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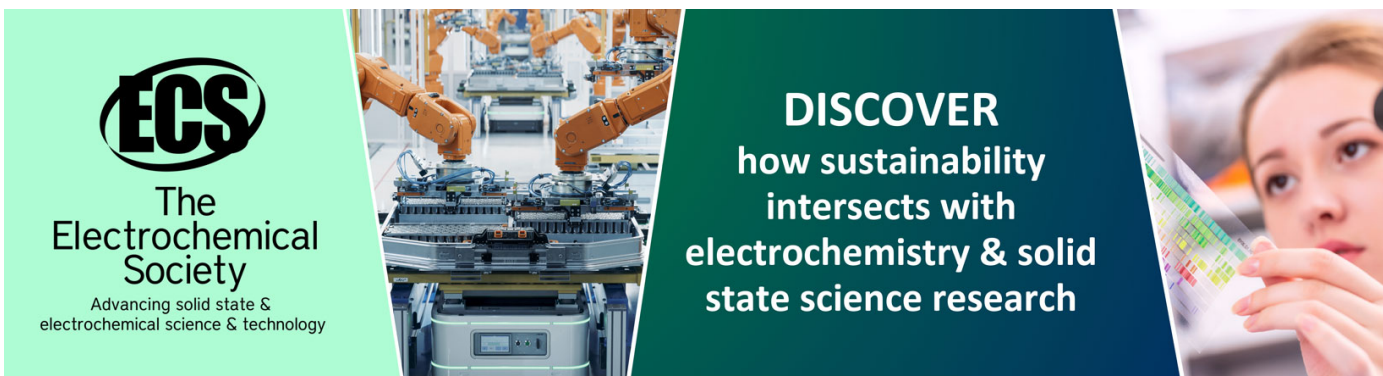
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One-step synthesis and deposition of ZnFe_2O_4 related composite films via SPPS route for photodegradation application

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Abstract

Binary spinel-type metal oxides (AB_2O_4) related materials, including ferrites (AF_2O_4), are attractive photocatalysts thanks to their excellent visible light response for the photodegradation of organic pollutants. Currently, these materials are synthesized via conventional chemical routes suffering from long preparation duration and multistep. Moreover, the photocatalysts are obtained as nano-powders from conventional chemical routes would introduce another drawback for their recycling and reuse. From an industrial perspective, it is desirable to develop an efficient and facile synthesis process to produce photocatalysts in a non-dispersible form. Herein, we demonstrate that the solution precursor plasma spray (SPPS) process is a single-step method for depositing photocatalytically active zinc ferrite-based films within several minutes. The influence of the precursor ratio on the microstructures and phase compositions of the ZnFe_2O_4 films was investigated by XRD and Raman analyses. In addition, two optimized ZnFe_2O_4 films were prepared by increasing the ZnO loading and tailoring injection pattern of the precursor solution. The surface morphologies and optical bandgap were also determined by SEM and UV–visible spectroscopy. The photocatalytic activities of the ZnFe_2O_4 films were evaluated through the degradation of the Orange II dye and of tetracycline hydrochloride under UV or visible light irradiation. The results show that compositional ratios and composition distribution of the ZnFe_2O_4 films prepared via SPPS played a key role on the photocatalytic activity. The SPPS route was demonstrated to be a promising method for the synthesis and the deposition of metal oxide (i.e. perovskite type and spinel type) films within a single-step for functional applications.

Supplementary material for this article is available [online](#)

Keywords: solution precursor plasma spray, zinc ferrite, composite films, photocatalytic degradation

(Some figures may appear in colour only in the online journal)

Introduction

The growth of the population and the industrial development generate increasing risks of water pollution on ecosystems

and human beings [1]. Therefore, there is a growing interest in the development of efficient and low cost processes to remove organic pollutants from water using advanced oxidation processes (AOPs) [2]. The photocatalytic degradation of pollutants is a promising and 'green' AOP since it

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Table 1. Precursor solution parameters for reference ZnO and ZnFe₂O₄ related films.

Sample name	Zinc salt (M)	Iron salt (M)	Solvent type	Solution pattern
ZnO	0.2	0	Water	Pure
ZnFe ₂ O ₄ -01	0.04	0.08	Ethanol	Mixture
ZnFe ₂ O ₄ -02	0.06	0.08	Ethanol	Mixture
ZnFe ₂ O ₄ -03	0.08	0.08	Ethanol	Mixture
ZnFe ₂ O ₄ -A	0.2	0.04	Ethanol	Mixture
ZnFe ₂ O ₄ -B	0.2	0.04	Ethanol	Separated

consumes no chemical reagents but simply uses light irradiation, operates in ambient conditions and boasts high efficiency and reasonable cost [3–11]. In this respect, metal oxide semiconductors, such as TiO₂ and ZnO, have received great attention due to their outstanding photocatalytic activities [12–14]. However, due to their high bandgap (3.2 eV and 3.37 eV for TiO₂ and ZnO, respectively), these materials can only be photo-activated by UV light which accounts for only 4% of the solar spectrum [15]. Ferrite-type spinels (AFe₂O₄) exhibit narrower bandgaps (~2.0 eV), which increases their absorption of solar photons [16, 17]. For example, zinc ferrite (ZnFe₂O₄) absorbs photons in the visible-light range, exhibits a high photochemical stability and is therefore a promising photocatalyst for the degradation of aqueous pollutants [18, 19].

Spinel ferrite-type photocatalysts are currently prepared via a series of conventional routes that include sol-gel [19], solvothermal [20], co-precipitation [21] and electrochemical methods [22], which are of long duration, that generally require multi-step processes and that exhibit limited efficiency. In addition, all these methods generate photocatalysts in the form of nano-powders that require a filtration for their recovery and reuse and thus that generate an additional threat to the human health and the environment [23–27]. Replacing such dispersed photocatalysts by film-formed ones is also highly desirable to industrialization [23–29]. In the present work, we have used the solution precursor plasma spray (SPPS) process to simultaneously synthesize and deposit spinel ZnFe₂O₄ based films. In this technology, a direct-current plasma plume generated by a primary gas (e.g. argon) and secondary gas (e.g. hydrogen) is employed to heat the precursor solution and accelerate it onto a solid substrate, which allows the preparation of catalytic films within several minutes [30]. Compared to other conventional thermal spray technologies, the SPPS process promotes the formation of porously finer structured metal oxide films [31]. To the best of our knowledge, only a few studies have been devoted so far to the preparation of spinel-type materials via SPPS, especially in view of photocatalytic applications [32, 33].

In this work, ZnFe₂O₄ films were deposited by the SPPS route. The influence of the precursor solution concentration and of the Zn/Fe ratio on the properties of the films was investigated. Two optimized ZnFe₂O₄ films and a reference ZnO film were also prepared. These ZnFe₂O₄ films were

**Scheme 1.** Schematic illustration of the synthesis and deposition of ZnFe₂O₄ related films by the SPPS route.

characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. UV–visible spectrophotometry was used to determine their optical bandgaps. The photocatalytic performances of those films were evaluated through the degradation of Orange II dye and of tetracycline hydrochloride under UV or visible light irradiation.

