Microwave-Assisted Synthesis of Chalcopyrite/Silver Phosphate Composites with Enhanced Degradation of Rhodamine B under Photo-Fenton Process

Shun-An Chang 1, Po-Yu Wen 1, Tsunghsueh Wu 2,* and Yang-Wei Lin 1,*

1 Department of Chemistry, National Changhua University of Education, 1 Jin-De road, Changhua City 50007, Taiwan; jack556yes@gmail.com (S.-A.C.); bba02123@gmail.com (P.-Y.W.)
2 Department of Chemistry, University of Wisconsin-Platteville, 1 University Plaza, Platteville, WI 53818-3099, USA
* Correspondence: wut@uwplatt.edu (T.W.); linywjerry@cc.ncue.edu.tw (Y.-W.L.);
Tel.: +1-608-342-6018 (T.W.); +886-4-7232105-3553 (Y.-W.L.)

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Abstract: A new composite by coupling chalcopyrite (CuFeS$_2$) with silver phosphate (Ag$_3$PO$_4$) (CuFeS$_2$/Ag$_3$PO$_4$) was proposed by using a cyclic microwave heating method. The prepared composites were characterized by scanning and transmission electron microscopy and X-ray diffraction, Fourier-transform infrared, UV–Visible diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy. Under optimum conditions and 2.5 W irradiation (wavelength length > 420 nm, power density = 0.38 W cm$^{-2}$), 96% of rhodamine B (RhB) was degraded by CuFeS$_2$/Ag$_3$PO$_4$ within a 1 min photo-Fenton reaction, better than the performance of Ag$_3$PO$_4$ (25% degradation within 10 min), CuFeS$_2$ (87.7% degradation within 1 min), and mechanically mixed CuFeS$_2$/Ag$_3$PO$_4$ catalyst. RhB degradation mainly depended on the amount of hydroxyl radicals generated from the Fenton reaction. The degradation mechanism of CuFeS$_2$/Ag$_3$PO$_4$ from the photo-Fenton reaction was deduced using a free radical trapping experiment, the chemical reaction of coumarin, and photocurrent and luminescence response. The incorporation of CuFeS$_2$ in Ag$_3$PO$_4$ enhanced the charge separation of Ag$_3$PO$_4$ and reduced Ag$_3$PO$_4$ photocorrosion as the photogenerated electrons on Ag$_3$PO$_4$ were transferred to regenerate Cu$^{2+}$/Fe$^{3+}$ ions produced from the Fenton reaction to Cu$^{+}$/Fe$^{2+}$ ions, thus simultaneously maintaining the CuFeS$_2$ intact. This demonstrates the synergistic effect on material stability. However, hydroxyl radicals were produced by both the photogenerated holes of Ag$_3$PO$_4$ and the Fenton reaction of CuFeS$_2$ as another synergistic effect in catalysis. Notably, the degradation performance and the reusability of CuFeS$_2$/Ag$_3$PO$_4$ were promoted. The practical applications of this new material were demonstrated from the effective performance of CuFeS$_2$/Ag$_3$PO$_4$ composites in degrading various dyestuffs (90–98.9% degradation within 10 min) and dyes in environmental water samples (tap water, river water, pond water, seawater, treated wastewater) through enhanced the Fenton reaction under sunlight irradiation.

Keywords: CuFeS$_2$/Ag$_3$PO$_4$; Fenton process; degradation; sunlight; environmental water samples

1. Introduction

Recently, concerns have been raised worldwide toward the harm caused by residual organic pollutants in surface water and groundwater, threatening ecosystems and aquatic species [1–3]. Among the many sources of water pollution, wastewater from the printing and dyeing industry is a major concern. The decolorization and degradation of most chromophores in dyes are difficult because of their stable aromatic structures, leading to prolonged toxic effects and environmental hazards [4–6]. Furthermore, dyes can absorb sunlight and reduce water clarity, preventing photosynthesis in
aquatic plants, decreasing dissolved oxygen in water, affecting microbial diversity, and disrupting the self-purification capacity of water [7]. The removal of these deleterious and hazardous pollutants from industrial wastewater has become an urgent environmental need in the world [8].

Many studies have evaluated the removal of organic dyes by using photocatalytic degradation, ideally using sunlight, with the vision of sustainable water treatment. TiO$_2$ is the most widely used photocatalytic semiconductor because of its nontoxic and stable nature, with a relatively low cost and abundant production resulting from a mature manufacturing process [9,10]. However, its absorption and photocatalytic activity depends entirely on ultraviolet light, which restricts its application in large-scale wastewater treatment [11–13]. Studies have been attempting to identify efficient sunlight-responsive photocatalysts, and Ag$_3$PO$_4$ with a quantum efficiency of >90%, is considered an excellent candidate that is sunlight responsive [14–16]. However, it experiences considerable photocorrosion during photolysis. In addition to the photocatalytic method, Cu/Fe-bearing solids such as chalcopyrite (CuFeS$_2$) have been widely used as catalysts in advanced oxidation processes (AOPs) for wastewater treatment [17–21]. In general, AOPs are based on Fenton’s chemistry, which utilizes hydroxyl radicals produced from the Fenton reaction between H$_2$O$_2$ and Cu$^+/Fe^{2+}$ ions to degrade organic dyes (Equations (1)–(6)) [22,23]. However, the reusability of CuFeS$_2$ is a challenge due to its dissolution during water treatment and the slow kinetics of Fe$^{2+}$ regeneration:

$\text{CuFeS}_2(s) + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{Cu}^{2+} + 2\text{SO}_4^{2–} + 8\text{H}_2\text{O} + 2\text{H}^+$  \hspace{1cm} (1)

$\text{CuFeS}_2(s) + 16\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 17\text{Fe}^{2+} + \text{Cu}^{2+} + 2\text{SO}_4^{2–} + 16\text{H}^+$  \hspace{1cm} (2)

$\text{CuFeS}_2(s) + 4\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{Cu}^{2+} + 2\text{SO}_4^{2–}$  \hspace{1cm} (3)

$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}$.  \hspace{1cm} (4)

$\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + \text{O}_2^– + 2\text{H}^+$  \hspace{1cm} (5)

$\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{OH}^- + \text{OH}$.  \hspace{1cm} (6)

$\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+$  \hspace{1cm} (7)

$\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{OH}$.  \hspace{1cm} (8)

