
Research article

Comparative study of CoFe_2O_4 - and Fe_3O_4 -coupled Ag_3PO_4 composites: interfacial coupling, photocatalytic stability, and magnetic recoverability

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Abstract: Silver phosphate (Ag_3PO_4 , APO) is a highly active visible-light photocatalyst, but its practical application is hindered by photocorrosion and the difficulty of post-reaction recovery. In this study, we aimed to clarify how the nature of the magnetic ferrite phase influences the interfacial coupling, photocatalytic behavior, stability, and recoverability of APO-based composites. For this purpose, APO was composited with CoFe_2O_4 (CFO) and Fe_3O_4 (FFO) through an in-situ hydrothermal route, and the resulting composites were comparatively examined by X-ray diffraction, Raman spectroscopy, field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), ultraviolet–visible (UV–Vis) diffuse reflectance spectroscopy, photocatalytic degradation of methylene blue (MB), cycling tests, and vibrating sample magnetometry. The results showed that both ferrites were successfully integrated without altering the APO crystal framework. CFO nanoparticles were more finely and uniformly distributed on APO than FFO, indicating a closer interfacial association in the APO/CFO system. Although pure APO exhibited the highest initial activity, APO/CFO retained a higher degradation rate than APO/FFO at appropriate ferrite loadings. At higher ferrite contents, both systems showed reduced activity because of optical shielding and aggregation. More importantly, APO/CFO displayed markedly better operational stability, retaining over 90% of its degradation efficiency after three cycles, whereas APO/FFO deactivated more rapidly. Magnetic measurements, together with a representative magnetic separation test, indicated that the

composites could be recovered under an external magnetic field. These results indicate that the practical functionality of APO-based magnetic composites depends more strongly on the quality of interfacial coupling than on the mere presence of a magnetic phase.

Keywords: silver phosphate; magnetic photocatalyst; interfacial coupling; CoFe_2O_4 ; photocorrosion; heterojunction

1. Introduction

Silver phosphate (APO) has attracted considerable attention in photocatalysis because of its narrow band gap (~ 2.4 eV) and exceptionally high quantum efficiency for water oxidation and degradation of organic pollutants. However, the practical application of APO remains limited by its intrinsic photocorrosion [1–3]. During photocatalytic operation, photogenerated electrons may reduce Ag^+ ions in the crystal lattice to metallic silver (Ag^0), leading to rapid deactivation [1]. In addition, when used as a dispersed powder, APO is difficult and costly to recover from treated water [3–5].

To address these two limitations, the integration of APO with magnetic nanoparticles, particularly spinel ferrites, has become an attractive strategy [6]. Such a combination not only enables rapid recovery of the photocatalyst under an external magnetic field, but is also expected to create heterointerfaces that may promote interfacial charge separation and thereby help mitigate photocorrosion [1–3,7,8].

Magnetic ferrites have been widely considered attractive partners for Ag_3PO_4 because they can introduce magnetic recoverability while affecting charge separation at the heterointerface [1,6]. Among them, Fe_3O_4 has been frequently used because of its facile synthesis, low cost, and soft magnetic behavior, which is favorable for redispersion after magnetic collection [9,10]. CoFe_2O_4 , in contrast, is a harder ferrite with stronger magnetization and higher structural stability, and has been explored in photocatalyst design as a magnetic component with potentially stronger interfacial interaction [11–13]. Although both ferrites have been individually coupled with Ag_3PO_4 or other visible-light photocatalysts, their roles are often discussed mainly in terms of magnetic recovery or overall photocatalytic performance. A more direct comparison of how these two ferrites differently affect the interfacial structure, functional stability, and practical recoverability of the same Ag_3PO_4 host remains limited.

Accordingly, a more fundamental question remains open: how does the nature of the magnetic ferrite phase affect the interfacial coupling and the structural preservation of APO? In practice, not all magnetic nanoparticles play equivalent roles when coupled with the same photocatalytic host. To clarify this issue, we provide a direct and systematic comparison between two composite systems, $\text{Ag}_3\text{PO}_4/\text{CoFe}_2\text{O}_4$ (APO/CFO) and $\text{Ag}_3\text{PO}_4/\text{Fe}_3\text{O}_4$ (APO/FFO). Using the same APO host and the same in-situ hydrothermal integration route, we evaluate how these two ferrite phases differently influence the structural evolution, morphology, and interfacial characteristics of the resulting composites. More importantly, we focus on how the coupling between APO and the two magnetic phases affect stability and practical recoverability, rather than simply identifying the sample with the highest initial photocatalytic activity. We aim to clarify whether practical functionality in heterojunction photocatalysts is governed mainly by interfacial coupling and the associated charge-transfer pathway or by the mere presence of magnetism.

2. Materials and methods

All chemicals were of analytical grade and used as received without further purification. The reagents included $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, FeCl_2 , FeCl_3 , AgNO_3 , Na_2HPO_4 , NaOH , citric acid, and ethanol. Methylene blue (MB) was used as the model organic pollutant.

CoFe_2O_4 (CFO) nanoparticles were synthesized by a sol–gel route followed by calcination. Stoichiometric amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1:2 molar ratio), together with citric acid, were dissolved in deionized water. The mixture was stirred continuously at 80 °C for 2 h to form a homogeneous sol, followed by the dropwise addition of ethanol. After being maintained at 80 °C for another 3 h, the resulting wet gel was dried at 100 °C and then calcined at 900 °C for 5 h to obtain CFO nanopowder. For comparison, Fe_3O_4 (FFO) nanoparticles were prepared by a conventional co-precipitation method. A mixed aqueous solution of FeCl_2 and FeCl_3 was heated to 70–80 °C under an argon atmosphere, and NaOH solution was added dropwise under vigorous stirring until the pH reached 12–14. The black suspension was aged for 1.5 h, and the resulting FFO nanoparticles were collected, washed with ethanol, and dried at 80 °C.