Experimental procedures

Solution precursor preparation

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, purum, ≥98%) and iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma-Aldrich, ACS, 98.0%-101.0%) were used as the precursors for the ZnFe₂O₄ phase. A reference pure ZnO film was prepared from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. We also studied the influence of various solution and spraying parameters on the composition phases and microstructures of the ZnFe₂O₄ films via SPPS process:

- for the ZnFe₂O₄ films, the effect of the Zn/Fe ratio was studied;
- for the optimized ZnFe₂O₄ films, higher ratio of ZnO/ZnFe₂O₄ or separated injection pattern of solution precursors instead of mixture solutions were employed.

Plasma spray conditions

A direct-current plasma torch (F4, OerlikonMetco, Switzerland) attached to a six-axis robotic arm (ABB, Switzerland) was employed to deposit the ZnFe₂O₄ films on commercial alumina plates (33 mm × 34 mm × 2 mm). The corresponding solutions of precursors were driven by a flow of pressurized nitrogen through a stainless steel injector. The resultant films were noted as ZnFe₂O₄-01, ZnFe₂O₄-02 and ZnFe₂O₄-03 according to the different solution parameters (as listed in table 1). The two optimized ZnFe₂O₄ samples were named as ZnFe₂O₄-A and ZnFe₂O₄-B, respectively, by adjusting the chemical ratios or tailoring the surface morphologies. The other spraying parameters (plasma power, spraying distance, feeding rate, moving velocity of the robotic arm) were kept constant. The schematic diagram of direct

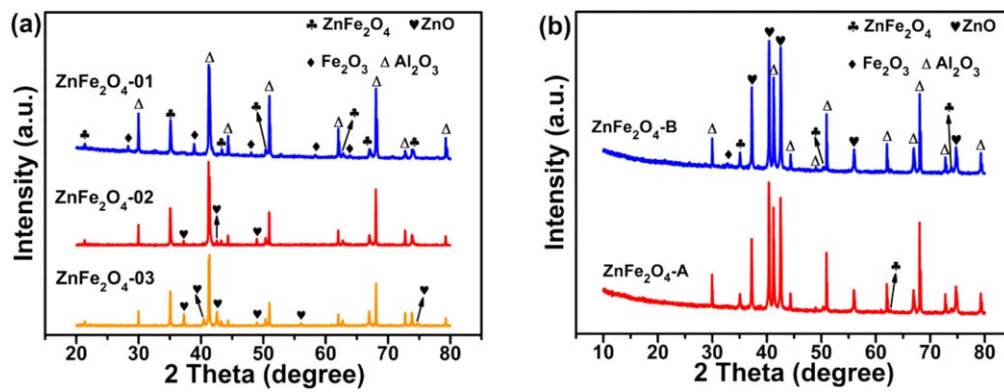


Figure 1. XRD patterns of (a) ZnFe₂O₄ films when varying the concentration of the precursor solutions and (b) optimized ZnFe₂O₄ samples.

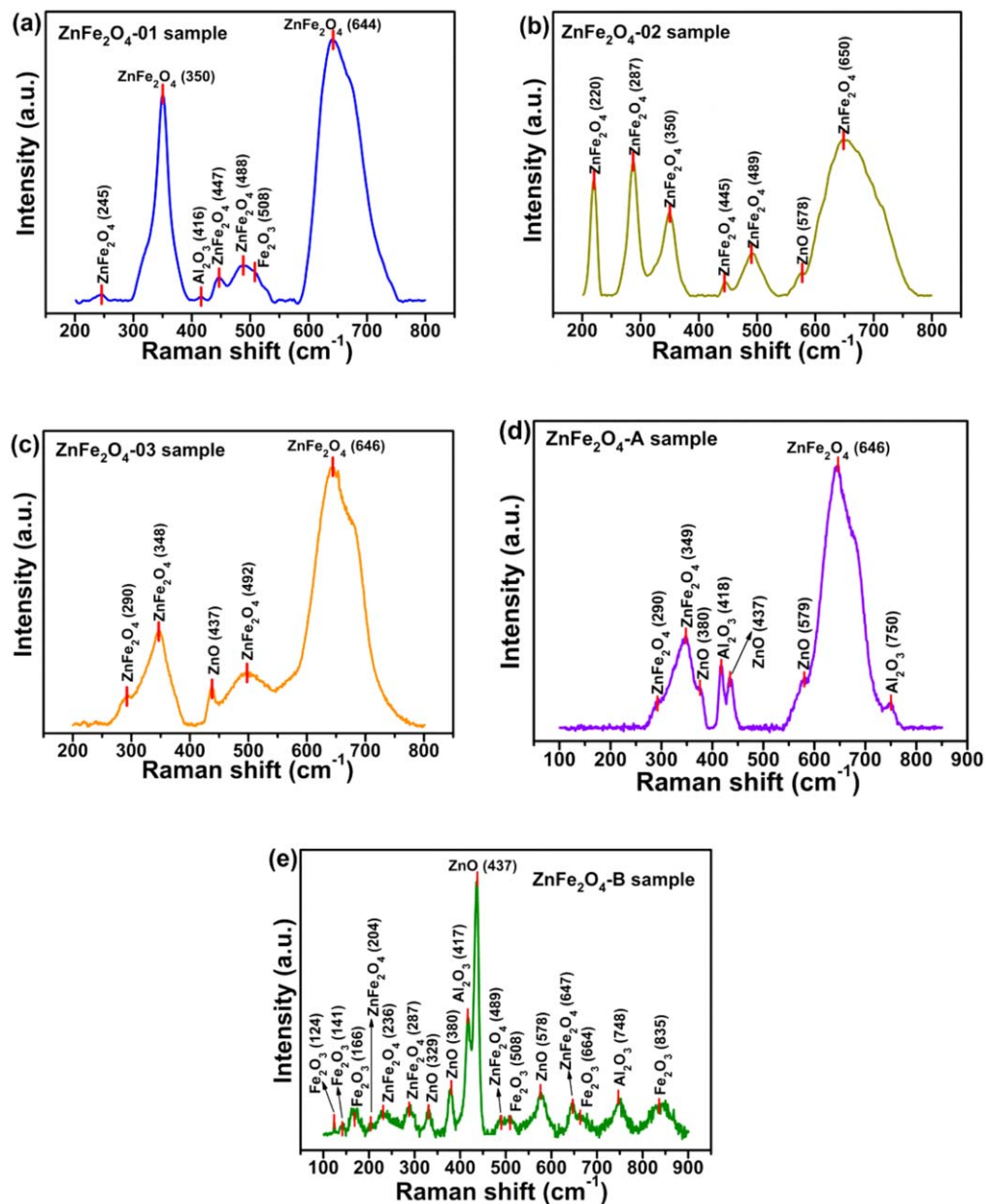


Figure 2. Raman spectra of (a) ZnFe₂O₄-01, (b) ZnFe₂O₄-02, (c) ZnFe₂O₄-03, (d) ZnFe₂O₄-A and (e) ZnFe₂O₄-B samples.