To address CuFeS$_2$ reusability, attempts have been made to regenerate the Fenton catalysts with UV and/or visible-light irradiation, known as the photo-Fenton process [19,24,25]. Under UV and/or visible-light irradiation, Fe$^{3+}$ complexes are formed from the Fenton reaction (Equation (7)) to produce both Fe$^{2+}$ and hydroxyl radicals (Equation (8)). The photogenerated Fe$^{2+}$ ions can catalyze the Fenton reaction to form Fe$^{3+}$, thus demonstrating the recyclability of Fenton catalysts (Equation (4)). For instance, Dotto et al. demonstrated that the prepared citrate–CuFeS$_2$ materials possessed 90% catalytic efficiency for bisphenol A (BPA) degradation with a 15 min photo-Fenton process for its rapid generation of hydroxyl radicals and efficient H$_2$O$_2$ consumption [24]. Dotto et al. also reported that the catalytic efficiency and stability was sustained after four consecutive photoregeneration cycles. However, the preparation of the novel CuFeS$_2$ samples requires a high power and expensive microwave reactor (1400 W, 200 °C, 7 min). In another simpler attempt in material preparation, Pastrana-Martinez et al. used the mineral of CuFeS$_2$ mined from Jendouba, Tunisia, to catalyze tyrosol (TY) degradation by using a UV light-emitting diode (LED)-assisted photo-Fenton reaction [19]. Higher total organic carbon (TOC) conversions (85.0%) and lower iron leaching (0.89 mg·L$^{-1}$) were attained when the purified CuFeS$_2$ samples were used in the photo-Fenton-like process within 60 min (0.50 mM TY at stoichiometric H$_2$O$_2$ concentrations). However, UV light irradiation is not considered sustainable because it requires a high energy input. The limitations of the methods used in all these studies underline the need to improve the visible-light absorption ability and efficiently boost the degradation performance and stability of CuFeS$_2$. To our knowledge, CuFeS$_2$ coupled with other semiconductors has not been examined in the Fenton process under visible-light irradiation.
Here, we synthesized CuFeS$_2$ coupled with Ag$_3$PO$_4$ (CuFeS$_2$/Ag$_3$PO$_4$) through cyclic microwave heating to address the challenges in material preparation, the stability of materials, and degradation performance. The breakthrough in our synthesis is that CuFeS$_2$/Ag$_3$PO$_4$ could be prepared using a domestic 336 W microwave oven within 12 min. Our previous report indicated that Ag$_3$PO$_4$ is an efficient photocatalyst responsive to visible light and sunlight, so incorporating Ag$_3$PO$_4$ into the CuFeS$_2$ Fenton reaction system might greatly increase the visible-light absorption while improving the regeneration of Fe$^{2+}$/Cu$^+$ ions. Here, we used CuFeS$_2$/Ag$_3$PO$_4$ composites for the degradation of organic dyes (rhodamine B (RhB), methyl red (MR), rhodamine 6G (R6G), fluorescein, and propidium iodide (PI)). We also proposed that the degradation mechanism of CuFeS$_2$/Ag$_3$PO$_4$ and the reactive species and successfully demonstrated the regeneration of the CuFeS$_2$ catalyst and the application of CuFeS$_2$/Ag$_3$PO$_4$ in the treatment of environmental samples.

2. Materials and Methods

2.1. Preparation of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

All chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA) and were of analytical grade and thus used without further purification. First, 0.212 g of AgNO$_3$ was added to 20 mL of deionized water (18.2 M Ω cm) with stirring. Then, a colorless Ag(NH$_3$)$_2$$^+$ ion solution was produced by adding 6.2 mL of 14 M NH$_3$ solution dropwise into the AgNO$_3$ solution. After 30 min stirring, 3.5 mL of H$_3$PO$_4$ (14.6 M) was used to neutralize the mixed solution to pH 7.0, and the solution was stirred again for 30 min in the dark. The yellow precipitate was filtered and subsequently rinsed with copies of deionized water and anhydrous ethanol. Finally, the as-synthesized Ag$_3$PO$_4$ was dried at 55 °C for 12 h [26].

CuFeS$_2$ was prepared using the cyclic microwave heating method [27]. First, 19.7 mg of CuCl, 25.35 mg of FeCl$_3$ and 48.46 mg of L-cysteine were added to 20 mL of deionized water with stirring for 15 min. Then, the mixed solution underwent 10 cycles of 36 s heating and a 36 s pause in a domestic microwave oven (power: 336 W). After the black precipitate was cooled to room temperature, it was rinsed with deionized water and anhydrous ethanol. Finally, the as-synthesized CuFeS$_2$ was dried at 55 °C for 12 h. Cu$_9$S and Fe$_2$S$_3$ were prepared following similar method without adding FeCl$_3$ and CuCl precursor, respectively. The CuFeS$_2$/Ag$_3$PO$_4$ with a molar ratio of 2.5:1 was prepared as followed: 20 mg of Ag$_3$PO$_4$, 19.7 mg of CuCl, 25.35 mg of FeCl$_3$, and 48.46 mg of L-cysteine were added to 20 mL of deionized water with stirring for 15 min. Then, the mixed solution underwent 10 cycles of 36 s heating and a 36 s pause in a domestic microwave oven (power: 336 W). After the black precipitate was cooled to room temperature, it was rinsed with deionized water and anhydrous ethanol. Finally, the prepared CuFeS$_2$/Ag$_3$PO$_4$ was dried at 55 °C for 12 h and the weight of CuFeS$_2$/Ag$_3$PO$_4$ was 41.7 mg. Thus, the weight percentage of CuFeS$_2$ in CuFeS$_2$/Ag$_3$PO$_4$ was 52%. In this condition, we estimated the weight of CuFeS$_2$ and Ag$_3$PO$_4$ in the CuFeS$_2$/Ag$_3$PO$_4$ was 21.7 mg and 20 mg, respectively. Therefore, the molar ratio of CuFeS$_2$/Ag$_3$PO$_4$ was calculated to be 2.5:1 [27]. In addition, the preparation of CuFeS$_2$/Ag$_3$PO$_4$ with different molar ratios (0.4:1 and 1:1) followed the same method and was prepared by decreasing the adding amounts of CuCl and FeCl$_3$ precursors at 20 mg Ag$_3$PO$_4$.

2.2. Characterization of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

The morphological and compositional characteristics of all as-prepared samples were observed with scanning electron microscopy (SEM) on a HITACHI-S-4300 (Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM) on a 1200EX II (JEOL, Tokyo, Japan) equipped with a QUANTAX Annular XFlash QUAD FQ5060 (Bruker Nano, Berlin, Germany). The crystallographic texture of the samples was measured through powder X-ray diffraction (XRD) on SMART APEX II (Bruker AXS, Billerica, MA, USA) using Cu Kα radiation (λ = 1.5406 Å). Fourier-transform infrared (FT-IR) spectra were obtained using an Agilent Cary 600 FT-IR spectrometer (Agilent Technologies, Santa Clara, CA, USA). An Evolution 2000UV–Vis spectrophotometer (Thermo Fisher Scientific Inc., Madison, WI, USA)
with integrating spheres and reflectance standard material BaSO$_4$ was applied to obtain the UV–Vis diffuse reflectance spectroscopy (DRS). The binding energy of elements was determined through X-ray photoelectron spectroscopy (XPS) on a VG ESCA210 (VG Scientific, West Sussex, UK).