The magnetic composites were synthesized by an in-situ hydrothermal method. In a typical procedure, pre-synthesized ferrite nanoparticles were dispersed in an aqueous Na_2HPO_4 solution and magnetically stirred for 10 min. Separately, an aqueous AgNO_3 solution was prepared and stirred for 10 min, then added dropwise to the ferrite/phosphate suspension. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave and heated at 160 °C for 3 h. After cooling to room temperature, the precipitates were collected, washed thoroughly with deionized water and ethanol, and dried. Using this procedure, two series of composites with APO-to-ferrite molar ratios ranging from 9:1 to 5:5 were prepared and denoted as APO/CFO-9:1 to APO/CFO-5:5 and APO/FFO-9:1 to APO/FFO-5:5, respectively.

The photocatalytic performance of the prepared samples was evaluated through the degradation of MB under simulated solar irradiation using an ABET SunLite solar simulator (Model 11002) equipped with an AM 1.5 filter. Before each experiment, the irradiation intensity was calibrated using the reference cell supplied with the system, and the light intensity at the sample surface was adjusted to 1 Sun (100 mW cm^{-2}). In a typical experiment, 0.06 g of catalyst was ultrasonically dispersed in 30 mL of deionized water for 1 h. Then, 30 mL of a 20 ppm MB solution was added, giving a final MB concentration of 10 ppm. Before illumination, the suspension was stirred in the dark for 30 min to establish adsorption–desorption equilibrium. A modest but sample-dependent decrease in MB concentration was observed during this stage, indicating that the adsorption behavior was not identical for all samples. This variation may be related to differences in the accessible APO surface, ferrite dispersion, and nanoparticle aggregation. During irradiation, 3 mL aliquots were withdrawn at 10 min intervals, and the catalyst particles were removed by centrifugation at 4000 rpm. The residual MB concentration was determined from the absorbance at 665 nm using a Jasco V670 spectrophotometer (Japan). For reusability tests, the used catalyst was collected with an external magnet, washed, dried, and reused in subsequent degradation cycles under identical conditions.

The crystal structures of the synthesized samples were analyzed by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (Germany) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were recorded at room temperature on a LabRAM HR Evolution system (Horiba France SAS, France) equipped with a 785 nm laser. The morphology and elemental composition were examined by field-emission scanning electron microscopy (FESEM, Hitachi S-4800) operated at 5 kV and equipped

with an energy-dispersive X-ray spectroscopy (EDS) detector. Ultraviolet–visible diffuse reflectance spectra (UV–Vis DRS) were measured using a Jasco V770 spectrophotometer (Japan) equipped with an integrating sphere. The magnetic properties of the samples were evaluated at room temperature using a vibrating sample magnetometer (VSM).

3. Results and discussion

The crystal structures and phase purities of the as-synthesized samples were first examined by XRD. As shown in Figure 1, the diffraction patterns of pure APO, CFO, and FFO are consistent with the standard cubic phase of Ag_3PO_4 (JCPDS No. 06-0505) and the spinel phases of CoFe_2O_4 (JCPDS No. 22-1086) and Fe_3O_4 (JCPDS No. 19-0629), respectively. In the composite samples, the main reflections of both the APO and the corresponding ferrite phases coexist [5,7,14,15] without any obvious impurity peaks. The nearly unchanged peak positions of Ag_3PO_4 indicate that the primary crystal framework of APO remains stable during the composite formation process [1,16].

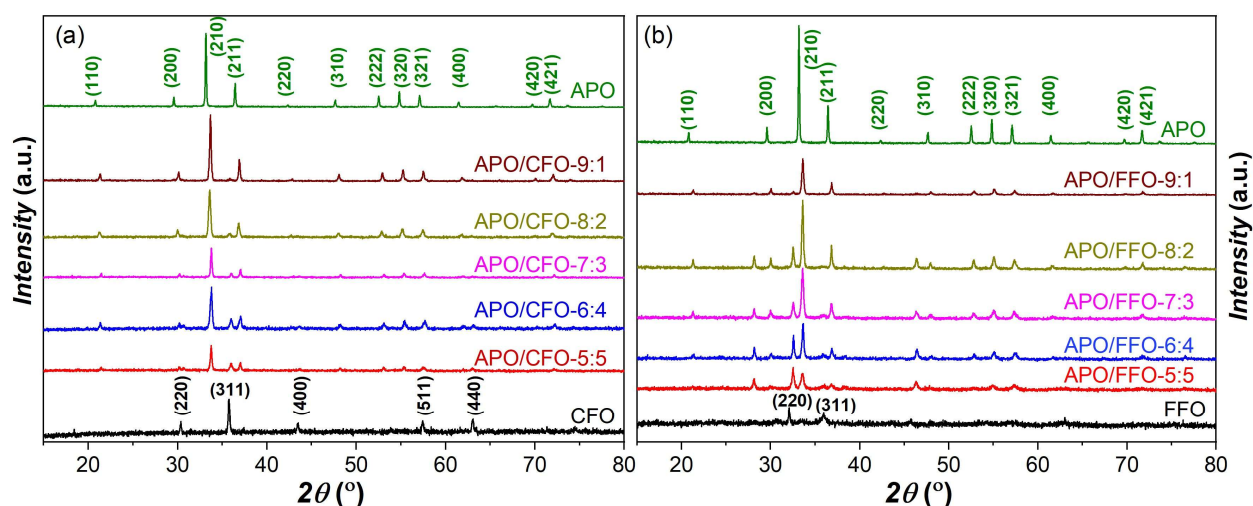


Figure 1. XRD patterns of (a) pure APO, pure CFO, and APO/CFO composites with varying molar ratios (from 9:1 to 5:5); and (b) pure APO, pure FFO, and APO/FFO composites with varying molar ratios (from 9:1 to 5:5).

