

Article

Pulsed-Laser Induced Photolysis of Synthesizing Magnetic Fe₃O₄ Nanoparticles for Visible-Light Photocatalysis

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Abstract: Our report is the first example describing the successful synthesis of magnetic Fe₃O₄ nanoparticles (NPs), for which we used pulsed-laser induced photolysis (PLIP). Compared with the previous method of using pulsed-laser ablation of a target, or strong energy of pulsed-laser light to decompose precursors in generating a solvated-ion reaction, the PLIP method used here is dependent on hydrogen peroxide (H₂O₂) to generate a hydrolysis reaction. Energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were used to demonstrate the Fe₃O₄ crystalline structure of the synthesized NPs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images revealed that the average size of the NPs was about 20–50 nm. Regarding their magnetic characteristics, the synthesized NPs exhibited a saturation magnetization of 5.62 emu/g, remanence of 3.82 emu/g, and coercive force of 49.8 Oe. The photocatalytic experiments confirmed that the synthesized magnetic Fe₃O₄ NPs have visible light-degradation effects based on their ability to photocatalytically degrade methylene blue (MB). The MB degradation efficiency was 60–80% under white-light exposure for 180 min. This study presents a new route for synthesizing magnetic Fe₃O₄ NPs for their potential use in photocatalysis.

Keywords: photolysis; pulsed-laser; magnetic nanoparticles; visible-light photocatalysis



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1. Introduction

In recent years, the release of chemicals and harmful substances has resulted in the pollution of water sources, and this poses a threat to the lives of animals and plants; therefore, there is a need to develop advanced materials to detect or degrade hazardous organic chemical dyes [1–3]. Most of the methods for degrading textile dyes, such as biological filtration [4], adsorption and sedimentation, ion exchange [5,6], ultraviolet [7], and ozone [8,9] treatment methods, are prohibitively expensive, unavailable, and ineffective. Advances in photodegradation technology have attracted scientists to use this technique for degrading dyes because of its higher efficiency and feasibility compared with other traditional methods [10,11].

From the point of view of materials, the photocatalysis of semiconducting materials is considered a promising way to remove various organic pollutants from wastewater through the conversion of the toxic substances into safe small molecules via highly reactive radicals (OH[−], H⁺) for [12]. An ideal photocatalyst should be nontoxic, inexpensive, stable, readily available, and highly photoactive. However, it has not been possible so far to

obtain these advantages within a photocatalyst that also has high surface area, stability, photocatalytic activity, and biocompatibility; these excellent properties have only been found in nanomaterial-based photocatalysts [13–16]. Among the various types of nanomaterials, iron-oxide nanoparticles (IrO NPs) have excellent catalytic and reducing properties for application in wastewater treatment, and they have the advantage of being easy to separate compared with other nanomaterials, which require very expensive centrifugation processing [17]. The applications of IrO NPs range from the removal of heavy metals [18,19], dyes [20–22], and antibiotics [23–25] from water sources to other uses in biomedical fields. Regarding the application of IrO NPs as photocatalysts, the mechanism by which dyes undergo photodegradation via UV light irradiation is due to the rapid transfer of photo-generated electrons, resulting in the efficient separation of electrons and holes. The hole itself is a strong oxidant that can be oxidized and adsorbed on the surface of IrO NPs to generate $\text{HO}^\bullet$ radicals. The free radicals adsorbed on the surfaces of IrO NPs are strong oxidants that not only oxidize the adsorbed organics but also diffuse into the bulk solution and oxidize the organics. After a series of oxidation processes, organic compounds can finally be converted into harmless end products via CO_2 and H_2O [26,27].

Due to the excellent properties of IrO NPs, their synthesis has attracted considerable interest. Past studies have also confirmed that IrO NPs can be fabricated by various methods, such as thermal reaction, chemical reduction, and green synthesis methods [28]. However, the synthesis of monodispersed IrO NPs in solvents remains a challenge because of the inherent aggregation properties of these NPs. Significant effort has also been devoted to overcoming the aggregation problem; however, these methods are time-consuming, inefficient, and complicated to operate, sometimes requiring harsh chemical-reaction conditions and/or the addition of different chemical reagents, such as reducing agents and surfactants [29–32]. The generation of NP dispersions in a liquid environment using high-energy lasers is an efficient method for synthesizing NPs directly in liquids. The earliest examples were based on pulsed-laser-ablation techniques, in which a laser beam was directly irradiated on a solid material immersed in a liquid solution, ablating the surface to produce NPs of the same elemental composition as the solid material [33–35]. Indeed, the synthesis of NPs in a liquid environment has advantages due to widely controllable experimental conditions and changes in reactants.