### 2.3. Degradation Procedure by Using Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

RhB degradation was used to assess the degradation activity of the prepared samples. The photoreactor PCX-50C (Beijing Perfectlight Technology Co. Ltd., Beijing, China) was equipped with a low-power white LED irradiation (2.5 W, power density = 0.38 W·cm$^{-2}$, wavelength > 420 nm). For the photo-Fenton reaction, 20 mg of the prepared catalyst samples was added into the RhB solution (20 ppm, 50 mL), and the solution was stirred in the dark for 30 min. Before 10 min, to turn the light on and add H$_2$O$_2$, we measured the absorbance to check the adsorption ability of the prepared samples. Subsequently, the LED lamp was turned on and 200 µL of H$_2$O$_2$ (35%) was added. After given time intervals, 1 mL of suspension was taken, quenched immediately by adding 0.1 mM Na$_2$S$_2$O$_3$ and filtered by a 0.22 µm syringe filter organic membrane to remove the catalyst sample. The concentration of RhB was measured using a Synergy H1 hybrid multimode microplate reader (BioTek Instruments, Winooski, VT, USA) at its characteristic absorption peak of 550 nm. Similar processes were performed for other dyestuffs (MR, R6G, fluorescein, and PI). The RhB degradation (20 ppm, 50 mL) for the photocatalytic and Fenton reactions was performed using the same protocols (20 mg catalysts) as mentioned above, but without the addition of H$_2$O$_2$ and LED light irradiation, respectively. After the experiment, TOC concentration was determined on an Elementar Acquaray TOC analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany) to evaluate the extent of mineralization.

### 2.4. Evaluation of Charge Separation and Recombination Rate of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

The charge separation efficiency and recombination rate of electron–hole pairs for the prepared composites were evaluated according to our earlier reports [28–30]. Photocurrent was measured to evaluate the charge separation efficiency of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites under constant white LED irradiation at 60 s intervals. To determine the recombination rate of electron–hole pairs, the photoluminescence (PL) spectra of samples were obtained using $\lambda_{ex}$ = 250 nm with a Varian Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Santa Clara, CA, USA).

### 2.5. Free Radical Trapping Experiment of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

To investigate the active species generated during RhB degradation over Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$, the trapping experiment was conducted using ethylenediaminetetraacetate (EDTA), tert-butanol (t-BuOH), and p-benzoquinone (BQ) (each 1 mM) as the capturing agent for holes, hydroxyl radicals, and oxygen radicals, respectively. The implemented trapping experimental procedure was identical to the steps mentioned in the degradation section except for the capturing agent being added at each run.

### 3. Results and Discussion

#### 3.1. Morphology and Crystal Phase of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

The morphology of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites was analyzed through SEM and TEM (Figure 1). As shown in Figure 1, Ag$_3$PO$_4$ appears as tetrapod-like structures, with its four cylindrical arms being approximately 7–10 µm in length and with its average diameter being 2–3 µm. The CuFeS$_2$ crystals appear irregular and sheet-like with sizes of 0.2–2 µm. As for the prepared Ag$_3$PO$_4$/CuFeS$_2$ composites, CuFeS$_2$ sheets were randomly deposited on the Ag$_3$PO$_4$ surface, and this deposition has no effect on the morphology and chemical composition of the Ag$_3$PO$_4$ particles. The corresponding magnified TEM image revealed clear lattice fringes with a d spacing of 0.249 and 0.312 nm, which are in good agreement with the (210) and (112) lattice planes of Ag$_3$PO$_4$ and CuFeS$_2$, respectively. The energy dispersive spectrometer (EDS) spectra of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$...
CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$ composites (Figure 2) confirm the presence of Ag, P, O, Cu, Fe, and S elements in their crystals accordingly. In addition, we also found C element in the presence of CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$ composites. This is because we used L-cysteine precursor in the preparation of CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$ composites.

![Figure 1. SEM and TEM images of (A) Ag$_3$PO$_4$; (B) CuFeS$_2$; and (C) CuFeS$_2$/Ag$_3$PO$_4$ composites.](image)

The XRD spectra of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites are displayed in Figure 3. From the black curve of Ag$_3$PO$_4$, the diffraction peaks at 21.5°, 30.1°, 33.4°, 36.7°, 42.5°, 48.7°, 53.6°, 55.3°, 57.5°, 62.4°, 65.1°, 70.7°, 72.2°, 74.6°, and 78.2° were identified and assigned to the (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (330), (420), (421), (332), and (442) faces of the cubic Ag$_3$PO$_4$, respectively (JCPDS No. 06-0505) [26]. The XRD pattern of CuFeS$_2$ is presented in the red curve of Figure 3, and the diffraction peaks at 28.9°, 46.4°, and 56.2° corresponded well to the (112), (220), and (312) faces of the tetragonal chalcopyrite CuFeS$_2$, respectively (JCPDS No. 01-0842) [27]. As a confirmation of good composite quality, the diffraction patterns of the prepared CuFeS$_2$/Ag$_3$PO$_4$ composites match with the patterns of Ag$_3$PO$_4$ and CuFeS$_2$. According to Scherer’s equation, the average crystallite size of Ag$_3$PO$_4$ and CuFeS$_2$ was 55.8 and 43.5 nm, respectively. In addition, they did not change in the CuFeS$_2$/Ag$_3$PO$_4$ composites (Ag$_3$PO$_4$: 57.0 nm, CuFeS$_2$: 46.5 nm).
3.2. Optical Property of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

The FT-IR spectra of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites are shown in Figure 4. The IR spectrum for Ag$_3$PO$_4$ shows four major peaks located at 560, 1012, 1670, and 3200 cm$^{-1}$, which corresponded to the PO$_4^{3-}$ stretching and O–H bending vibration, respectively.
The O–H bending in the prepared Ag$_3$PO$_4$ may be attributed from Ag$_3$PO$_4$ adsorbed water from the air. For CuFeS$_2$, it shows three peaks located at 1045, 1640, and 3400 cm$^{-1}$, which corresponded to the C=S stretching and O–H bending vibration, respectively. The O–H bending in the prepared CuFeS$_2$ may be attributed from CuFeS$_2$ adsorbed water from the air. The C=S stretching in the prepared CuFeS$_2$ may be attributed from the L-cysteine precursor. In addition, the EDS spectra for CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$ composites also confirmed the presence of C element. For CuFeS$_2$/Ag$_3$PO$_4$ composites, the spectrum exhibited PO$_4^{3-}$, C=S, and O–H vibration peaks in the present on their crystals.