For the APO/CFO composites (Figure 1a), the characteristic CFO (311) reflection appears at around 35.7° . As the CFO content increases, this peak becomes progressively more distinct, and its relative intensity with respect to the adjacent APO (211) reflection also increases. Notably, the CFO (311) peak shows a slight shift toward higher 2θ values in the composite samples compared to pure CFO. This behavior suggests a small decrease in the lattice spacing of CFO and is consistent with compressive microstrain induced by an interfacial lattice mismatch between CFO and APO [12,17,18]. Therefore, these observations suggest a stronger structural interaction in the APO/CFO system.

For the APO/FFO composites (Figure 1b), the incorporation of FFO is indicated by the appearance of the FFO (220) and (311) reflections at about 32.5° and 35.9° , respectively. However, compared to the APO/CFO system, the FFO peaks are broader and weaker, and their positions exhibit negligible shifting relative to pure FFO. This suggests a lower crystallinity or smaller coherent domain size of Fe_3O_4 in the composite, together with a weaker structural perturbation at the APO/FFO interface [19].

Overall, the XRD results indicate that both ferrites can be successfully integrated with the APO matrix without altering the APO crystal phase. Furthermore, the APO/CFO system exhibits stronger structural perturbation than APO/FFO, which supports the view of stronger interfacial coupling in the CFO-based composite.

The surface morphology and microstructure of the as-synthesized materials were examined by FESEM, as shown in Figure 2. The pure APO sample consists of well-defined quasi-spherical particles with an average diameter of 196 ± 58 nm (Figure 2a,d). Their relatively smooth surfaces are consistent with the good crystallinity indicated by the XRD results. In contrast, the pure CFO and FFO samples are composed of agglomerated nanoparticles with average sizes of 19 ± 5 and 23 ± 7 nm, respectively (Figure 2b,c). The smaller particle size of CFO may favor finer dispersion on the larger APO surface. The nanoscale ferrite particles also provide the magnetic component required for post-reaction recovery, as further supported by the VSM results.

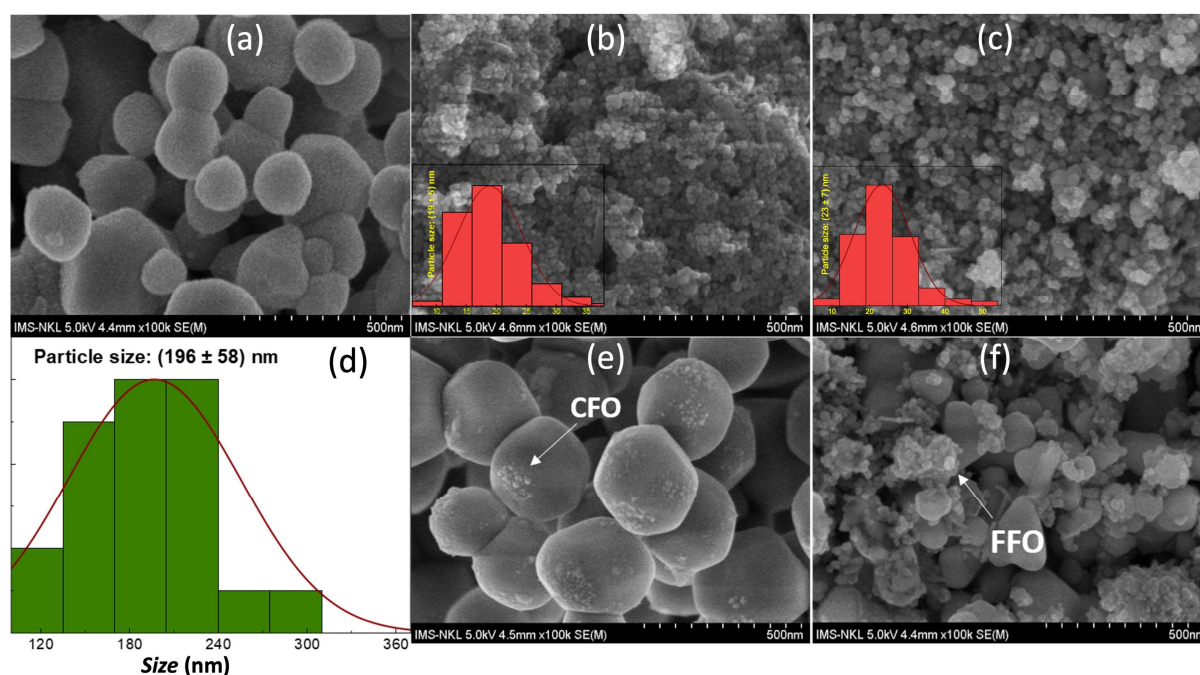


Figure 2. FESEM micrographs of (a) APO; (b) CFO; and (c) FFO; (d) particle size distribution of APO; FESEM micrographs of (e) APO/CFO-7:3; and (f) APO/FFO-7:3. The insets in (b) and (c) show the corresponding particle size histograms of CFO and FFO. All FESEM images were recorded at 100,000 $\times$ magnification.