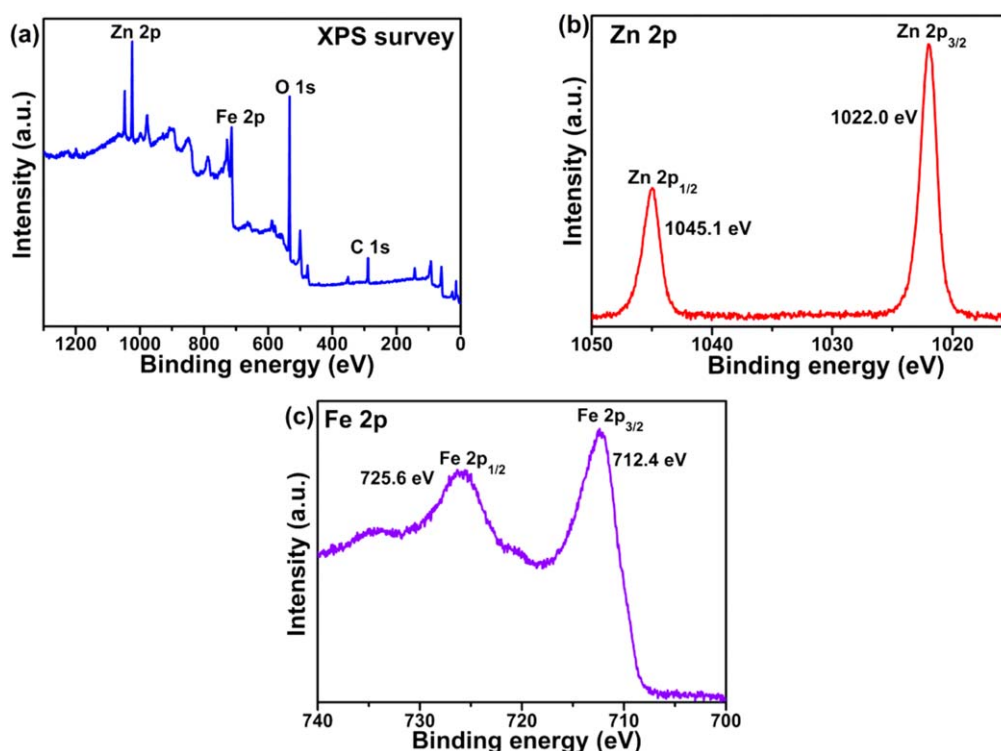


Figure 3. XPS spectra of the ZnFe_2O_4 sample: (a) survey spectrum; (b) Zn 2p spectrum; and (c) Fe 2p spectrum.

synthesis and deposition of ZnFe_2O_4 films via SPDS route was illustrated in scheme 1.

Characterization of the coatings

The surface morphologies of the ferrite films were examined by SEM (JEOL, JSM-5800LV). The compositions of the samples were determined by XRD (Bruker AXS D8 focus, Germany) using a cobalt anticathode ($\lambda = 1.78897 \text{ \AA}$) with a scanning speed of 0.1° s^{-1} and Raman spectrum (XploRA PLUS Raman Microscope, Horiba Jobin Yvon) with the excitation occurring at 532 nm. Their optical properties were evaluated by UV–visible absorption spectroscopy and diffuse reflectance spectroscopy using a UV–visible spectrophotometer (Shimadzu, UV-2600). The optical energy bandgap values were estimated based on Kubelka–Munk equation, resorting to the Tauc plot method [34]. XPS (Thermo K-Alpha+) with Al $K\alpha$ radiation source (1486.6 eV) was performed to examine the composition and metal oxidation states of the sample. All the binding energies were calibrated by using the contaminant carbon (C 1s) 284.6 eV as a reference.

Photocatalytic testing

The photocatalytic performances of the ZnFe_2O_4 films were evaluated through the photodegradation of Orange II or tetracycline hydrochloride at room temperature either under the UV light irradiation produced by an Hg-Xe lamp or under visible light. The visible light irradiation was produced by a Xe lamp equipped with an ultraviolet cutoff filter ($\lambda > 420 \text{ nm}$). The light intensities used were 15 mW cm^{-2}

for UV light and 7.5 mW cm^{-2} for visible light. In a typical run, a set of five identical film pieces representing in total 60 mg of photocatalysts was placed into a Petri dish containing 60 ml of Orange II aqueous solution (5 mg l^{-1}). Before irradiation, the liquid was magnetically stirred for 120 min in the dark to reach the adsorption–desorption equilibrium. During the subsequent light irradiation, 1 ml of the liquid was extracted at regular time intervals to evaluate the remaining concentration of Orange II ($\lambda_{\text{abs}} = 485 \text{ nm}$) or tetracycline ($\lambda_{\text{abs}} = 381 \text{ nm}$) using a Thermo Scientific Evolution 220 spectrophotometer. The photodegradation percentage was calculated as follows:

$$D(\%) = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where C_0 is the initial concentration and C_t is the concentration of the pollutant after irradiation time t , respectively.

Results and discussion

Effect of solution parameters on the compositions of the resultant films

The XRD patterns of the various ZnFe_2O_4 films are shown in figure 1. Due to the very thin thickness (about $2.5 \mu\text{m}$) and porous microstructure (as shown in figure 4, *vide infra*) of these films, the XRD pattern of the underlying Al_2O_3 substrate (PDF card No. 74-1081) was also detected. Figure 1(a) illustrates the effect of the ratio between zinc and iron salt in the precursor solutions on the compositions of the resultant