![Figure 4. FT-IR spectra of different samples: Ag$_3$PO$_4$ (black); CuFeS$_2$ (red); and CuFeS$_2$/Ag$_3$PO$_4$ composites (blue).](attachment:figure4.png)

To study the optical absorption characteristics of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites, UV–Vis DRS was performed, as shown in Figure 5. The absorption band-edge for Ag$_3$PO$_4$, CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$ is at approximately 525, 427, and 487 nm, respectively. The bandgap energy (E$_g$) of Ag$_3$PO$_4$ is theoretically estimated to be 2.38 eV using the equation $\alpha = A(h\nu - E_g)^n$ (n = 1 for Ag$_3$PO$_4$). Furthermore, the band-edge potentials for the conduction band (CB) and valence band (VB) can be calculated as $E_{VB} = \chi - E_H + 0.5 E_g$ and $E_{CB} = E_{VB} - E_g$, respectively; here, $\chi$ is the electronegativity of the constituent atom (5.96 eV for Ag$_3$PO$_4$) and $E_H$ is the energy of the free electrons relative to the standard hydrogen reduction potential (approximately 4.5 eV). Thus, $E_{VB}$ and $E_{CB}$ of Ag$_3$PO$_4$ can be estimated to be 2.65 and 0.27 eV, respectively.

As another quality assurance method, the XPS analysis of the prepared Ag$_3$PO$_4$, CuFeS$_2$, CuFeS$_2$/Ag$_3$PO$_4$ composites (Figures 6–8, full scan) revealed that the prepared composites contained their own elements: Ag, P, O, Cu, Fe, and S. High-resolution XPS revealed Ag 3d, P 2p, O 1s, Cu 2p, Fe 2p, and S 2p in CuFeS$_2$/Ag$_3$PO$_4$ composites (Figure 8B–G, respectively). In Figure 8B, the binding energies are located at 367.8 and 373.3 eV, corresponding to Ag$^{+}$ 3d$_{5/2}$ and Ag$^{+}$ 3d$_{3/2}$, respectively. Furthermore, the peak at 132.9 eV correspond to P$^{5+}$ 2p (Figure 8C). O 1s spectra can be deconvoluted into two component peaks of 531.8 and 530.7 eV (Figure 8D). The peak centered at 530.7 eV associated with the O$_2$ in Ag$_3$PO$_4$. The other peak centered at 531.8 eV the presence of –OH group or a water molecule absorbed on the surface of the prepared composites. In Figure 8E, the peaks at 932.3, 934.2, 952.2, and 953.8 eV corresponded to Cu$^{+}$ 2p$_{3/2}$, Cu$^{2+}$ 2p$_{3/2}$, Cu$^{+}$ 2p$_{1/2}$, and Cu$^{2+}$ 2p$_{1/2}$, respectively. The peaks at 712.5, 718.2, 722.5, and 731.8 eV corresponded to Fe$^{2+}$ 2p$_{3/2}$, Fe$^{3+}$ 2p$_{3/2}$, Fe$^{2+}$ 2p$_{1/2}$ and
Fe$^{3+}$ 2p$_{3/2}$, respectively (Figure 8F), whereas that at 162.5 and 167.8 eV corresponded to S$^{2-}$ 2p and S$^{6+}$ 2p, respectively (Figure 8G).

**Figure 5.** (A) UV–Vis diffuse reflectance spectroscopy (DRS) spectra and (B) Tauc’s plots of different samples: Ag$_3$PO$_4$ (black), CuFeS$_2$ (red), and CuFeS$_2$/Ag$_3$PO$_4$ composites (blue).
Figure 6. XPS spectra of Ag$_3$PO$_4$: (A) full scan; (B) Ag$^{3d}$; (C) P$^{2p}$; and (D) O$^{1s}$. Deconvolution of XPS peak for O$^{1s}$ element represented in different color line.

Figure 7. XPS spectra of CuFeS$_2$: (A) full scan; (B) Cu$^{2p}$; (C) Fe$^{2p}$; and (D) S$^{2p}$. Deconvolution of XPS peaks for Cu$^{2p}$, Fe$^{2p}$ and S$^{2p}$ elements represented in different color line.
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Figure 8. XPS spectra of CuFeS₂/Ag₃PO₄: (A) full scan; (B) Ag₃d; (C) P₂p; (D) O₁s; (E) Cu₂p; (F) Fe₂p; and (G) S₂p. Deconvolution of XPS peaks for O₁s, Cu₂p, Fe₂p, and S₂p elements represented in different color line.

3.3. Degradation Performance of Ag₃PO₄, CuFeS₂, and CuFeS₂/Ag₃PO₄

To evaluate the degradation activity of the prepared Ag₃PO₄, CuFeS₂, and CuFeS₂/Ag₃PO₄ composites, RhB was selected as the target pollutant. Figure 9 shows the concentration ratio (C/C₀, where C₀ and C represented the RhB concentration at the initial condition and at time t, respectively) of RhB by using Ag₃PO₄, CuFeS₂, and CuFeS₂/Ag₃PO₄ composites under three different degradation conditions: photocatalytic, Fenton, and photo-Fenton. First, under 30 min LED light irradiation...
3.3. Degradation Performance of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

To evaluate the degradation activity of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites, RhB was selected as the target pollutant. Figure 9 shows the concentration ratio (C/C$_0$, where C$_0$ and C represented the RhB concentration at the initial condition and at time t, respectively) of RhB by using Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites under three different degradation conditions: photocatalytic, Fenton, and photo-Fenton. First, under 30 min LED light irradiation (Figure 9A), the degradation efficiencies of RhB in CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$ are only 8.9% and 16.9%, respectively, whereas the efficiency reaches 39.5% in the presence of Ag$_3$PO$_4$. This suggests that the photocatalytic performance of Ag$_3$PO$_4$ is better than that of CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$, attributable to the reactive radical formation from the effective photoinduced charge separation for RhB degradation. Nevertheless, these reactive radicals must be determined in a later experiment.

