respectively [10]), it can be seen that Cu$_2$O/ZnWO$_4$ composites have matching energy levels. The staggered energy level structure contributes to the fast separation of photo-generated carriers.

The possible mechanism of improved photocatalytic performance of Cu$_2$O/ZnWO$_4$ composite formed by Cu$_2$O nanoparticles loading on ZnWO$_4$ was deduced based on above experimental results, as seen in Figure 12. This can be explained as follows: Under visible irradiation, Cu$_2$O could stimulate the generation of photogenerated hole pairs while the electrons on the conduction band can quickly migrate to the conduction band of ZnWO$_4$ at the close interface of the composites since the conduction band of Cu$_2$O is more negative than the conduction band of ZnWO$_4$. Then the electrons transferred to the ZnWO$_4$ react with the adsorbed oxygen molecules to produce O$_2^−$ radicals and participate in the photocatalytic oxidation degradation and the organic pollution process photocatalytic reaction. Simultaneously, after the transition stay in the Cu$_2$O valence band hole, another active species can directly oxidize organic pollutants involved in the reaction. Furthermore, this photo-assisted electron transfer method can effectively avoid the photo-generated carrier recombination, improve the utilization of the quantum pair, and promote the photocatalytic activity of the composite. This is consistent with the PL, photoelectric experiment results, and the active species of the quenching experiment.

![Figure 12. Schematic illustration of photo-generated carriers’ transportation for Cu$_2$O/ZnWO$_4$ composite.](image)

4. Conclusions

The surface of ZnWO$_4$ nanorods was decorated with Cu$_2$O nanoparticles (Cu$_2$O/ZnWO$_4$) prepared through the precipitation method. The 5 wt % Cu$_2$O/ZnWO$_4$ composites displayed the best
photocatalytic performance under visible light irradiation and the degradation rate of MB solution was 91%. The improvement in the photocatalytic performance of Cu$_2$O/ZnWO$_4$ composites due to the Cu$_2$O nanoparticles not only promoted the absorption and utilization of visible light, but also facilitated the migration of photogenerated charge carriers due to the matched level structure and the intimately contacted interface. In addition, the O$_2^-$ and holes were predicted to be the main active species in the photocatalytic degradation process based on free-radical scavenging experiments. In conclusion, the Cu$_2$O/ZnWO$_4$ composite is a highly efficient and stable photocatalyst that can effectively degrade organic pollutants in order to protect the environment.

Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (No. 51672081), Hebei Natural Science Funds for the Joint Research of Iron and Steel (B2016209348).

Author Contributions: Lingyu Tian, Yulan Rui and Weijia An conceived and designed the experiments; Lingyu Tian, Kelei Sun and Wenquan Cui analyzed the data; Lingyu Tian, Yulan Rui and Weijia An wrote the paper. All authors reviewed and approved the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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