The representative morphologies of APO/CFO-7:3 and APO/FFO-7:3 are shown in Figure 2e,f, respectively. In both systems, ferrite nanoparticles can be observed together with the larger APO particles, indicating the formation of composite structures. The ferrite particles attached to APO remain in the same general size range as the corresponding pure CFO and FFO samples. However, a difference can be seen in their dispersion behavior. In the APO/CFO composite, the CFO nanoparticles appear more finely and more evenly distributed on the APO surface. By contrast, in the APO/FFO composite, the FFO nanoparticles show a stronger tendency to aggregate into larger and more isolated clusters.

This morphological difference is consistent with the XRD results, which suggest a stronger structural perturbation in the APO/CFO system than in APO/FFO. Overall, the FESEM observations suggest

that CFO is more closely associated with the APO surface than FFO, which may contribute to the better structural stability and functional performance observed for the CFO-based composite [16,20,21].

To further verify the elemental composition of the as-synthesized materials, EDS was performed. As shown in Figure 3, the composite samples exhibit the expected characteristic signals of the APO matrix, including Ag, P, and O, together with those of the corresponding ferrite phases. In the APO/CFO series, Fe and Co signals are observed, whereas in the APO/FFO series, the Fe signal is present along with the APO-related elements.

A gradual increase in the relative intensities of the ferrite-related peaks can be observed from the 9:1 to the 5:5 compositions, which is consistent with the increasing ferrite content in the composite samples. No obvious impurity peaks are detected in either system. These EDS results therefore support the successful incorporation and coexistence of APO and ferrite phases, in agreement with the XRD, Raman, and FESEM observations.

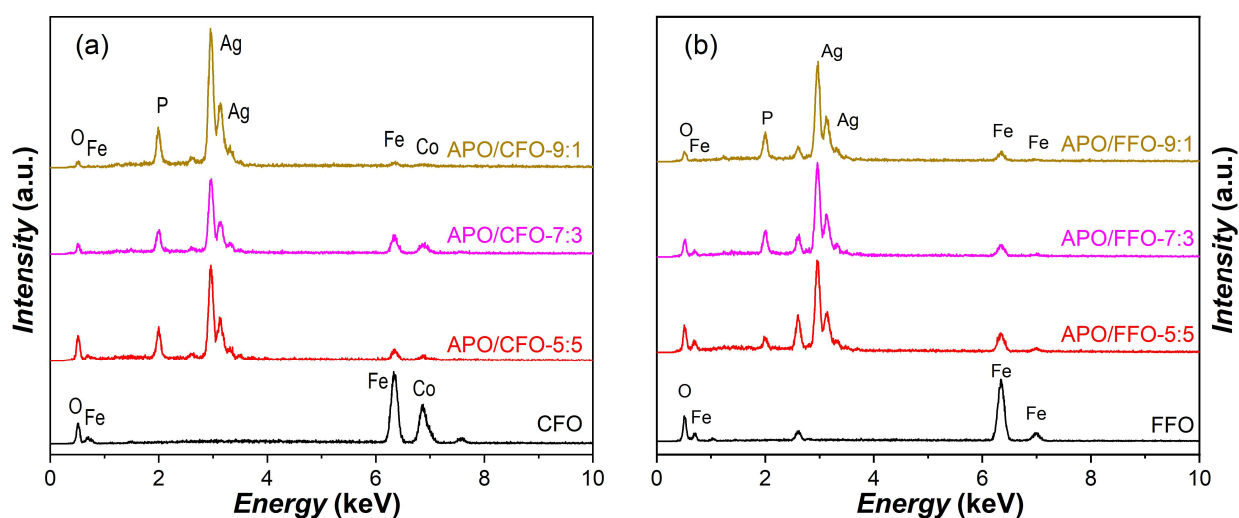


Figure 3. EDS spectra of representative (a) APO/CFO; and (b) APO/FFO composites with varying molar ratios (9:1; 7:3 and 5:5).

To further examine the local structural features of the composites, Raman spectroscopy was performed, and the spectra were normalized for comparative analysis (Figure 4). The pristine APO sample exhibits a strong characteristic band at around 908 cm^{-1} , which is assigned to the symmetric stretching vibration (ν_1) of the PO_4^{3-} tetrahedra [5]. For the pure ferrites, CFO shows relatively weak spinel-related Raman features, whereas FFO gives a stronger Raman response under identical measurement conditions. In the FFO spectrum, several low-wavenumber bands at about 225 , 292 , and 410 cm^{-1} are characteristic of $\alpha\text{-Fe}_2\text{O}_3$, suggesting partial surface oxidation of Fe_3O_4 during the Raman measurement [22]. In the composite samples, the coexistence of APO and ferrite phases remains evident.

The relative Raman intensities do not vary linearly with the nominal phase ratios. This behavior is likely related to the highly localized probing volume of the Raman laser, together with the non-uniform surface distribution of ferrite nanoparticles. In the APO/CFO series, the spectra remain largely dominated by the APO band at 908 cm^{-1} because the CFO-related Raman features are relatively weak. In contrast, the APO/FFO series shows a progressively stronger ferrite contribution, and the

overlap between FFO- and APO-related bands becomes more pronounced at higher FFO loadings. Therefore, in this case, the Raman intensities should be interpreted qualitatively rather than quantitatively.