Another method for making NPs by pulsed laser is to use water-based metal salts. When the laser light pulse reacts with the metal salts, metal NPs are formed by the reduction of metal ions. The reduction reaction can occur continuously due to the supplementation of electrons from the ionized metal salts [36]. The resulting electron density is high, and a wide variety of noble-metal nanoparticles and multi-metal-alloy nanoparticles can be easily fabricated and continuously produced. Previous studies have shown that spherical IrO NPs can be synthesized from ferrocene/hexane solutions by femtosecond near-infrared laser-light pulses (800 nm, 40 fs) [37,38]. These studies also presented the size distribution, elemental ratios, and structural information of these IrO NPs. A nanosecond UV pulsed laser (355 nm, 8 ns) was also used in one study for comparison; however, there are no experimental results demonstrating that these IrO NPs possess any magnetism. Here, we utilize, for the first time, the pulsed-laser-induced photolysis (PLIP, 532 nm, 15 ns) in the synthesis of magnetic Fe_3O_4 NPs. Previous studies have successfully used this method to fabricate Au NPs, Au-graphene, and Au- TiO_2 nanocomposites (NCPs) [39]. Compared with other laser-ablation methods, the PLIP method is more flexible in allowing a wider choice of precursor to be dissolved in a suitable solvent. By adding different NPs to the precursor solution, NCPs could be easily fabricated by using the PLIP method. For synthesizing magnetic NPs, the precursor used here was ferrocene/acetone, which is different from the previously used ferrocene/hexane solution. By introducing an oxidant, hydrogen peroxide (H_2O_2), into the precursor, the magnetic Fe_3O_4 NPs were formed through the photolysis process induced by pulsed-laser irradiation. At the same time, we demonstrate that the PLIP-synthesized Fe_3O_4 NPs are efficient in visible-light catalysis. This study provides another synthetic route for magnetic Fe_3O_4 NPs for their application in photocatalysis.

2. Results and Discussion

2.1. PLIP Fabrication of Magnetic Fe₃O₄ NPs

Figure 1 shows a schematic diagram of Fe₃O₄ NP fabrication using the PLIP method. This method primarily involves the addition of H₂O₂ into ferrocene/acetone precursors and the triggering of a photolysis reaction through the energy of pulsed-laser light. Figure 1 also shows a photograph of the suspended Fe₃O₄ NPs without (right) and with (left) magnetic separation.

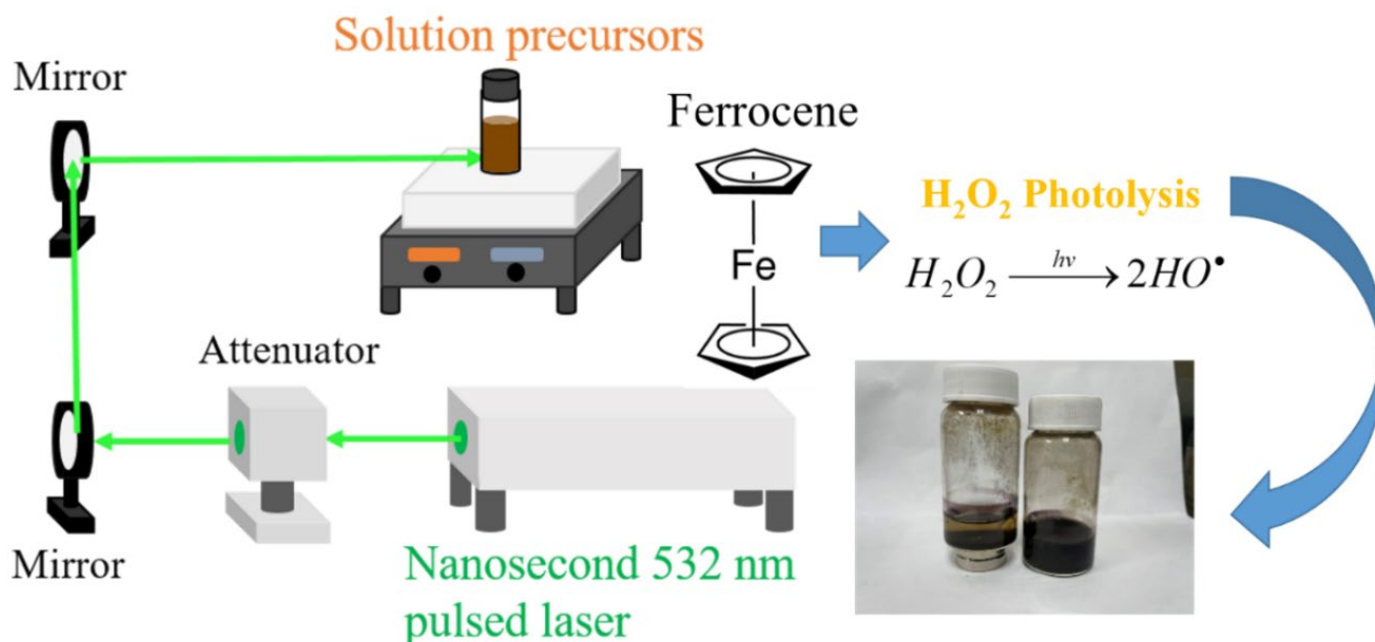


Figure 1. Schematic of experimental setup and precursors used for fabricating Fe₃O₄ NPs through pulsed-laser-induced photolysis (PLIP). The photograph also shows the Fe₃O₄ NPs separated from DI water under a magnet.

2.2. SEM, XRD, and XPS Characteristics of Fabricated Fe₃O₄ NPs

The X-ray diffraction (XRD) patterns of the PLIP-fabricated magnetic Fe₃O₄ NPs are shown in Figure 2, which reveals the formation of magnetite with well-defined crystallinity. The diffraction peaks, (311), (400), and (440), match well with the normal characteristic diffractions of the Fe₃O₄ inverse spinel structure [40,41]. The broadening of the Bragg peaks indicates the formation of Fe₃O₄ nanoparticles. Here, the (311) peak with the highest intensity was used to calculate the particle size of the Fe₃O₄ (30 nm) according to the Debye–Scherrer equation [41].