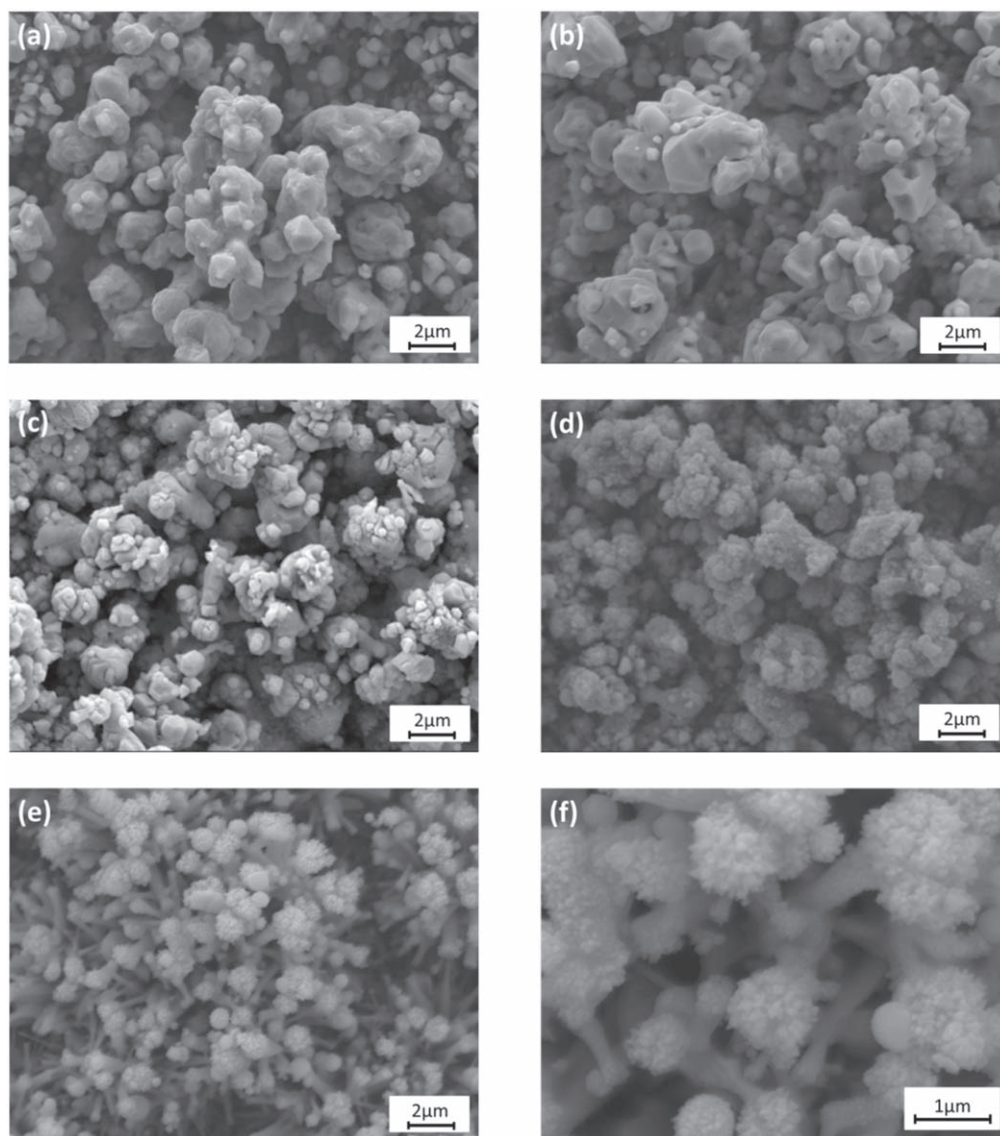
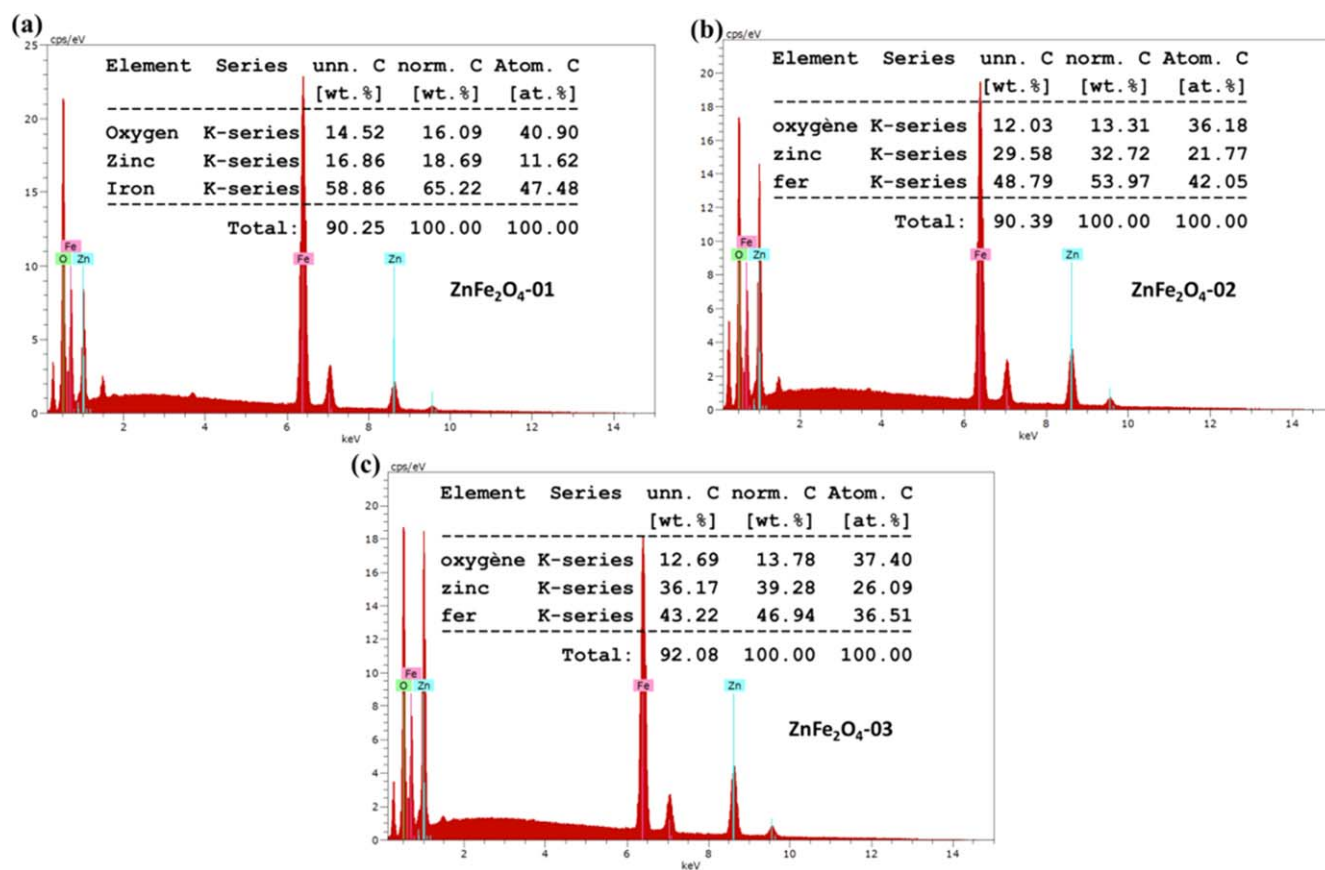
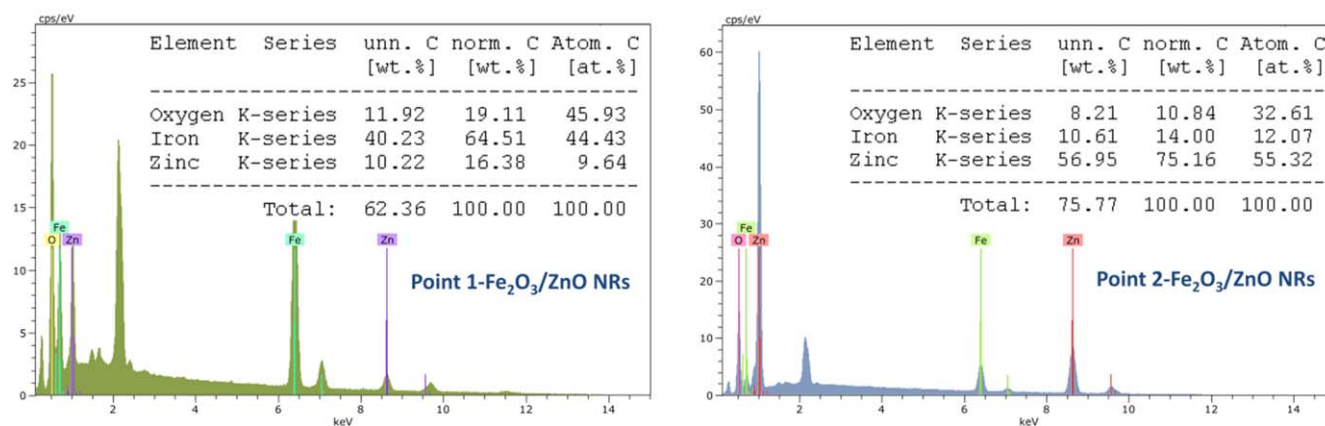
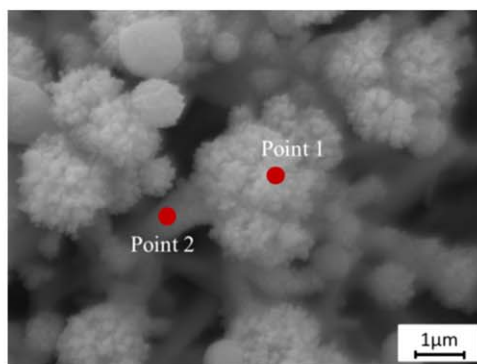