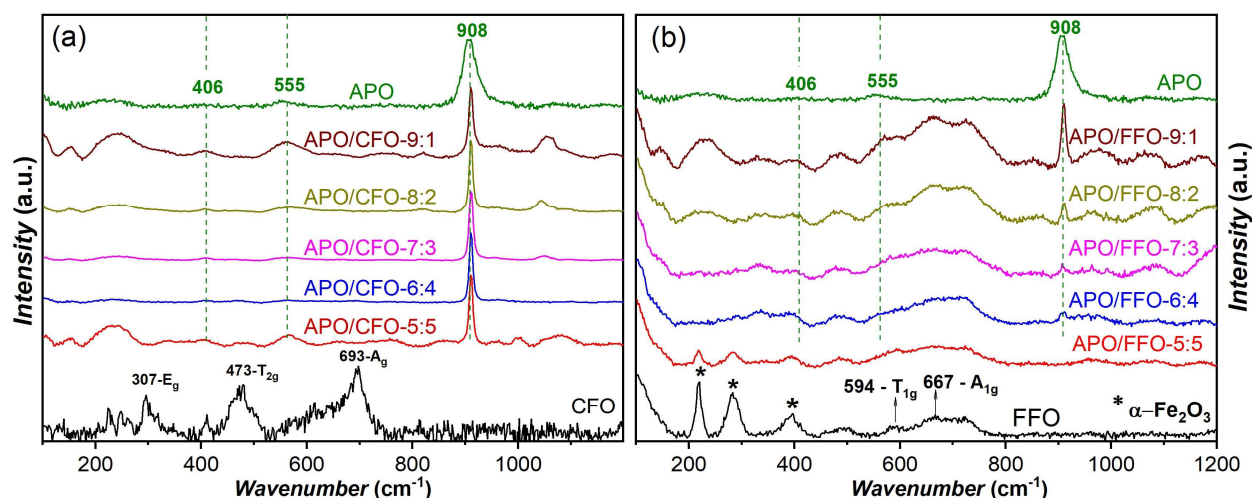


Figure 4. Raman spectra of (a) pure APO, pure CFO, and the APO/CFO composites with varying molar ratios (from 9:1 to 5:5); and (b) pure APO, pure FFO, and the APO/FFO composites with varying molar ratios (from 9:1 to 5:5).

A more meaningful feature is the spectral profile of the APO band at around 908 cm⁻¹. In the APO/CFO composites, this band becomes noticeably narrower than in pure APO. A similar tendency can also be seen in APO/FFO-9:1 and APO/FFO-8:2, but it becomes difficult to follow at higher FFO contents because of increasing spectral overlap and baseline distortion. To quantitatively support this observation, the primary APO band in the APO/CFO series was fitted with a Gaussian function using a linear baseline. The fitted full width at half maximum (FWHM) decreases markedly from 29.3 cm⁻¹ for pure APO to 8.7–10.6 cm⁻¹ for the APO/CFO composites. This confirms a clear narrowing of this band. In addition, the fitted peak center shows a slight shift toward higher wavenumber, from 907.4 cm⁻¹ for pure APO to about 910.7 cm⁻¹ for the APO/CFO composites. This slight blue shift is consistent with the presence of local compressive strain, in agreement with the XRD results [5,18]. In solid-state materials, peak narrowing is generally associated with reduced local structural disorder or a more uniform local bonding environment. In this context, the sharper APO band suggests that ferrite incorporation, especially in the APO/CFO system, is associated with a more ordered local environment for the PO₄³⁻ units. This interpretation is consistent with the XRD and FESEM results and further supports the view that APO/CFO system exhibits stronger structural perturbation and closer surface integration than in the APO/FFO system.

Figure 5 shows the optical absorption properties of the APO, APO/CFO, and APO/FFO powder samples. The pure APO sample exhibits a typical absorption edge in the visible region at approximately 488 nm, which corresponds to an estimated intrinsic band gap (E_g) of about 2.54 eV [3,5,23,24]. In contrast, pure CFO and FFO show broad absorption over the visible range, which is consistent with their intrinsically narrow band gaps and dark macroscopic appearance.

Upon ferrite incorporation, the APO/CFO and APO/FFO composites display a pronounced increase in background absorption intensity across the visible spectrum. This behavior is primarily attributed to the strong intrinsic absorption of the dark ferrite nanoparticles, which significantly

contributes to the average macroscopic optical response of the composite powders. Consequently, the intrinsic absorption edge of APO becomes less distinct in the mixed systems.