The surface morphology of the Fe₃O₄ NPs were observed by SEM, and the obtained image is shown in Figure 3a. The Fe₃O₄ NPs synthesized using the PLIP technique have spherical structures and a tendency to agglomerate. This agglomeration phenomenon is likely to have been caused by van der Waals forces and magnetic attraction between the NPs. The images obtained by the EDS analysis (Figure 3b) confirmed that the elemental ratio of the Fe₃O₄ NPs is about 2.35:4 (Figure 3c), which is close to the ideal ferrite-to-oxygen ratio of 3:4.

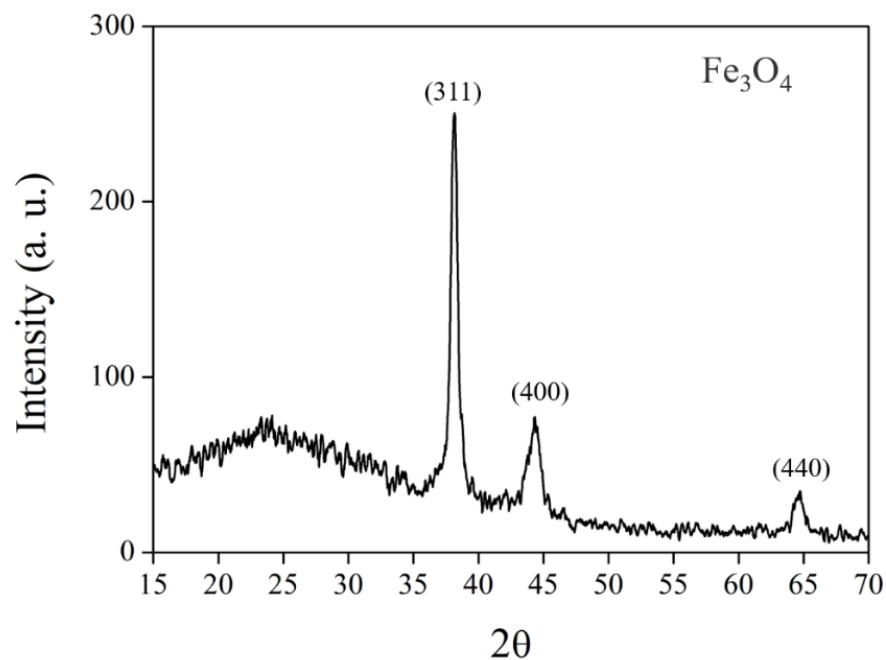


Figure 2. XRD pattern of PLIP-synthesized magnetic NPs indicating the Fe_3O_4 crystalline structure.

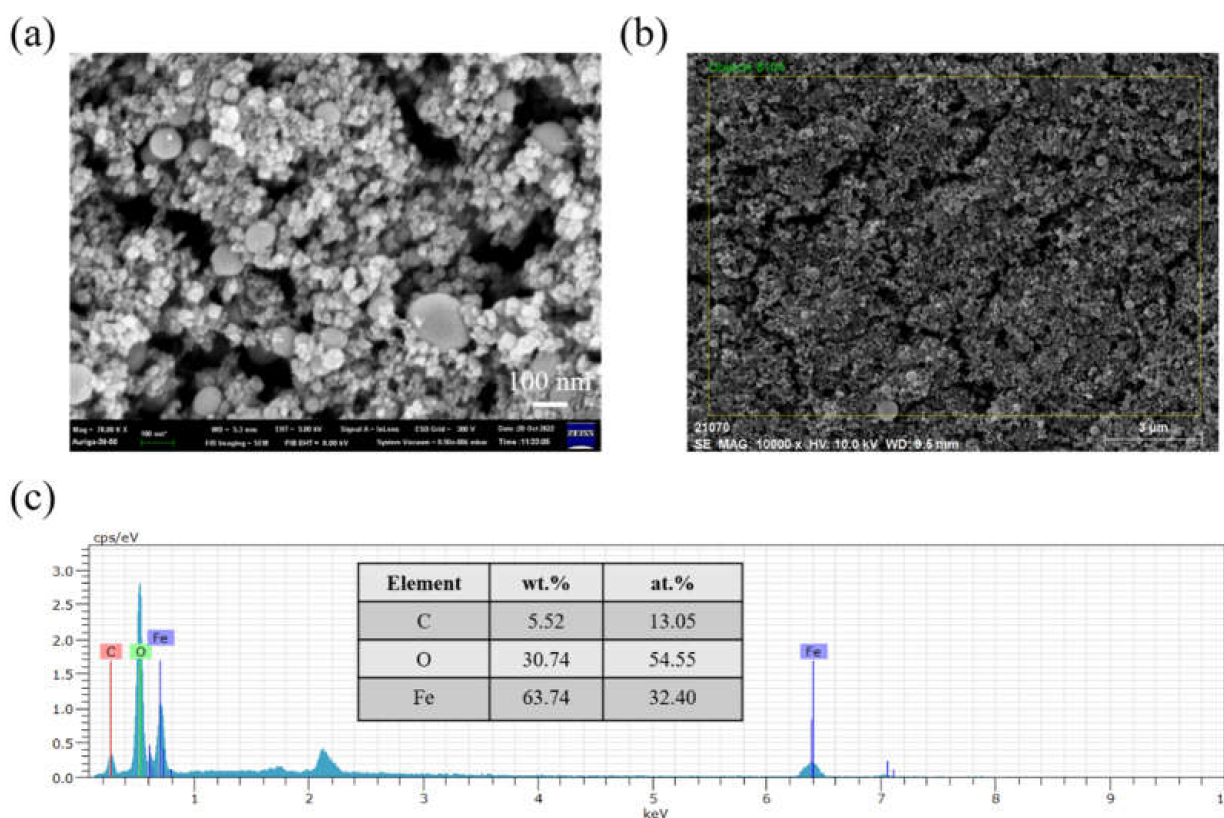


Figure 3. (a) SEM image; (b) SEM image corresponding to (c) EDS analysis of Fe_3O_4 NPs.