CuFeS$_2$/Ag$_3$PO$_4$ is responsive to visible light caused by its diluted amount of Ag$_3$PO$_4$, resulting in a weaker degradation performance than that of pure Ag$_3$PO$_4$. Second, the degradation efficiency of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites through the Fenton reaction in the dark was studied (Figure 9B). The RhB concentration barely changes in the presence of Ag$_3$PO$_4$, but the RhB degradation efficiency reaches 76.1% and 93.7% within 1 min in the presence of CuFeS$_2$ and CuFeS$_2$/Ag$_3$PO$_4$, respectively. This is due to the production of hydroxyl radicals that degrade RhB from the oxidation of the Cu$^+$/Fe$^{3+}$ ions on the CuFeS$_2$ to the formation of Cu$^{2+}$/Fe$^{3+}$ ions in the presence of H$_2$O$_2$. Finally, the degradation performance of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites was evaluated with the photo-Fenton reaction in the presence of H$_2$O$_2$, and the results are shown in Figure 9C. The degradation efficiency of Ag$_3$PO$_4$ reaches 25% with a 10 min photo-Fenton reaction, whereas that of CuFeS$_2$ reaches 87.7% within 1 min. Notably, the degradation efficiency of CuFeS$_2$/Ag$_3$PO$_4$ reaches 96% within 1 min. Moreover, the relative standard deviation of the degradation performance for three different batches of the prepared composites was less than 9%, indicating the high reproducibility of the preparation methods for the proposed composites. In addition, we also analyzed the degradation performances of Cu$_2$S, Fe$_2$S$_3$, Cu$_2$S/Ag$_3$PO$_4$ and Fe$_2$S$_3$/Ag$_3$PO$_4$ composites. As shown in Figure 10, the RhB degradation efficiency reaches 75.2%, 86.5%, 81.4% and 90.4% within 1 min in the presence of Cu$_2$S, Fe$_2$S$_3$, Cu$_2$S/Ag$_3$PO$_4$ and Fe$_2$S$_3$/Ag$_3$PO$_4$, respectively. These results suggested that the addition of CuFeS$_2$/Ag$_3$PO$_4$ promotes the production of hydroxyl radicals through the photo-Fenton reaction to degrade RhB at a higher efficiency than CuFeS$_2$, Cu$_2$S, Fe$_2$S$_3$ alone, indicating a synergistic effect between CuFeS$_2$ and Ag$_3$PO$_4$. Figure 9D–F showed the corresponded pseudo-first-order linear transform of RhB degradation under photocatalytic reaction, Fenton reaction and photo-Fenton reaction by Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites. The apparent rate constants for RhB degradation by Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites are listed in Table 1.

Table 1. Pseudo-first-order rate constants for rhodamine B (RhB) degradation by Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites at different conditions.

| Series         | Degradation Mode       | Pseudo-First-Order Kinetic Equation | k(min$^{-1}$) | R$^2$ |
|----------------|------------------------|-----------------------------------|--------------|------|
| Ag$_3$PO$_4$   | Photocatalytic reaction| $y = 0.016x + 0.048$              | 0.016        | 0.96 |
|                | Fenton reaction         | $y = 0.0026x + 0.0088$            | 0.0026       | 0.92 |
|                | Photo-Fenton reaction   | $y = 0.0047x + 0.055$             | 0.0047       | 0.80 |
| CuFeS$_2$      | Photocatalytic reaction| $y = 0.0007x - 0.039$             | 0.0007       | 0.72 |
|                | Fenton reaction         | $y = 1.5x - 0.16$                 | 1.5          | 0.93 |
|                | Photo-Fenton reaction   | $y = 2.8x - 0.29$                 | 2.8          | 0.94 |
| CuFeS$_2$/Ag$_3$PO$_4$ | Photocatalytic reaction| $y = 0.018x - 0.0015$            | 0.018        | 0.94 |
|                | Fenton reaction         | $y = 2.2x - 0.156$                | 2.2          | 0.99 |
|                | Photo-Fenton reaction   | $y = 3.3x - 0.0322$               | 3.3          | 0.97 |
Figure 9. (A) Photocatalytic reaction; (B) fenton reaction; and (C) photo-Fenton reaction for RhB degradation by different samples: Ag$_3$PO$_4$ (black), CuFeS$_2$ (red), and CuFeS$_2$/Ag$_3$PO$_4$ composites (blue). The pseudo-first order linear transform of RhB degradation under (D) photocatalytic reaction, (E) Fenton reaction and (F) photo-Fenton reaction by different samples: Ag$_3$PO$_4$ (black), CuFeS$_2$ (red), and CuFeS$_2$/Ag$_3$PO$_4$ composites (blue).

To maximize the degradation performance of CuFeS$_2$/Ag$_3$PO$_4$, the following factors were systematically studied: the molar ratio of CuFeS$_2$ to Ag$_3$PO$_4$, the mechanical mixing of CuFeS$_2$ and Ag$_3$PO$_4$ particles, and the added amounts of H$_2$O$_2$ and CuFeS$_2$/Ag$_3$PO$_4$. Figure 11A presents the plots of the RhB concentration ratio ($C/C_0$) against the reaction time for CuFeS$_2$/Ag$_3$PO$_4$ prepared at different precursor molar ratios from CuFeS$_2$ to Ag$_3$PO$_4$. The degradation efficiency can be visually related to the highest drop in the RhB concentration ratio in the plots during the reaction. The higher molar ratio of the precursors used to make CuFeS$_2$/Ag$_3$PO$_4$ resulted in higher degradation efficiency as the hydroxyl radicals generated from the photo-Fenton reaction dominated the RhB degradation.
Above the 2.5:1 ratio, the suspension of excessive black CuFeS$_2$ particles in the CuFeS$_2$/Ag$_3$PO$_4$ solution was observed. This raised a concern as the excessive CuFeS$_2$ particles were not coupled with Ag$_3$PO$_4$ during the synthesis, and they cannot be regenerated during the photolysis. CuFeS$_2$/Ag$_3$PO$_4$ with the molar ratio of 2.5:1 was therefore selected as the optimal condition for this study. The second experiment was performed by mechanically mixing both CuFeS$_2$ and Ag$_3$PO$_4$ particles with the molar ratio of 2.5:1 to prove the synergistic effect within CuFeS$_2$/Ag$_3$PO$_4$ in the enhanced degradation activity (Figure 11B). The degradation efficiency for the mechanically mixed sample with 10 min photocatalytic, Fenton, and photo-Fenton reactions is 4.2%, 83.5%, and 87.7%, respectively—all evidently lower than that for composites formed with cyclic microwave heating (Figure 9). These results strongly suggest that the coupling interaction between CuFeS$_2$ and Ag$_3$PO$_4$ is critical for the significantly enhanced degradation activity of CuFeS$_2$/Ag$_3$PO$_4$ composites. Then, because the amount of H$_2$O$_2$ is key for the photo-Fenton reaction, its content in the degradation process may influence the performance of CuFeS$_2$/Ag$_3$PO$_4$ composites. As shown in Figure 11C, the degradation efficiency increased with an increase in the H$_2$O$_2$ amount up to 200 µL, above which the degradation efficiency decreased, probably because excess reactive radicals react with one another. Thus, we selected 200 µL of H$_2$O$_2$ as the optimum required amount of H$_2$O$_2$. Then, the degradation efficiency at different amounts of CuFeS$_2$/Ag$_3$PO$_4$ composites was evaluated. As shown in Figure 11D, the degradation efficiency increased with an increase in the CuFeS$_2$/Ag$_3$PO$_4$ amount of up to 20 mg, above which the degradation efficiency plateaued. On the basis of this result, 20 mg of CuFeS$_2$/Ag$_3$PO$_4$ was used for further investigations. Finally, the degradation efficiency for a higher RhB concentration at 20 mg CuFeS$_2$/Ag$_3$PO$_4$ was evaluated. As shown in Figure 11E, the degradation efficiency at a higher RhB concentration decreased within 10 min of photo-Fenton reaction. However, the degraded RhB amount was higher at a higher RhB concentration. The results also indicated that the maximum degraded amount of RhB at 20 mg CuFeS$_2$/Ag$_3$PO$_4$ was 54.9 ppm.