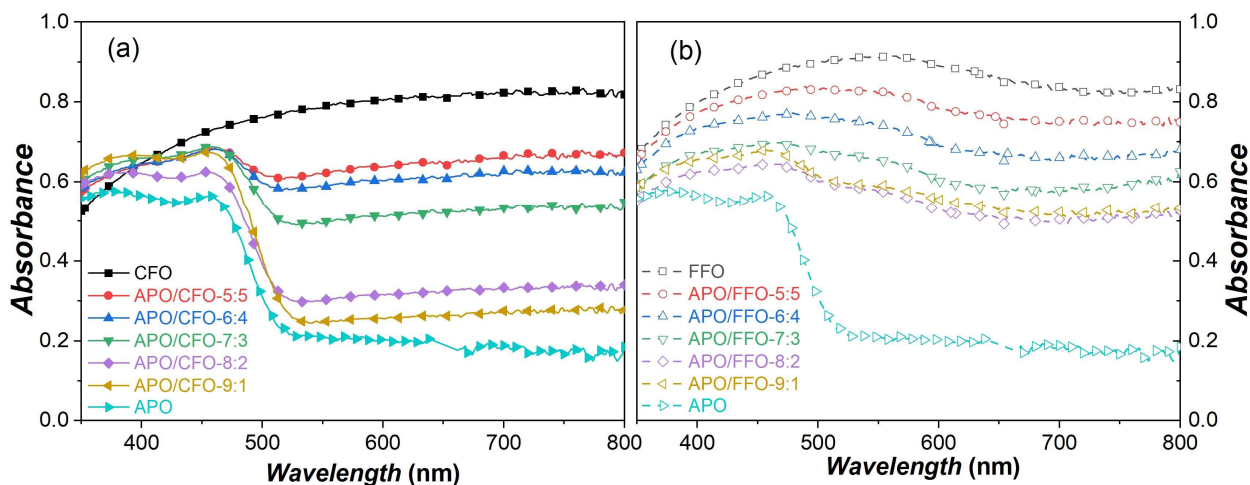


Figure 5. UV–Vis absorption spectra of (a) the APO/CFO; and (b) the APO/FFO composites with varying molar ratios (from 9:1 to 5:5), together with pure APO and their corresponding pure ferrite references.

Although subtle perturbations near the absorption edge can be observed, they are relatively limited and challenging to quantify because of the elevated background absorption. Therefore, rather than over-interpreting complex electronic band-structure modifications, these results are used to confirm the successful integration of the ferrite phases. This integration effectively enhances the overall visible-light harvesting capacity of the composites, a property that is beneficial for driving solar-simulated photocatalytic reactions.

The photocatalytic performances of the two series of samples, APO/CFO and APO/FFO, were evaluated by monitoring the degradation of MB under simulated solar irradiation, as shown in Figure 6. The pure APO sample exhibits the highest intrinsic activity, achieving complete degradation within about 15 min. In comparison, the APO/CFO composites (Figure 6a) show a composition-dependent decrease in photocatalytic rate with increasing CFO content. The APO/CFO-9:1 sample required about 75 min for complete degradation, while APO/CFO-8:2 required about 105 min, and APO/CFO-7:3 extended to nearly 165 min. At higher CFO loadings, the degradation became slower. This decrease in activity, despite the increased visible-light absorption background, can be reasonably related to morphological and optical effects. As indicated by the SEM and UV–Vis absorption spectra, higher CFO loadings tend to increase ferrite aggregation and optical shielding, which reduce the exposed photoactive APO surface and may lower the effectiveness of the APO/CFO interface. In addition, these aggregates may act as recombination sites for photogenerated charge carriers.

The APO/FFO composites (Figure 6b) showed much poorer photocatalytic activity. Complete MB degradation required about 5 h for APO/FFO-9:1, about 6.5 h for APO/FFO-8:2, and more than 7 h at higher FFO loadings. This strong reduction in activity is consistent with the weaker structural interaction suggested by the XRD results, the more aggregated morphology observed by FESEM, and the less distinct absorption-edge behavior in the absorption spectra. Taken together, these results suggest that the APO/FFO interface is less effective than APO/CFO in preserving the photocatalytic function of APO.