The binding energy, which reveals the surface composition of the PLIP-synthesized NPs, was further verified by XPS analysis, and the results are shown in Figure 4. The observed spectra of the NPs show characteristic peaks at 531.5, 712.5, and 725.5 eV corresponding to O 1s, Fe 2p_{3/2}, and Fe 2p_{1/2}, respectively (Figure 4a). The observed satellite peak (718.6 eV) was also observed as evidence of the oxidation state in the Fe_3O_4 NPs

(Figure 4b). Figure 4c shows the O 1s peak observed at 529.7 eV (green curve) and 530.2 eV (pink curve) corresponding to the energy for binding of oxygen to iron in the Fe_3O_4 lattice, whereas the shoulder at 531.6 eV (blue curve) indicating the presence of chemisorbed species (OH^-) on the sample surface [40].

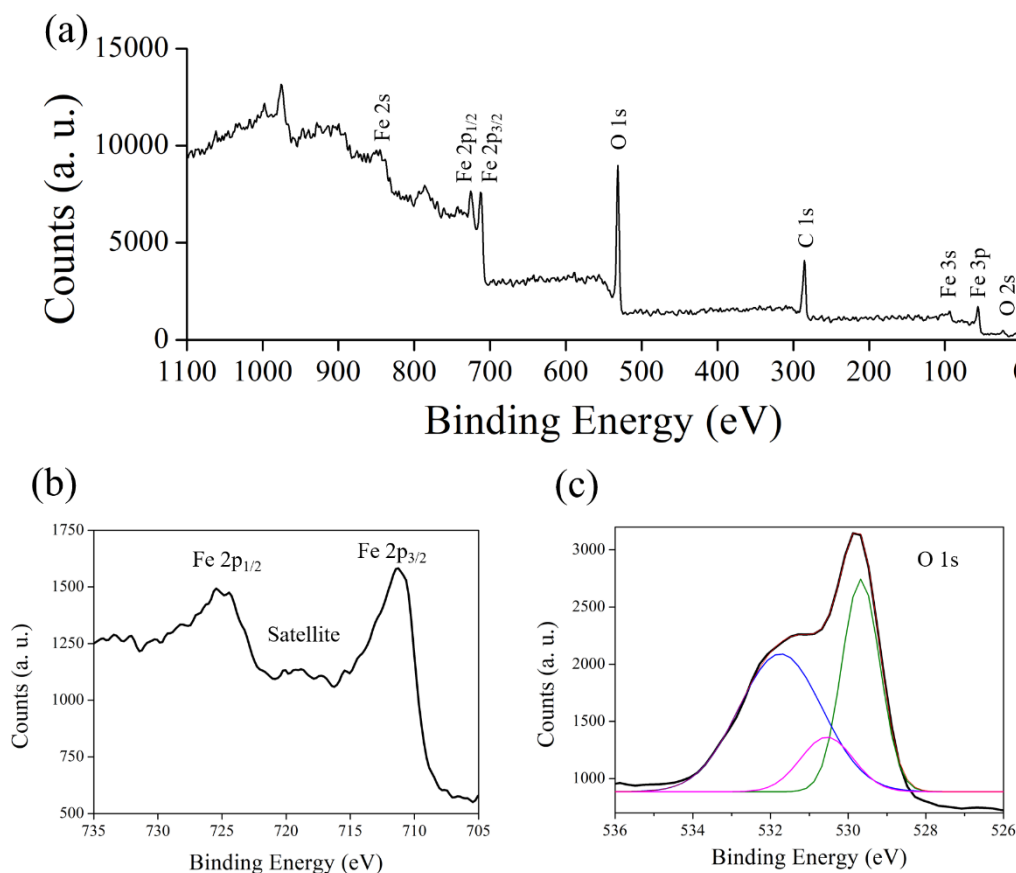


Figure 4. XPS patterns of PLIP-synthesized magnetic Fe_3O_4 NPs showing (a) full spectrum, (b) Fe 2p, and (c) O 1s.

2.3. TEM, SQUID VSM and Absorption Characteristics of Fabricated Fe_3O_4 NPs

Through the high energy of the pulsed laser, the chemical substances in the liquid were reacted to finally produce NPs, which mainly rely on the photochemical reaction of the reactants. In the case of the IrO NPs, when a high-energy pulsed laser reacts with a precursor, metal NPs are formed by the oxidation of metal ions due to the ionization of solvent [36]. For example, ferrocene/xylene, ferrocene/benzene, and ferrocene/hexane have been used to fabricate IrO NPs containing iron cores covered with or without a carbon shell [36,37]. Compared with the previous method of using a pulsed laser as high-energy light source to complete ionization of the solvent, our PLIP method uses a pulsed laser to initiate the photolysis process. The metal ions (Fe^{2+}) were oxidized with the addition of H_2O_2 in the precursor solution. Figure 5a,b show TEM micrographs of the NPs fabricated using pulsed laser (532 nm, 15 ns) for 60 min with ferrocene, as the precursor, in acetone/ H_2O_2 solution via the PLIP method. The TEM images clearly show high-contrast spherical NPs surrounded by low-contrast organic aggregate particles. It should be noted that carbon shells were not observed in the TEM images. The size distribution of the fabricated Fe_3O_4 NPs was between 20 and 50 nm. Figure 5c shows the SQUID VSM measurement of the synthesized NPs, indicating the hysteresis loop of the Fe_3O_4 NPs at 300 K. The magnetic nanoparticles synthesized by this laser method had a saturation magnetization of 5.62 emu/g, remanence of 3.82 emu/g, and coercive force of 49.8 Oe. Previous studies have shown that low remanence or coercive force aid in the