According to the literature, deethylation and chromophore cleavage are analogous competitive photodegradation reactions during the photocatalytic decomposition of organic pollutants. Based on the literature, the hypsochromic shifts (blue shift of the maximum absorption band) are attributed to the formation of a series of N-deethylated intermediates of RhB [31,32]. In this study, the absorption at 550 nm for RhB decreased with the increase in the reaction time and exhibited a slight hypsochromic shift (dash line in Figure 12A). Therefore, a possible method to degrade RhB is through chromophore cleavage, which can be observed with an insignificant hypsochromic shift in the UV–Vis spectra. Another approach to study organic compound degradation is to measure the TOC of the solution before and after the reaction. Figure 12B plots the temporal evolution of TOC content with RhB degradation by CuFeS$_2$/Ag$_3$PO$_4$. Initially, the color vanished in the RhB solution with the photo-Fenton reaction for

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**Figure 10.** Photo-Fenton reaction for RhB degradation by different samples: (A) Cu$_2$S (black) and Fe$_2$S$_3$ (red); and (B) Cu$_2$S/Ag$_3$PO$_4$ (black) and Fe$_2$S$_3$/Ag$_3$PO$_4$ (red) composites.
1 min; the TOC content decreased to 13.5 ppm (decomposing only 2.17% of the original concentration (13.8 ppm)). The decomposition of RhB with CuFeS$_2$/Ag$_3$PO$_4$ increased to as high as 78.3%, but only 3.0 ppm TOC remained in the solution with a 30 min photo-Fenton reaction. Evidence from both experimental approaches strongly supports RhB chromophore cleavage and CO$_2$ production as the predominant pathways of degradation by CuFeS$_2$/Ag$_3$PO$_4$.

3.4. Degradation Mechanism of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$

In photodegradation, the rate and the stability of electron–hole pairs generated from the excitation source are critical factors to be considered in the development of ideal photocatalysts. In this study, the separation efficiency and recombination rate of the electron–hole pairs for the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites were investigated through photocatalytic degradation without any H$_2$O$_2$. Figure 13A shows the photocurrent density of Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ under LED light irradiation; all samples produced a sharp photocurrent peak on turning the light on and no peak as the light turned off, with photocurrent response during the on/off cycles. Under LED light irradiation, the current density decreased in the following order: Ag$_3$PO$_4$ > CuFeS$_2$/Ag$_3$PO$_4$ > CuFeS$_2$. This result is consistent with the photocatalytic degradation results shown in Figure 9A, indicating that the differences in the photodegradation activity was due to the differences in the optoelectrical properties of selected materials. In addition, the different noise levels and shape forms of the photocurrent density for different composites may be attributed to the different size and morphology of the composites deposited on the fluorine-doped tin oxide (FTO) substrates. As a further experiment, the intensity of PL emission for three materials was measured to quantify the recombination rate of the electron–hole pairs; a lower rate implies a lower luminescence emission intensity and higher photocatalytic activity. Figure 13B presents the PL emission spectra of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites at $\lambda_{ex} = 250$ nm. The emission intensity of CuFeS$_2$ was the weakest due to the lowest yield of electron–hole pairs but not due to a low recombination rate. The difference in the emission intensity between Ag$_3$PO$_4$ and CuFeS$_2$/Ag$_3$PO$_4$ is nonsignificant, indicating comparable electron–hole pair recombination rates. This demonstrates the ability of CuFeS$_2$/Ag$_3$PO$_4$ to generate electron–hole pairs with a low recombination rate, providing critical information to understand the mechanism discussed later.
To maximize the degradation performance of CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4}, the following factors were systematically studied: the molar ratio of CuFeS\textsubscript{2} to Ag\textsubscript{3}PO\textsubscript{4}, the mechanical mixing of CuFeS\textsubscript{2} and Ag\textsubscript{3}PO\textsubscript{4} particles, and the added amounts of H\textsubscript{2}O\textsubscript{2} and CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4}. Figure 11A presents the plots of the RhB concentration ratio (C/C\textsubscript{0}) against the reaction time for CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} prepared at different precursor molar ratios from CuFeS\textsubscript{2} to Ag\textsubscript{3}PO\textsubscript{4}. The degradation efficiency can be visually related to the highest drop in the RhB concentration ratio in the plots during the reaction. The higher molar ratio of the precursors used to make CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} resulted in higher degradation efficiency as the hydroxyl radicals generated from the photo-Fenton reaction dominated the RhB degradation. Above the 2.5:1 ratio, the suspension of excessive black CuFeS\textsubscript{2} particles in the CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} solution was observed. This raised a concern as the excessive CuFeS\textsubscript{2} particles were not coupled with Ag\textsubscript{3}PO\textsubscript{4} during the synthesis, and they cannot be regenerated during the photolysis. CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} with the molar ratio of 2.5:1 was therefore selected as the optimal condition for this study. The second experiment was performed by mechanically mixing both CuFeS\textsubscript{2} and Ag\textsubscript{3}PO\textsubscript{4} particles with the molar ratio of 2.5:1 to prove the synergistic effect within CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} in the enhanced degradation activity (Figure 11B). The degradation efficiency for the mechanically mixed sample with 10 min photocatalytic, Fenton, and photo-Fenton reactions is 4.2%, 83.5%, and 87.7%, respectively—all evidently lower than that for composites formed with cyclic microwave heating (Figure 9). These results strongly suggest that the coupling interaction between CuFeS\textsubscript{2} and Ag\textsubscript{3}PO\textsubscript{4} is critical for the significantly enhanced degradation activity of CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} composites. Then, because the amount of H\textsubscript{2}O\textsubscript{2} is key for the photo-Fenton reaction, its content in the degradation process may influence the performance of CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} composites. As shown in Figure 11C, the degradation efficiency increased with an increase in the H\textsubscript{2}O\textsubscript{2} amount up to 200 \( \mu \text{L} \), above which the degradation efficiency decreased, probably because excess reactive radicals react with one another. Thus, we selected 200 \( \mu \text{L} \) of H\textsubscript{2}O\textsubscript{2} as the optimum required amount of H\textsubscript{2}O\textsubscript{2}. Then, the degradation efficiency at different amounts of CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} composites was evaluated. As shown in Figure 11D, the degradation efficiency increased with an increase in the CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} amount of up to 20 mg, above which the degradation efficiency plateaued. On the basis of this result, 20 mg of CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} was used for further investigations. Finally, the degradation efficiency for a higher RhB concentration at 20 mg CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} was evaluated. As shown in Figure 11E, the degradation efficiency at a higher RhB concentration decreased within 10 min of photo-Fenton reaction. However, the degraded RhB amount was higher at a higher RhB concentration. The results also indicated that the maximum degraded amount of RhB at 20 mg CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} was 54.9 ppm.