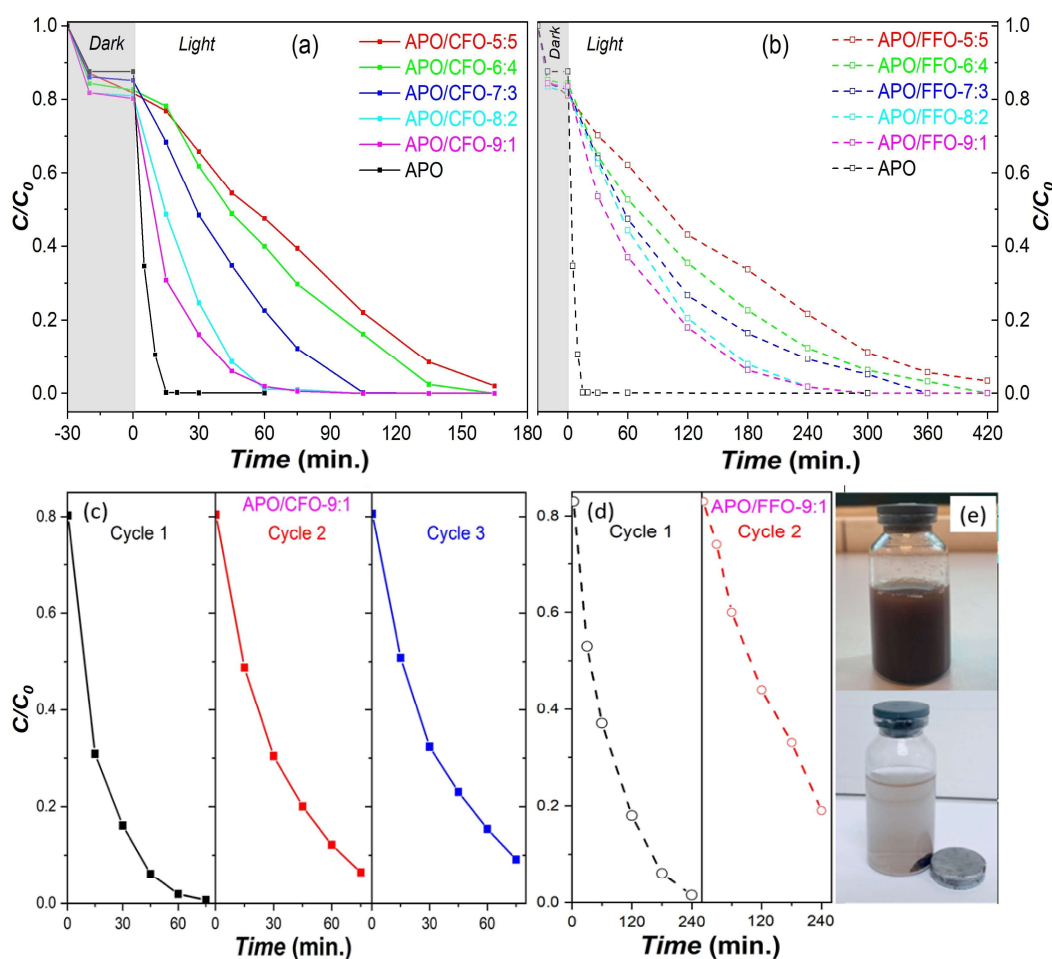


Figure 6. Photocatalytic degradation of MB under solar-simulated irradiation: degradation profiles of (a) the APO/CFO; and (b) the APO/FFO composites with varying molar ratios (from 9:1 to 5:5); reusability tests of (c) the APO/CFO-9:1; and (d) the APO/FFO-9:1 composites; (e) a photo demonstrating the representative magnetic separation test of the APO/FFO-9:1 sample.

The practical applicability of the composites was further examined through reusability tests (Figure 6c,d). The representative APO/CFO-9:1 composite maintains high degradation efficiency over three consecutive cycles, whereas the representative APO/FFO-9:1 composite shows a much faster decrease in activity. The better operational stability of APO/CFO is consistent with its stronger interfacial coupling, which may favor interfacial charge separation and help reduce photocorrosion in the Ag_3PO_4 lattice during repeated use. In contrast, the faster activity loss in APO/FFO suggests that its weaker interface is less effective in maintaining photocatalytic performance during repeated use. After the degradation cycles, the composites can be recovered from the aqueous suspension with an external magnet (Figure 6e), consistent with the magnetic response discussed below.

Overall, these results show that introducing a magnetic ferrite phase leads to a trade-off with the initial reaction rate of pure APO. However, between the two ferrites studied here, CFO provides a more favorable balance between photocatalytic function, reusability, and magnetic recoverability than FFO.

To better position our results within the literature, the photocatalytic performance of the APO/CFO composite was compared with several related Ag_3PO_4 -based photocatalysts previously reported for MB degradation, as summarized in Table 1. Although the irradiation sources and

experimental conditions are not identical, the comparison shows that the present APO/CFO system exhibits competitive photocatalytic activity under simulated sunlight. More importantly, the value of this work lies not only in the degradation efficiency, but also in the direct comparison between CoFe_2O_4 and Fe_3O_4 as two magnetic ferrite partners for the same Ag_3PO_4 host.

Table 1. Comparison of the photocatalytic performance of the APO/CFO composite with related Ag_3PO_4 -based photocatalysts reported in the literature for MB degradation.

No.	Reported system	Irradiation source	Reaction conditions	Best photocatalytic performance	Ref.
1	$\text{Ag}_3\text{PO}_4\text{-ZnO}$	UV (365 nm) and visible source (544 nm)	20 mg photocatalyst in 50 mL of 10 ppm MB solution	92.8% MB degradation within 120 min	[25]
2	$\text{Ag}_3\text{PO}_4/\text{Fe}_3\text{O}_4/\text{Chitosan}$	Visible light irradiation	30 mg photocatalyst in 50 mL of 10^{-4} M MB solution	95% MB degradation within 120 min	[26]
3	Biochar/ $\text{NiFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$	LED lamp (10 W)	26 mg photocatalyst in 10 mL of 10 ppm MB solution	94% MB degradation within 90 min	[27]
4	$\text{ZnO}/\text{Ag}_3\text{PO}_4$	Visible light	50 mg photocatalyst in 50 mL of 10^{-5} M MB solution	97.14% MB degradation within 120 min	[28]
5	Iodine-doped Ag_3PO_4	Blue LED (3 W)	100 mg photocatalyst in 100 mL of 10 ppm MB solution	>97.14% MB degradation within 15 min	[29]
6	Chlorophyll@ Ag_3PO_4	Blue LED (3 W)	100 mg photocatalyst in 100 mL of 10 ppm MB solution	>99% MB degradation within 15 min	[30]
7	APO/CFO	Simulated sunlight	60 mg photocatalyst in 60 mL of 10 ppm MB solution	>99% MB degradation within 75 min	This work

An explanation for this difference is that the photocatalytic behavior of the two composite systems is governed not only by the presence of a magnetic phase, but also by the quality of the heterointerface formed with APO. In the APO/CFO series, the XRD results suggest stronger structural perturbation, while FESEM shows finer and more uniform ferrite distribution on the APO surface. Together with the more pronounced modification of the optical absorption behavior, these observations indicate that CFO forms a closer and more effective interface with APO than FFO. Such an interface is more favorable for interfacial charge separation after light excitation and may therefore help preserve the photocatalytic function of APO during repeated use. In contrast, the weaker structural interaction and more aggregated morphology of APO/FFO are less favorable for this process, which is consistent with its much poorer photocatalytic and cycling performance.