Figure 4. SEM images and surface morphologies of (a) ZnFe_2O_4 -01, (b) ZnFe_2O_4 -02, (c) ZnFe_2O_4 -03, (d) ZnFe_2O_4 -A and (e), (f) ZnFe_2O_4 -B samples.

films. The characteristic XRD peaks of the ZnFe_2O_4 phase (PDF card No. 77-0011) are always observed with low intensity due to its weak thickness and porous microstructure. Although the ZnFe_2O_4 -01 sample was prepared using the stoichiometric ratio ($\text{Zn}/\text{Fe} = 0.5$), extra XRD peaks originating from Fe_2O_3 (PDF card No. 25-1402) were also detected. This impurity may originate either from the incomplete *in situ* association of $\text{Zn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ inside the plasma plume (see reaction (i) below) and/or the lower deposition efficiency of ZnO compared to Fe_2O_3 . With the increase of the Zn/Fe ratio to 0.75 (ZnFe_2O_4 -02 sample) in the precursors solution, the by-product changed from Fe_2O_3 to ZnO (PDF card No. 75-0576). This trend is strengthened when the Zn/Fe ratio was further increased up to 1 (ZnFe_2O_4 -03 sample) and the corresponding XRD peaks of ZnO became more obvious. These results show that pure ZnFe_2O_4 based films can be deposited with an atomic Zn/Fe ratio between 0.5 and 0.75 in the precursor solution.

Two ZnFe_2O_4 films with optimal atomic Zn/Fe ratio were also prepared using a single solution containing the two precursors or via separated injection pattern. The corresponding XRD patterns are shown in figure 1(b). In the ZnFe_2O_4 -A and ZnFe_2O_4 -B samples, the films are partly composed of ZnFe_2O_4 but the major component is ZnO , which is agreement with the solution composition. For the ZnFe_2O_4 -B sample, the reaction between pre-deposited ZnO and next Fe_2O_3 on the substrate allows the preparation of the ZnFe_2O_4 phase according to reaction (ii). Besides, during the deposition of the $\text{Fe}(\text{NO}_3)_3$ solution, it should be noted that the ZnFe_2O_4 thin films arising from reaction (ii) become the contacting barrier between ZnO and Fe_2O_3 . Therefore, the Fe_2O_3 phase was observed as well in the ZnFe_2O_4 -B films. The reference ZnO film is composed of pure wurtzite ZnO (PDF card No. 75-0576), as shown in figure S1, available online at stacks.iop.org/NANO/30/045707/mmedia.

Figure 5. Element ratios for (a) ZnFe₂O₄-01, (b) ZnFe₂O₄-02, (c) ZnFe₂O₄-03 samples.Figure 6. EDS analyses of ZnFe₂O₄-B films.

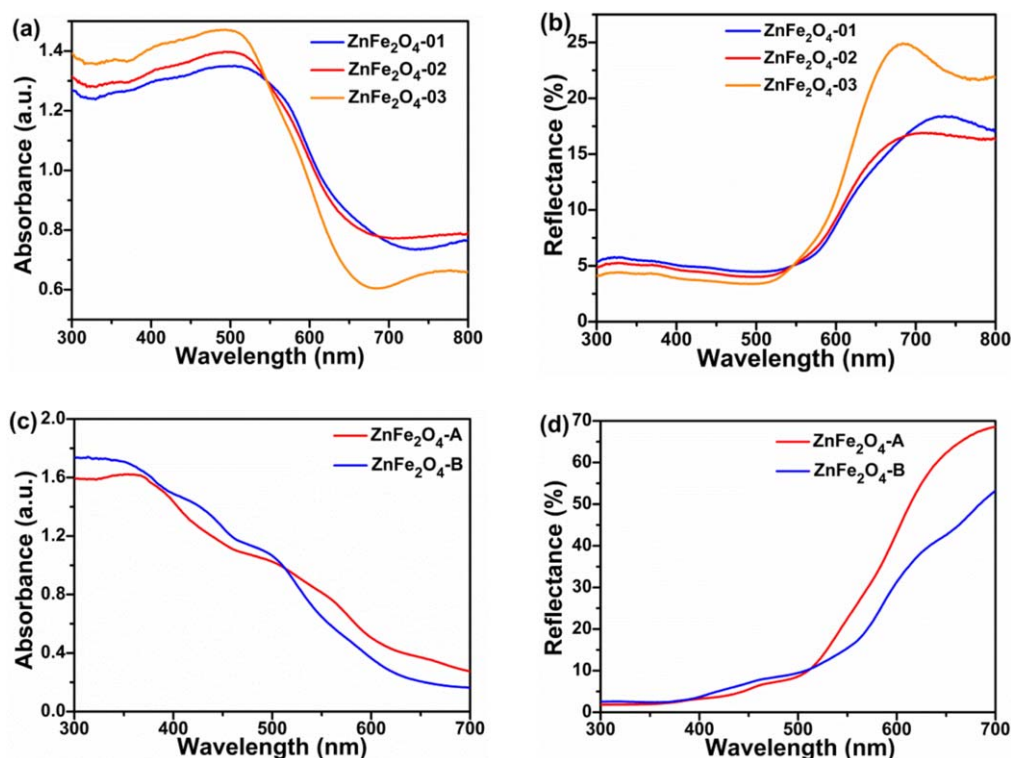


Figure 7. UV–visible absorption and diffuse reflectance spectra of (a), (b) ZnFe_2O_4 with different compositional ratios and (c), (d) optimized ZnFe_2O_4 films.

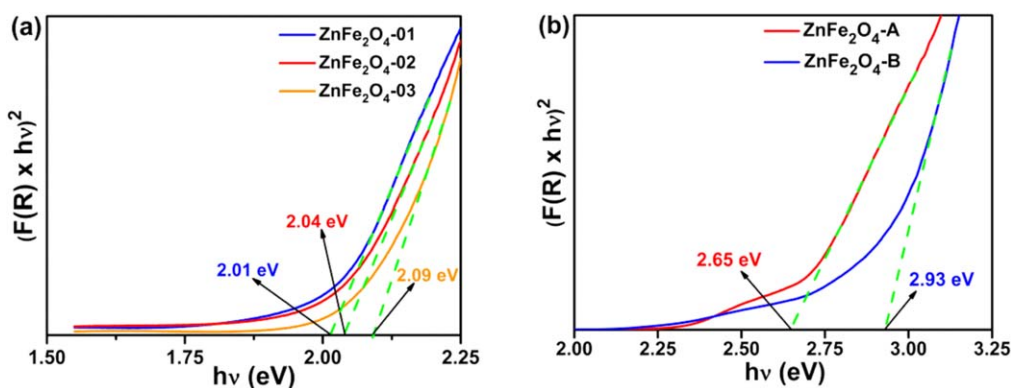
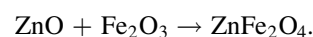


Figure 8. Plot of $(F(R) \times h\nu)^2$ versus $h\nu$ to determine the bandgaps of (a) ZnFe_2O_4 with different compositional ratios and (b) optimized ZnFe_2O_4 films.