dispersion of ferromagnetic nanoparticles in aqueous solutions [22]. Ferromagnetic NPs can rely on Brownian motion to break the chain-like structure created by the magnetic moment and form a hysteresis loop in a small area due to the low coercive force of the NP suspension. In this case, no significant magnetic interactions remained after removal of the external magnetic field, which is important for performing reproducible and reversible photocatalytic activities. Figure 5d shows the absorption spectra of magnetic Fe_3O_4 NPs dispersed in a DI water solution, indicating absorbance in the visible range, which favors visible-light photocatalytic activity.

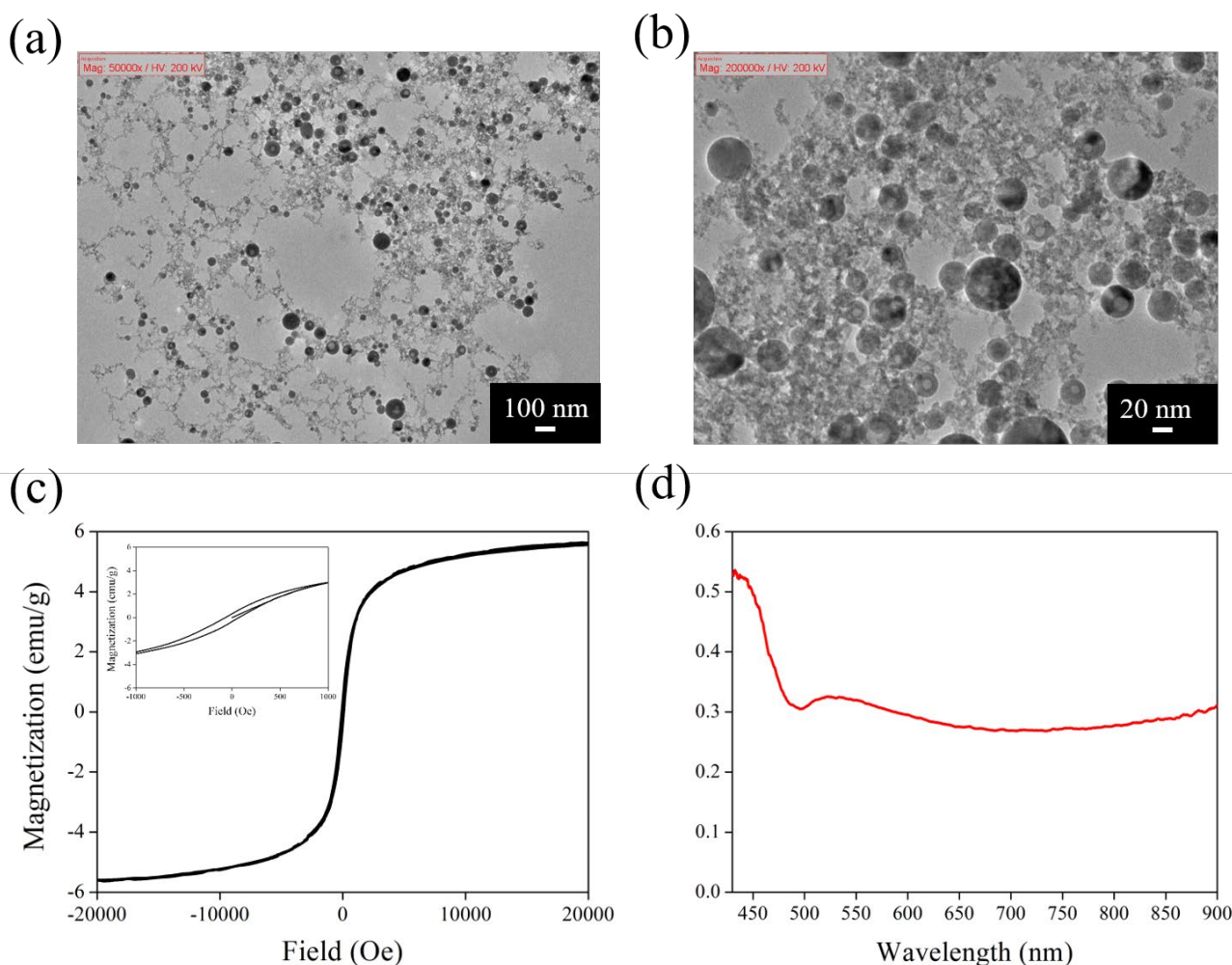


Figure 5. TEM images (a,b), (c) magnetization curve, and (d) absorption spectrum of magnetic Fe_3O_4 NPs synthesized by PLIP method using ferrocene as precursor.