Figure 11. Degradation of RhB under different conditions: (A) different molar ratios of CuFeS\textsubscript{2} to Ag\textsubscript{3}PO\textsubscript{4}; (B) different degradation procedures using the mechanical mixing of Ag\textsubscript{3}PO\textsubscript{4} and CuFeS\textsubscript{2} particles; (C) different amounts of H\textsubscript{2}O\textsubscript{2} by CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} composites; (D) different amounts of CuFeS\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} composites; and (E) different amounts of RhB.
Figure 12. (A) Temporal evolution of UV–Vis spectra of RhB and (B) the corresponding total organic carbon (TOC) content of RhB degradation by the prepared CuFeS$_2$/Ag$_3$PO$_4$ composites through the photo-Fenton reaction. Top image: photographs of the RhB solution under the photo-Fenton reaction at different irradiation time.
Figure 13. (A) Photocurrent density and (B) the photoluminescence (PL) spectra of different samples: Ag₃PO₄ (black), CuFeS₂ (red), and CuFeS₂/Ag₃PO₄ composites (blue).

As a key mechanistic study, the active species involved in the degradation reaction were identified systematically using the free radical trapping experiments (Figure 14). EDTA, BQ, and t-BuOH were used as holes, oxygen radicals, and hydroxyl radical scavengers, respectively. After adding EDTA to the reaction mixture, RhB degradation in Ag₃PO₄ samples was inhibited, indicating that holes are the major species involved in the photo-Fenton degradation (Figure 14A). In contrast to the Ag₃PO₄ sample, RhB degradation in CuFeS₂ and CuFeS₂/Ag₃PO₄ composites with the photo-Fenton reaction was inhibited by adding t-BuOH, indicating that hydroxyl radicals are the major active species (Figure 14B,C).
Figure 14. Free radical trapping experiment of (A) Ag₃PO₄, (B) CuFeS₂, and (C) CuFeS₂/Ag₃PO₄ composites. Ethylenediaminetetraacetate (EDTA), tert-butanol (t-BuOH), and p-benzoquinone (BQ) (each 1 mM) were scavengers for holes, oxygen radicals, and hydroxyl radicals, respectively.
Hydroxyl radical production was further detected using the fluorescent luminescence (FL) technique to study the photo-Fenton reaction. The FL emission spectra, excited at 370 nm in the coumarin solution in the absence and presence of the prepared samples, were evaluated for 10 min of irradiation. Figure 15 shows that an FL signal was observed at 460 nm for each sample and that the maximum FL intensity was observed in CuFeS$_2$/Ag$_3$PO$_4$. This suggests that CuFeS$_2$/Ag$_3$PO$_4$ produced the highest amount of hydroxyl radicals among these three materials, thereby leading to more chemical reactions with coumarin to generate fluorescence [33]. Hence, the hydroxyl radical was considered the direct reactive oxidation species in the CuFeS$_2$/Ag$_3$PO$_4$ composites for RhB degradation. Moreover, CuFeS$_2$/Ag$_3$PO$_4$ composites with maximal degradation activity produced excess reactive hydroxyl radicals than CuFeS$_2$, which is consistent with the previously discussed results.

![Figure 15. FL spectra of the different samples in the coumarin solution measured at $\lambda_{ex} = 370$ nm (each sample was illuminated for 10 min under visible light). Ag$_3$PO$_4$ (red), CuFeS$_2$ (blue), and CuFeS$_2$/Ag$_3$PO$_4$ composites (olive).](image)
of the charge separation efficiency, recombination rate of electron–hole pairs and the amount of the major reactive species were slight different, resulting in different degradation performance as shown in Figure 10.

Scheme 1. Transition of electrons and holes in the different degradation system of (A) Ag$_3$PO$_4$, (B) CuFeS$_2$, and (C) CuFeS$_2$/Ag$_3$PO$_4$.

3.5. Stability and Practical Applications of CuFeS$_2$/Ag$_3$PO$_4$

The stability of the catalyst is an essential parameter for the development of practical water treatment applications. To investigate the stability of the prepared Ag$_3$PO$_4$, CuFeS$_2$, and CuFeS$_2$/Ag$_3$PO$_4$ composites, the results of cyclic RhB degradation tests were evaluated (shown in Figure 16A); in each cycle, RhB and H$_2$O$_2$ were reintroduced into the catalyst. In this study, RhB degradation by Ag$_3$PO$_4$ and CuFeS$_2$/Ag$_3$PO$_4$ after ten cycles maintained a similar degradation efficiency (15.3% to 14% after ten cycles for Ag$_3$PO$_4$; 99.6% to 91.3% after ten cycles for CuFeS$_2$/Ag$_3$PO$_4$), whereas that by CuFeS$_2$ resulted in a considerable loss of efficiency (from 97.5% to 15.0% after ten cycles). Furthermore, the corresponding XRD results (Figure 16B) suggest a negligible change in the phase structure of Ag$_3$PO$_4$ and CuFeS$_2$/Ag$_3$PO$_4$ samples after the repeated reactions, indicating the good stability of the samples. However, the initial phase structure of CuFeS$_2$ disappeared after three reaction cycles. The SEM image shown in Figure 16D displays that the morphology of the CuFeS$_2$ sample changed from an irregular sheet to spherical shape, indicating that the Fenton reaction caused structural and chemical change for CuFeS$_2$ when it is used alone. Unlike CuFeS$_2$, the comparison of SEM images for Ag$_3$PO$_4$ and CuFeS$_2$/Ag$_3$PO$_4$ composites before and after reaction cycles only showed a slight change of morphology (Figure 16C,E). Evidently, the stability of CuFeS$_2$ in the
CuFeS$_2$/Ag$_3$PO$_4$ composite improved considerably because of its coupling with Ag$_3$PO$_4$ nanoparticles as the photogenerated electrons in the CB of Ag$_3$PO$_4$ reduce Fe$^{3+}$/Cu$^{2+}$ ions and keep them intact in CuFeS$_2$/Ag$_3$PO$_4$. This prevented the structural disintegration of CuFeS$_2$ during the Fenton reaction, effectively demonstrating its reusability for catalysis.