The composition of the ZnFe_2O_4 related thin films was further confirmed by Raman spectroscopy as shown in figure 2. Firstly, the signals appearing at 221, 246, 290, 350, 451, 487 and 647 cm^{-1} can be assigned to the ZnFe_2O_4 phase [35–37], and these signals can be observed in all the samples. ZnO has two Raman active modes centered at 330, 380, 437 and 578 cm^{-1} in figures 2(b)–(e), suggesting the presence of the ZnO phase in these samples [38, 39]. The peaks at 125, 141, 162, 508, 664 and 835 cm^{-1} correspond to Fe_2O_3 [40], and are detected in the ZnFe_2O_4 -01 and ZnFe_2O_4 -B samples. In accordance with the XRD analyses, the underlying Al_2O_3 was also detected with the peaks at 416 cm^{-1} and 750 cm^{-1} [41]. In addition, the peak at 328 cm^{-1} corresponding to single ZnO crystals [38], was only observed in ZnFe_2O_4 -B

sample, which is related to its microstructure (*vide infra*).



XPS measurements were used to further confirm the surface element composition and metal oxidation states of the SPPS-deposited ZnFe_2O_4 films. The signals of Zn, Fe and O can be detected from the full survey scan spectrum (figure 3(a)), which is consistent with the expected element composition of ZnFe_2O_4 phase [30, 42, 43]. The presence of C 1s peak at 284.6 eV can be assigned to carbon contamination and CO_2 adsorbed on the surface of the film [44]. The O 1s binding energy is observed at 530.1 eV, which is characteristic of oxygen in metal oxides (figure 3(a)) [42–44]. The Zn $2p_{3/2}$ and Zn $2p_{1/2}$ peaks at

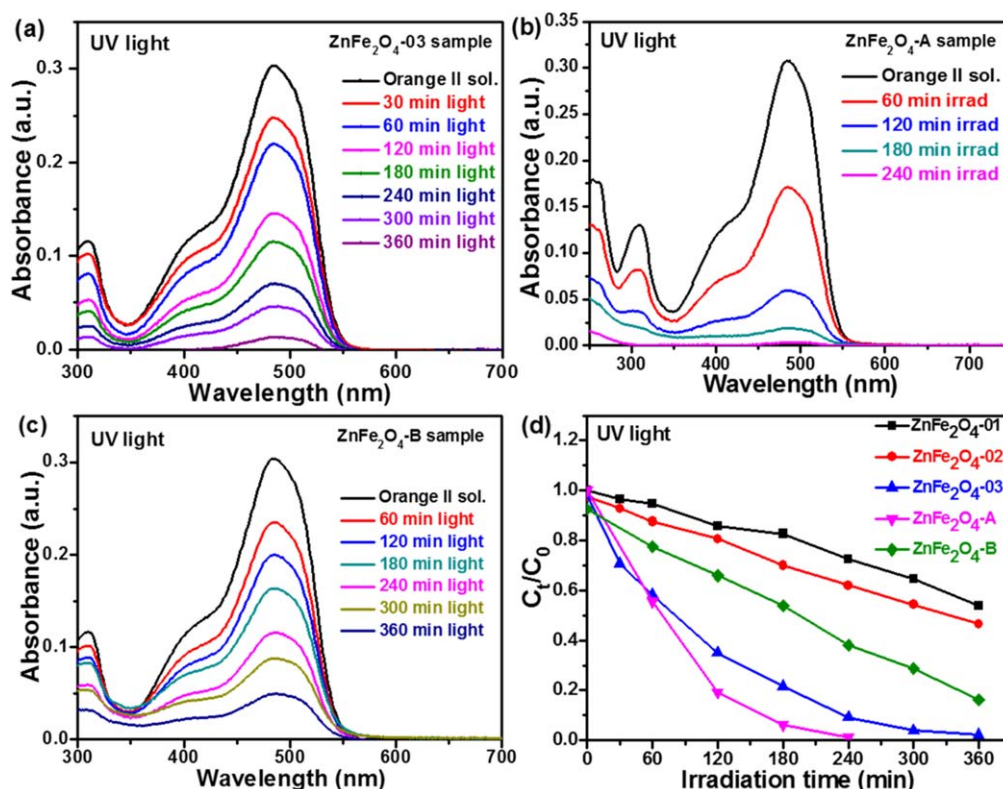


Figure 9. (a)–(c) UV–visible spectra of Orange II during its photodegradation under UV light in the presence of ZnFe₂O₄-03, ZnFe₂O₄-A and ZnFe₂O₄-B films, respectively, and (d) photodegradation performance of ZnFe₂O₄ photocatalysts for Orange II degradation under UV light in function of irradiation time.

1022.0 eV and 1045.1 eV, respectively, are indicative of Zn²⁺ in the composites (figure 3(b)) [19, 42–44]. As shown in figure 3(c), the peaks centered at 712.4 eV and 725.6 eV can be ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, which confirms that iron presents at the +3 oxidation state in the sample [19, 42–44]. XPS results further confirm the formation of ZnFe₂O₄ phase in the films.

Effect of solution parameters on the Microstructure of the ZnFe₂O₄ related films

For the zinc ferrite films prepared with different Zn/Fe ratio, porous surface morphologies were observed by SEM. Particles with smooth surface were observed for all the ZnFe₂O₄ samples. The particle sizes of ZnFe₂O₄ films rank as ZnFe₂O₄-02 > ZnFe₂O₄-01 > ZnFe₂O₄-03 as shown in figures 4(a)–(c). The complexity inherent to the SPPS spraying process is well-known due to the combination of diphasic physical and chemical processes. The different concentrations of Zn(NO₃)₂ in the raw solution will lead to different solution densities, degrees of supersaturation, mass and flight velocities of solution droplets, which could cause different flight path in the plasma plume. Moreover, since the temperature of plasma plume is quite non-uniform, the different flight paths could result in different heating profiles, which may also influence the particle sizes. In addition, the different composition in the films could also play a role in the various particle size, particle shapes and morphologies. For better explanation of the ranking, the Zn/Fe ratio in these three resultant films was further analyzed based on EDS spectrum as shown

in figure 5. Firstly, the Zn/Fe ratios of the ZnFe₂O₄-01, ZnFe₂O₄-02 and ZnFe₂O₄-03 films are 24.47% to 51.77% and 71.46% in mole, respectively, exhibiting the same trend as their original solution precursors. Moreover, it is clear that Zn/Fe ratio in the ZnFe₂O₄-02 sample is quite close the so stoichiometric ratio, suggesting formation of ZnFe₂O₄. It should be noted that synthesis of ZnFe₂O₄ phase from Zn(NO₃)₂ and Fe(NO₃)₃ is an exothermic reaction [45, 46]. As such, the more formed ZnFe₂O₄ phase will release more energy for the particle growth, resulting largest particles in the ZnFe₂O₄-02 sample. On the other hand, due to the more solute would be heated, decomposed and pyrolyzed from the solution of ZnFe₂O₄-03 films, less available energy would be allowed the growth of particles. Thus, particle size of ZnFe₂O₄-03 sample is smaller than that of ZnFe₂O₄-01 films. Furthermore, the Zn/Fe ratios in the ZnFe₂O₄-01, ZnFe₂O₄-02 and ZnFe₂O₄-03 samples were smaller than those of their corresponding solution precursors, which was possibly due to their different deposition efficiencies compared to the Zn(NO₃)₂ and Fe(NO₃)₃ solutions. It was found that the decomposition temperature of Zn(NO₃)₂ was higher than that of Fe(NO₃)₃ [47, 48], which could be the reason for the former's lower deposition efficiency.