2.4. Photocatalytic Activity of PLIP-Fabricated Fe_3O_4 NPs

Iron oxides are representative materials for single-phase magnetic catalysts, including magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$ and $\beta\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$), which spontaneously respond to the application of magnetic fields [16]. Most single-phase photocatalysts have low adsorption capacity in the visible-light range, resulting in poor catalytic efficiency. This problem can be solved through the creation of binary and ternary photo-sensitive ferrites [17]. Single-phase magnetic photocatalytic materials can also perform visible-light catalysis in photocatalytic systems containing strong oxidants, such as H_2O_2 , a catalytic reaction called photo-Fenton catalysis [17]. In the presence of light, photo-Fenton catalysts are bound and generate OH^- radicals, which greatly accelerate the degradation process. For potential photocatalytic applications, magnetic catalysts must have high saturation magnetization and low remanence such that they can rapidly respond to applied

magnetic fields and rapidly disperse in the liquid phase upon removal of the magnetic field. The single-phase magnetic NPs (magnetite, Fe_3O_4) synthesized by our proposed PLIP method were shown to be useful as visible-light-degradation catalysts without requiring the addition of a strong oxidant. Figure 6a shows the absorption spectra recorded for an MB solution containing magnetic nanoparticles under white-light irradiation. It can clearly be seen that the absorption spectrum decreased under continuous white-light illumination. Figure 6b compares the color change of the MB solution after 30 min white-light irradiation without and with the addition of magnetic NPs. It is obvious that the color of the MB solution becomes lighter with the addition of magnetic nanoparticles than without.

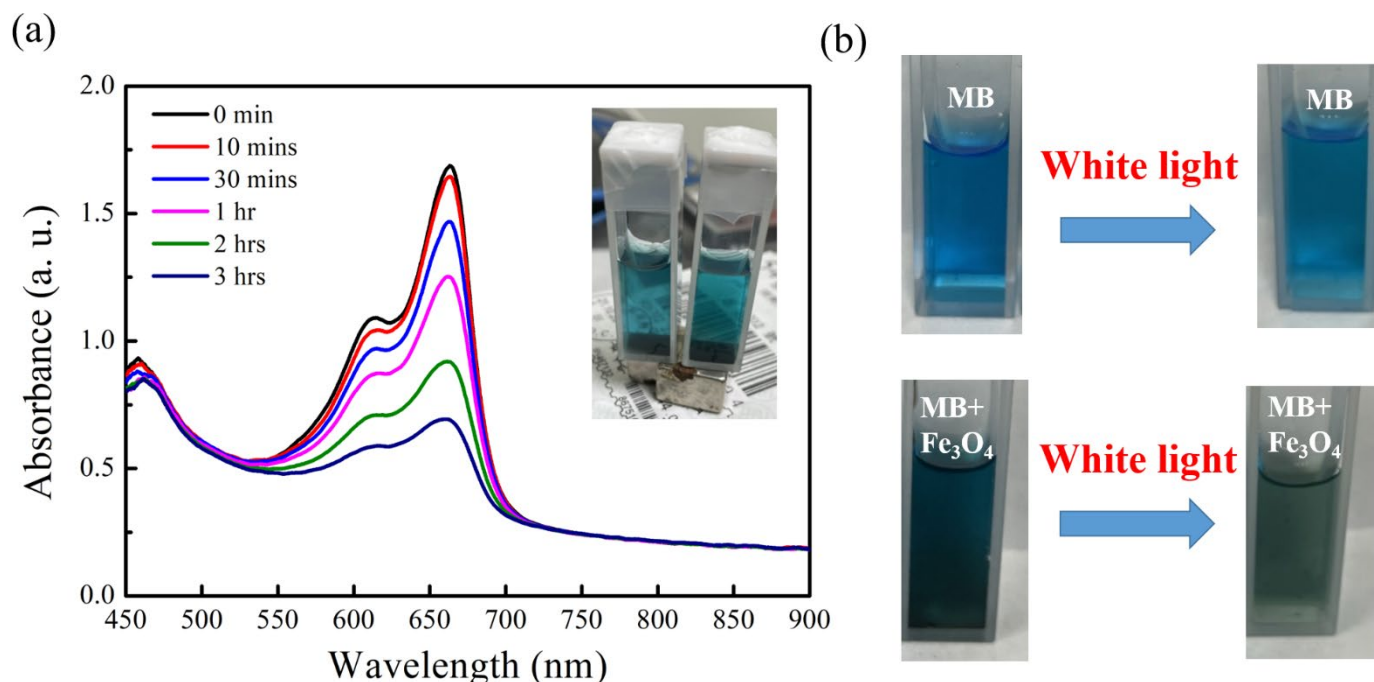


Figure 6. (a) Spectral change in methylene blue (MB) absorbance under white-light illumination. The photograph (inset) also shows the condensation of magnetic NPs under magnetization. (b) Photographs of MB without and with addition of magnetic Fe_3O_4 NPs after 30 min white-light illumination.

The magnetic NPs were applied to MB decolorization, and the recorded MB absorption spectra showed that the maximum absorption value of MB changed according to the recording time, as shown in Figure 7. The absorption of the MB without or with the addition of magnetic NPs under dark-room conditions remained unchanged. The absorption peak of the MB corresponded to about 18% photodegradation efficiency under white-light irradiation for 180 min, while the absorption peak of the MB solution with the addition of magnetic NPs showed 60% photocatalytic efficiency. We also tested using UV light in place of light irradiation and recorded the absorbance of the MB without and with the addition of magnetic NPs. As expected, without the addition of magnetic NPs, the absorbance of the MB had a change of only 10% under 180 min illumination of UV light. The addition of magnetic NPs had no effect on the enhancement of photocatalytic activity. Compared to a previous report where bare Fe_3O_4 was used without modification as the photocatalyst [42], the current demonstration had better performance. Furthermore, no leaching of iron into the solution was found.