To assess the practical applications of CuFeS$_2$/Ag$_3$PO$_4$, various organic dyes (MR, M6G, fluorescein, and PI) were degraded (Figure 17A). Compared with TiO$_2$ (P25), CuFeS$_2$/Ag$_3$PO$_4$ exhibited excellent degradation efficiency toward all selected dyestuffs, with nearly 95% degradation achieved within 10 min (except PI with only 78.5% degradation efficiency). In addition, the degradation performance of CuFeS$_2$/Ag$_3$PO$_4$ under sunlight irradiation was evaluated from November to December 2019 from 11:00 a.m. to 2:00 p.m. daily at the National Changhua University of Education, Changhua, Taiwan. As shown in Figure 17B, sunlight-induced RhB degradation in the absence and presence of CuFeS$_2$/Ag$_3$PO$_4$ was very poor without H$_2$O$_2$. However, using the sunlight-assisted Fenton reaction for RhB degradation achieved nearly 98.9% degradation efficiency within 1 min. This is because the combined UV and visible light in sunlight hastened the production of hydroxyl radicals in the presence of H$_2$O$_2$ and CuFeS$_2$/Ag$_3$PO$_4$. With the promise of the sunlight-assisted Fenton reaction, the pH effect in the water samples on the degradation performance of CuFeS$_2$/Ag$_3$PO$_4$ was also investigated. As shown in Figure 17C, the degradation efficiency decreased at pH 12.0 because the Fenton reaction was considerably hindered at a high pH as Fe$^{2+}$ cations form inactive porphyrin ferryl complexes (FeO$_2$) in the alkaline solution [24]. Finally, the prepared CuFeS$_2$/Ag$_3$PO$_4$ composites were used to degrade RhB in the environmental water samples (Figure 17D). CuFeS$_2$/Ag$_3$PO$_4$ exhibited excellent degradation efficiency through the photo-Fenton reaction for RhB degradation, with nearly 90% degradation within 1 min. A notable difference in the degradation time for RhB was observed for the seawater and treated wastewater samples (90% and 80% degradation within 10 min, respectively) compared with the other environmental water samples (100% degradation within 10 min) probably because of the presence of anions or radical scavengers in the seawater and treated wastewater samples that reduced the degradation activity of CuFeS$_2$/Ag$_3$PO$_4$. Nevertheless, the studies on the environmental water samples...
strongly support the benefits of this newly developed CuFeS$_2$/Ag$_3$PO$_4$-based photo-Fenton water treatment option.

![Figure 17](Nanomaterials 2020, 10, x FOR PEER REVIEW 21 of 25)

Figure 17. Photo-Fenton reaction of (A) different dyestuff by CuFeS$_2$/Ag$_3$PO$_4$ composites and P25; (B) different degradation procedures in the absence and presence of CuFeS$_2$/Ag$_3$PO$_4$ under sunlight irradiation; (C) different pH; and (D) different environmental water samples for RhB degradation by CuFeS$_2$/Ag$_3$PO$_4$.

4. Conclusions

The currently prepared CuFeS$_2$/Ag$_3$PO$_4$ composites exhibited higher RhB degradation efficiency through the photo-Fenton reaction than did Ag$_3$PO$_4$ and CuFeS$_2$ alone. This high enhancement in the degradation efficiency was attributed to the synergistic effect in material stability and the hydroxyl radical production. The constituent Ag$_3$PO$_4$ in the newly developed composite not only provides the visible-light absorption ability in degrading organic compounds but also acts as a rich electron source to stabilize the crystal structure of CuFeS$_2$ under light irradiation. Consequently, Cu$^{2+}$/Fe$^{3+}$ ions produced by the Fenton reaction can be reduced and regenerated into Cu$^+$/Fe$^{2+}$ ions, and the reactive hydroxyl radicals partially from the photogenerated holes of Ag$_3$PO$_4$ and predominantly from the Fenton reaction of CuFeS$_2$ can be continuously produced to degrade organic compounds. The CuFeS$_2$/Ag$_3$PO$_4$ composite has several attractive features not realized in the other reported photo-Fenton reactions (Table 2). First, the prepared CuFeS$_2$/Ag$_3$PO$_4$ composite had 96% RhB degradation performance under low-power white LED illumination within 1 min. In addition, various dyestuffs (MR, R6G, fluorescein, and PI) with 95% degradation efficiency could be achieved. Through sunlight-assisted Fenton reaction, the RhB degradation efficiency was further improved to 98.9%. For the recycling used ability, the CuFeS$_2$/Ag$_3$PO$_4$ composite is stable enough to be reused through the input of sustainable energy source. Hence, this study discovered the synergistic catalysis CuFeS$_2$/Ag$_3$PO$_4$ and successfully demonstrates the application of the sunlight-assisted Fenton reaction on environmental water samples. The current findings can be used for the applications of advanced oxidation technology in wastewater treatment in the future.
Table 2. Comparison of the degradation performance and practical applications using the photo-Fenton reaction.

| Samples                  | Preparation           | Degradation Performance                                                                 | Sunlight Irradiation | Target | Ref.       |
|--------------------------|-----------------------|----------------------------------------------------------------------------------------|----------------------|--------|------------|
| Citrate–CuFeS₂          | Microwave heating     | 90% degradation (0.2 g catalyst/50 ppm BPA) within 15 min (4 W fluorescent lamp)        | -                    | BPA    | [24]       |
| FS–TiO₂ disk            | Dip-coating method    | 95% degradation (50 ppm phenazone (PNZ)) within 180 min (36 W UV light)                 | 95% degradation of 50 ppm PNZ within 90 min | PNZ    | [34]       |
| Mined CuFeS₂            | Milling process       | 85% TOC conversion (1.0 g catalyst/0.5 mM tyrosol (TY)) within 60 min (10 W UV LED light) | -                    | TY     | [19]       |
| Fe–N–Ag–TiO₃ clay bead  | Surface impregnation method | -                                                                                     | 77% degradation of 50 ppm cephalaxin (CEX) within 60 min | CEX    | [35]       |
| FS/FA/TiO₂ clay bead    | Dip-coating method    | 89% degradation (50 ppm CEX) within 4 h (36 W UV light)                                 | 94% degradation (50 ppm CEX) within 3.5 h | CEX    | [36]       |
| Fe₂O₃–TiO₂ film         | Sol–gel method        | 80% degradation (10 ppm ciprofloxacin (CIPRO), sulfamethoxazole (SMX), and trimethoprim (TMP) mixture) within 240 min by a solar simulator (Solarbox Model 1500e) | -                    | CIPRO, SMX, TMP | [37] |
| CuFeS₂/Ag₃PO₄           | Cyclic microwave heating | 96% degradation (20 mg catalyst/20 ppm RhB) within 1 min (2.5 W white-light LED)        | 99.8% degradation (0.15 g catalyst/15 ppm MB) within 6 min | RhB, MR, R6G, Fluorescein, PI, phenol | This study |
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