For the two optimized ZnFe₂O₄ samples, their surface morphologies were different, suggesting that the injection pattern plays an important role in the microstructure of ZnFe₂O₄ related composite films generated via the SPPS process (figures 4(d)–(f)). For example, the ZnFe₂O₄-A sample exhibited conventional porous morphology composed

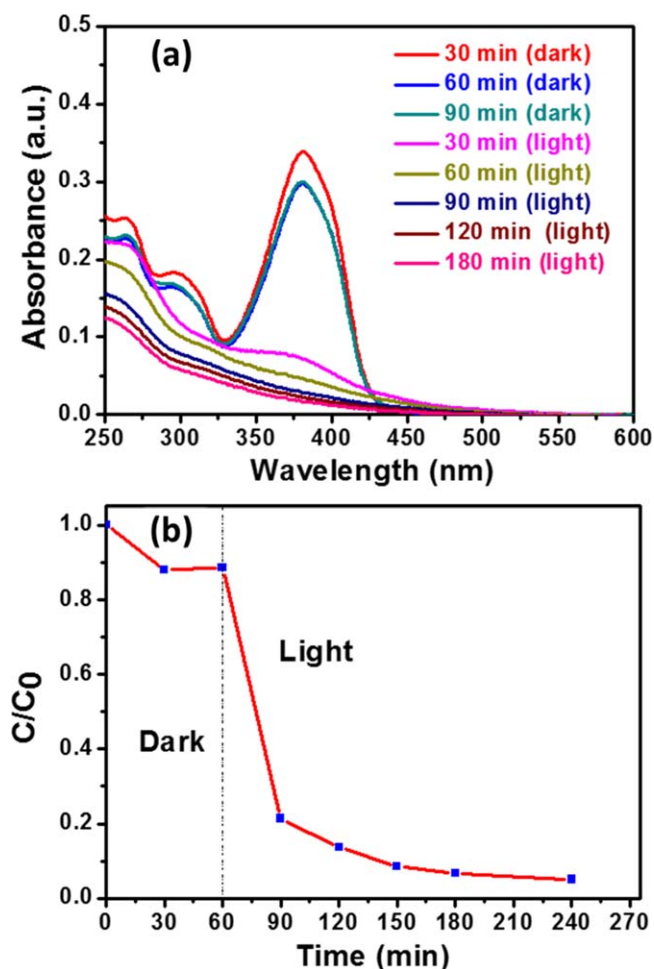


Figure 10. (a) Temporal evolution of TC UV-visible absorption spectra and (b) photocatalytic activity of the ZnFe₂O₄-A catalyst for the degradation of TC under UV light irradiation.

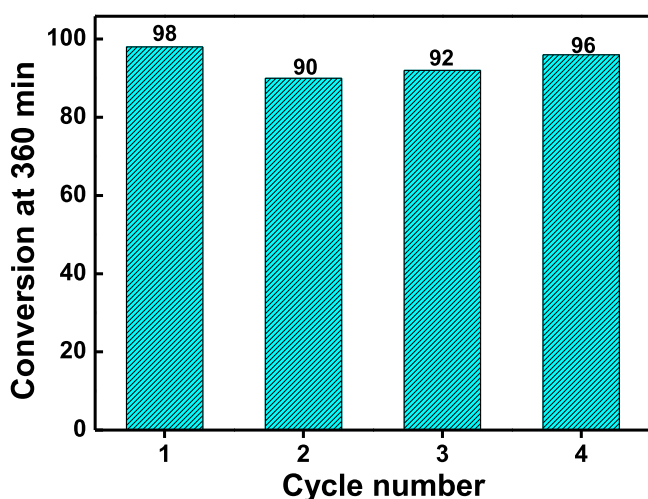


Figure 11. Recycling runs of the ZnFe₂O₄-A samples in the degradation of Orange II under UV light irradiation.

of numerous irregular fine particles. The ZnFe₂O₄-B film exhibits a hierarchical dandelion-like morphology and is partly composed of nanorods (NRs). In light of the deposition sequence of zinc and iron salts, the NRs should be mainly

composed by ZnO and the top fine particles should be predominately composed by ZnFe₂O₄ and Fe₂O₃ phases. This was confirmed by the EDS analysis shown in figure 6. The NRs-structured ZnO was observed in our previous studies [49]. The reference ZnO is composed of classic cauliflower-like microstructures and contains numerous irregular fine particles as shown in figure S2.

UV-visible analysis of the ferrite films

The UV-visible absorption and reflectance spectra of all the ZnFe₂O₄ related films are displayed in figure 7. The light absorption of the zinc ferrite films covers the visible region and extends to the near-infrared (figures 7(a) and (c)). Using the UV-visible diffuse reflectance spectra (figures 7(b) and (d)) and the Kubelka-Munk method [34], the corresponding bandgap energy (E_g) values were determined by extrapolating the plots at $(F(R) \times h\nu)^2 = 0$, as shown in figure 8. For the ZnFe₂O₄ films prepared by varying the ratio of precursors, the bandgap increases from 2.01 to 2.09 eV with the Zn/Fe molar ratio (as illustrated in figure 8(a)). This can be attributed to the different compositions in these ZnFe₂O₄ related films as indicated by XRD and Raman analyses, since ZnO has a larger bandgap (3.37 eV) than Fe₂O₃ (2.24 eV) [50]. The bandgaps determined for ZnFe₂O₄-A and ZnFe₂O₄-B samples are 2.65 and 2.93 eV, respectively (figure 8(b)). The decreased bandgap of ZnFe₂O₄-A likely originates from the simultaneous injection of the precursors which favors an optimal association of the ZnO and ZnFe₂O₄ phases in the resultant film. The increased bandgap values measured for ZnFe₂O₄-01, 02 and 03 samples is due to the compositional ratio between ZnO (or Fe₂O₃) and ZnFe₂O₄ phases. The bandgap value determined for the pure ZnO film is 3.18 eV (figure S3), which suggests a better photocatalytic performance for ZnFe₂O₄ films under visible light irradiation.