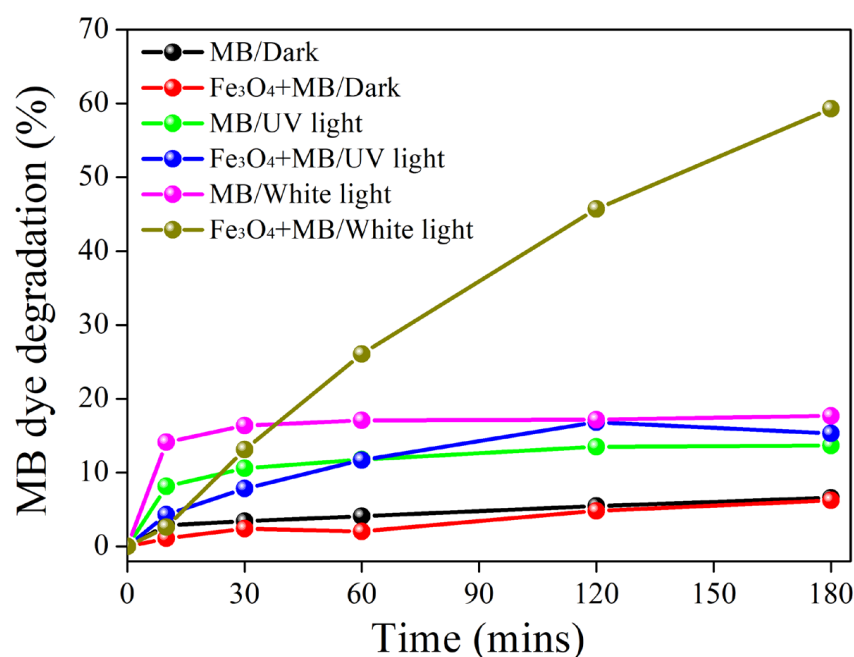


Figure 7. The MB degradation efficiency under different levels of environment and light irradiation.

Magnetic NPs can be easily recycled when used in photocatalysis, which is an advantage they have over other photocatalysts. After the first round of photocatalysis, the magnetic NPs were separated from the water using an external magnetic field and then recycled for reuse, as shown in Figure 8. We tried to recycle the synthesized magnetic Fe₃O₄ NP using magnet separation with reuse of the recycled magnetic NPs in the photodegradation of the MB, as shown in Figure 9. The degradation ability clearly decreased when the number of recycling cycles increased.

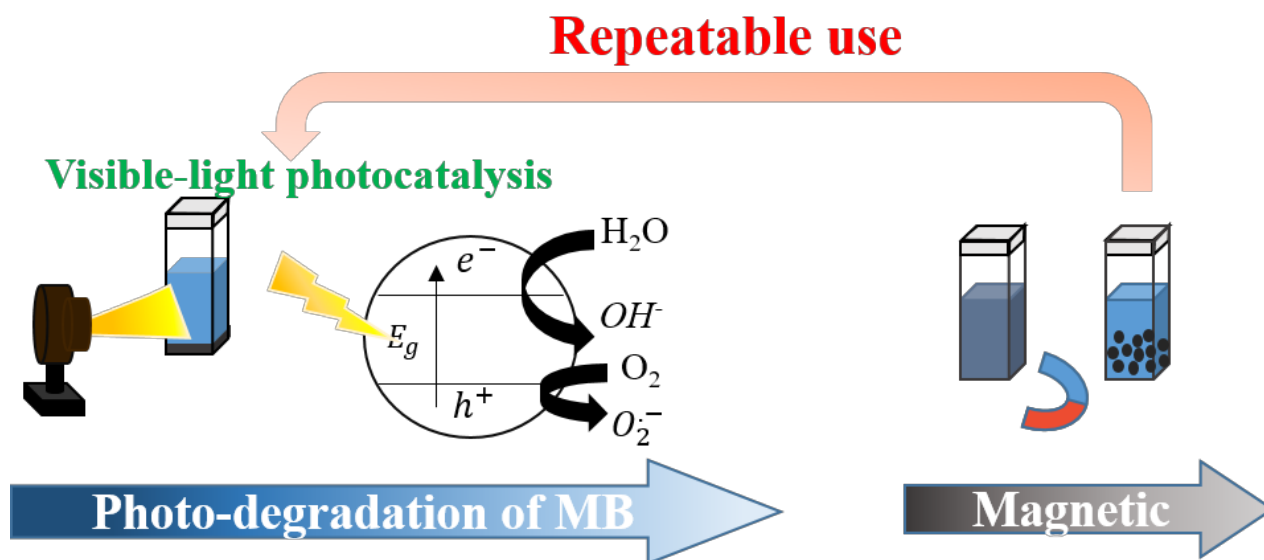


Figure 8. Schematic of possible reusability of magnetic NPs in visible-light photocatalysis.