The magnetic properties of the powder samples APO/CFO-7:3 and APO/FFO-7:3 are shown in Figure 7. The magnetization–field curves of the two ferrite-based systems exhibit distinctly different

magnetic behaviors, which are relevant to their recovery and reuse. For the pure FFO and the representative APO/FFO-7:3 composite, the saturation magnetization (M_s) is relatively low, and the coercivity (H_c) is very small. This indicates a soft magnetic response, which is favorable for easy redispersion after the external magnetic field is removed. However, the weak magnetic moment also implies a weaker magnetic driving force during separation. The low magnetization of FFO may be related to non-ideal crystallinity or magnetic ordering in the synthesized Fe_3O_4 nanoparticles, which is broadly consistent with the preceding structural analyses [12,18].

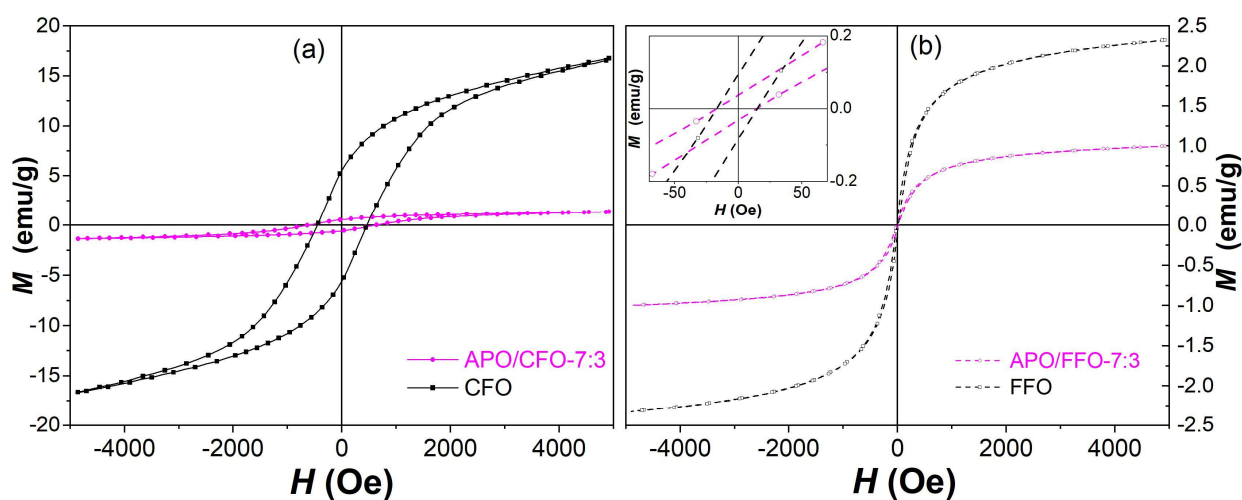


Figure 7. Room-temperature magnetization–field hysteresis loops of (a) pure CFO and APO/CFO-7:3; and (b) pure FFO and APO/FFO-7:3.

In contrast, the pure CFO and the representative APO/CFO-7:3 composite show a much stronger magnetic response, with an M_s roughly one order of magnitude higher than that of FFO. The CFO-based samples also exhibit a clear hysteresis loop with a coercivity of about 1500 Oe, which is typical of hard spinel ferrites [11,12]. This behavior is advantageous for rapid magnetic collection after the photocatalytic reaction. Furthermore, the finite coercivity and remanence suggest that the APO/CFO particles may show a stronger tendency toward magnetic aggregation after separation than the APO/FFO system.

From a practical viewpoint, the APO/FFO system may offer easier redispersion because of its very small coercivity, whereas the APO/CFO system is expected to enable easier magnetic collection because of its much larger magnetization. When these magnetic properties are considered together with the photocatalytic results, the APO/CFO system offers a more favorable practical balance, as it combines strong magnetic recoverability with better functional stability during repeated use.

4. Conclusions

In summary, a comparative study of APO/CFO and APO/FFO composites was carried out to clarify the role of the magnetic ferrite phase in heterojunction photocatalysts. The structural and morphological results suggest that CFO forms a closer interfacial association with the APO matrix than FFO, as reflected by the stronger structural perturbation, finer surface distribution, and more ordered local environment observed in the CFO-based system. In contrast, FFO shows a stronger tendency to aggregate, leading to a less uniform and more weakly coupled interface.

From a functional point of view, the incorporation of either ferrite introduces a trade-off by reducing the initial photocatalytic rate of pure APO, mostly because of optical shielding and aggregation effects. However, the APO/CFO system preserves the photocatalytic function of APO much better than APO/FFO and shows better operational stability during repeated use. In addition, CFO provides a much stronger magnetic response, which is advantageous for post-reaction recovery, whereas FFO shows softer magnetic behavior that may favor easier redispersion.

Overall, these results indicate that, in Ag_3PO_4 -based magnetic photocatalysts, the quality of interfacial coupling is more important than the mere presence of a magnetic phase in determining the balance between photocatalytic activity, operational stability, and magnetic recoverability.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

Acknowledgments

This work was supported by the scientific and technological project of the Ministry of Education and Training level (grant number B2026-SPH-03).

Author contributions

Do Chung Pham: conceptualization; data curation; writing—review & editing. Manh Hung Nguyen: methodology; visualization. Viet Tuyen Doan: visualization; writing—original draft. Thi Hang Lam: investigation. Thi Mai Oanh Le: data curation; writing—original draft. Van Minh Nguyen: supervision; funding acquisition.

Conflict of interest

The authors declare no conflict of interest.

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