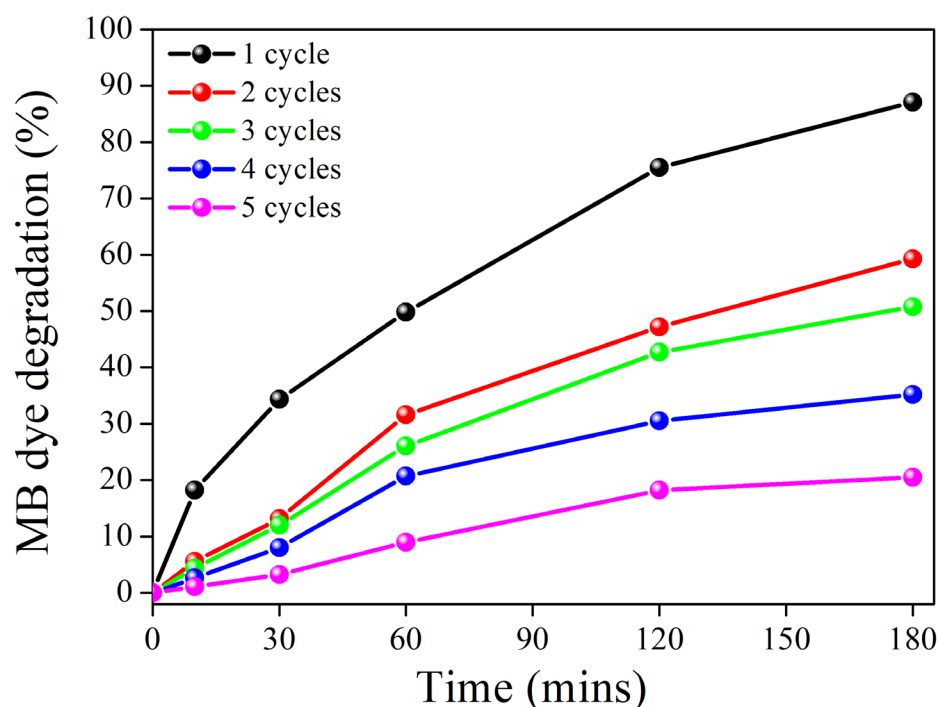


Figure 9. Cyclic testing of PLIP-synthesized magnetic Fe₃O₄ NPs in MB photodegradation under white-light exposure.

3. Materials and Methods

3.1. PLIP Synthesis

In this experiment, ferrocene and acetone were used to prepare a precursor solution, and hydrogen peroxide (H₂O₂) (35 wt.%, Acros) was added and mixed into the solution to initiate the photolysis process for synthesis of magnetic IrO NPs. The ferrocene/acetone precursor was prepared by mixing ferrocene (98%, Acros) powder (0.05g) into 5 mL acetone (95%, Acros) with sonication for 30 min. The ferrocene/acetone precursor exhibited a light orange color. H₂O₂ aqueous solution (0.25 mL) with a concentration of 35 wt.% was added into the ferrocene/acetone precursor and vigorously stirred for 30 min. The resulting solution was an orange-yellow color. The ferrocene/acetone/H₂O₂ solution was heated and stirred at 100 °C for 30 min. Next, the prepared solution was continuously irradiated using a Q-switched nanosecond pulsed green laser (532 nm) with a power of 57.5 J for 60 min until the solution turned a black-gray color. During the PLIP process, the prepared solution was stirred and heated at 80 °C. After finishing the PLIP process, a magnet was placed on the bottom, magnetization was used to separate the product, and the above solution was poured out and washed with acetone and DI water. In future studies, this process should be repeated about 2–3 times until the upper liquid is clear.

3.2. Characterization

X-ray diffraction (XRD) patterns of all the synthesized samples were obtained in the 2 θ range of 10–90° on a high-resolution X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany). The morphologies of the magnetic NPs were investigated through transmission electron microscopy (TEM) on a JEM-2100 transmission electron microscope (JEOL, Tokyo, Japan). The sample for magnetic characterization was prepared by adding NP solution on an 8 mm × 8 mm glass substrate. The hysteresis loops were recorded using a superconducting quantum interference device (SQUID) vibrating sample magnetometer (VSM) at room temperature.

3.3. Photocatalytic-Activity Test

A 0.1 mL volume of magnetic NP solution (1 mg/1 mL) was added to 2 mL MB solution (10^{-5} M) for photocatalytic evaluation. The absorption spectra of the sample were recorded under different light illuminations and times. The photocatalytic activity of the synthesized product was evaluated based on the degradation of MB in a homemade dark-room setup, under UV light-emitting diode (LED) (365 nm wavelength, 50 mW/cm²) and under a fiber white-light source (Thorlabs, OSL1, 180 W full light intensity). The absorption spectra were recorded using an Ocean Optics USB4000CG spectrometer. The photocatalytic degradation efficiency (DE) of MB was calculated by measuring the absorbance maximum value of the treated solutions at 664 nm under different times using the following equation:

$$DE = 100 - (A - A_0)/A_0 \times 100,$$

where A_0 is the initial absorbance of MB and A is the final absorbance of MB under different times of light exposure.

4. Conclusions

The present study is the first to successfully use the PLIP method to fabricate magnetic Fe₃O₄ NPs that degrade MB under visible-light illumination. The material characterization showed that the synthesized NPs had an Fe₃O₄ crystalline structure and particles 20–50 nm in diameter. The magnetic NPs dispersed in water solution showed broad absorbance in the visible-wavelength range, which is favorable for visible-light photocatalysis. The photocatalysis results demonstrated that the synthesized magnetic NPs had the ability to degrade MB at 60% degradation efficiency under 180 min of white-light illumination.

Author Contributions: Conceptualization, B.-Y.W., C.-M.C. and V.K.S.H.; methodology, B.-Y.W., S.-Y.H., Y.-S.H. and P.-C.W.; formal analysis, S.-Y.H., Y.-S.H. and V.K.S.H.; writing—original draft preparation, B.-Y.W. and S.-Y.H.; writing—review and editing, C.-M.C. and V.K.S.H.; supervision, B.-Y.W., C.-M.C. and V.K.S.H. All authors have read and agreed to the published version of the manuscript.

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

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