Photocatalytic activity under UV light irradiation and stability

The photocatalytic activity of ZnFe₂O₄ related samples was firstly assessed through the degradation of Orange II under UV light irradiation. In preliminary blank experiments conducted in the absence of ZnFe₂O₄ photocatalyst, no significant photodegradation of the Orange II dye is observed regardless of the light source used. In contrast, when using the ZnFe₂O₄-03 films a photocatalyst, the absorption peak of Orange II at 485 nm decays to almost 0 after 360 min irradiation (figure 9(a)), indicating an efficient decomposition of the dye. The evolution of the UV-visible absorption spectra of Orange II in contact with the ZnFe₂O₄-A and ZnFe₂O₄-B materials under UV irradiation are shown in figures 9(b) and 8(c), respectively. Almost complete degradation of the dye is observed using the ZnFe₂O₄-A catalyst after 240 min while only 80% of the dye is bleached using the ZnFe₂O₄-B film after 360 min irradiation.

The C_t/C_0 plots for all photocatalysts are shown in figure 9(d). Firstly, for ZnFe₂O₄-01, ZnFe₂O₄-02 and ZnFe₂O₄-03 samples, the photodegradation efficiency is improved when increasing the Zn/Fe ratio in the precursor

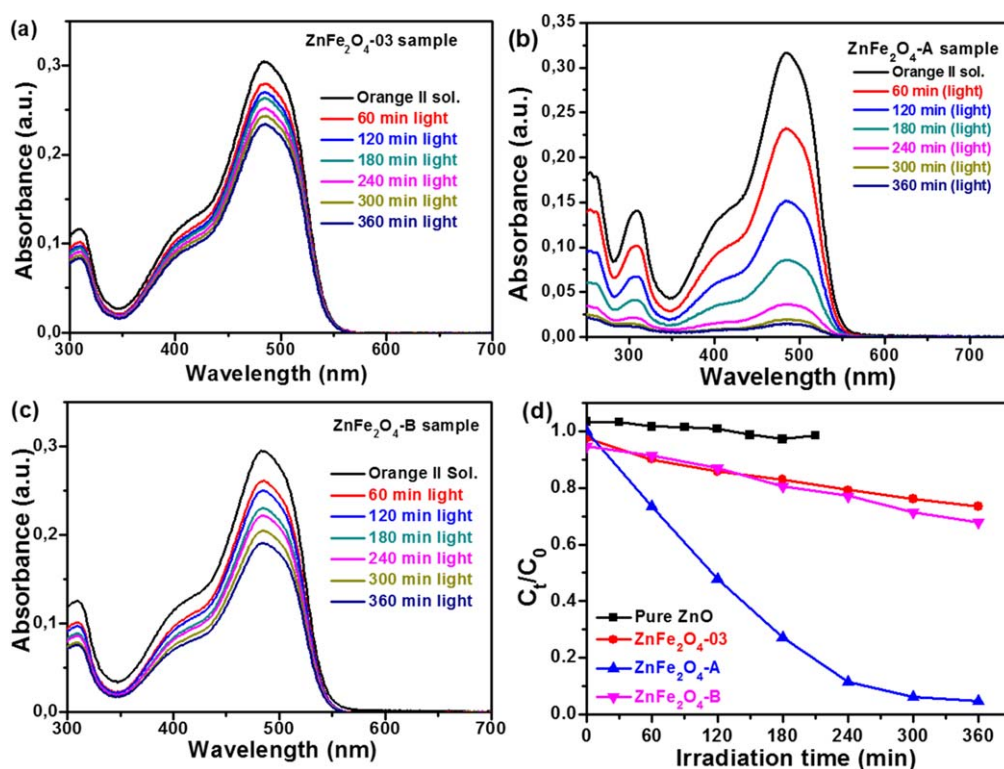


Figure 12. (a)–(c) UV–visible absorption spectra of Orange II during its photodegradation under visible light irradiation using Fe₂O₄-03, ZnFe₂O₄-A and ZnFe₂O₄-B samples and (d) photodegradation performance under visible light in function of irradiation time for the reference pure ZnO and the ZnFe₂O₄ related films.

solution. This result can be correlated to their different compositions. Indeed, although ZnFe₂O₄ and Fe₂O₃ benefit from a narrow bandgap, their photocatalytic activity is quite limited due to their poor photoelectric conversion and low valence band (VB) potential [51–54], suggesting limited utilization efficiency of photogenerated-holes and electrons and low oxidizing ability. When increasing the loading in Zn ratio (ZnFe₂O₄-A sample), almost 100% degradation was obtained within 240 min. This confirms that the ZnO/ZnFe₂O₄ ratio plays a key role in the photodegradation performance under UV light irradiation.

The plots of $\ln(C_0/C_t)$ versus time t are nearly linear with the irradiation time (figure S4), indicating that the photodegradation kinetics of Orange II at the surface of ZnFe₂O₄ related samples follow the pseudo-first-order model [55]:

$$\ln(C_0/C_t) = k_{app}xt, \quad (2)$$

where k_{app} is the pseudo-first-order rate constant (min^{-1}). The values determined for k_{app} are 0.001 min^{-1} , 0.002 min^{-1} and 0.010 min^{-1} for ZnFe₂O₄-01, ZnFe₂O₄-02 and ZnFe₂O₄-03 samples, respectively and confirms the high photoactivity of the ZnFe₂O₄-03 film. For the ZnFe₂O₄-A sample, k_{app} is as high as 0.018 min^{-1} , which is 18, 9 and 1.8 times higher than that determined for the ZnFe₂O₄-01, ZnFe₂O₄-02 and ZnFe₂O₄-03 samples, respectively. The k_{app} of the ZnFe₂O₄-B film decreased to 0.004 min^{-1} , further indicating that an appropriate combination of ZnFe₂O₄ and ZnO plays a much important role on the

photocatalytic activity than the nanostructured morphology in the ZnFe₂O₄ related films.

However, for the photodegradation driven by visible light, the presence of the ZnFe₂O₄ phase is highly desirable. For the ZnFe₂O₄-A sample, the weakly decreased performance (95%, 360 min) compared to the ZnFe₂O₄-03 films may be ascribed to the separated injection process, resulting in a modest association of ZnO and ZnFe₂O₄ phases. Generally, the ZnFe₂O₄/ZnO films exhibited enhanced photodegradation efficiency compared to the pure ZnO films (70%, 360 min) with similar microstructures as shown in figure S5.

The photocatalytic performance of the ZnFe₂O₄-A sample was also evaluated for the degradation of tetracycline hydrochloride (TC), an antibiotic of widespread use in human and veterinary medicine [56]. At neutral pH, TC exhibits two UV–visible absorption peaks located at 275 and 357 nm. Upon interaction with the ZnFe₂O₄-A catalyst, the UV–visible signals are red-shifted to 298 and 381 nm due to the deprotonating of one of the hydroxyl groups of TC by the photocatalyst. The temporal evolution of the TC spectral change demonstrate that the ZnFe₂O₄-A catalyst exhibit also a high efficiency for the degradation of TC (95% after 180 min UV light irradiation) (figures 10(a)–(b)). The pseudo first-order rate constant of TC decomposition over the ZnFe₂O₄-A catalyst is 0.02 min^{-1} .

The stability of the photocatalyst is of importance both for practical applications and economic costs. The stability of the ZnFe₂O₄-A material was evaluated by carrying out the

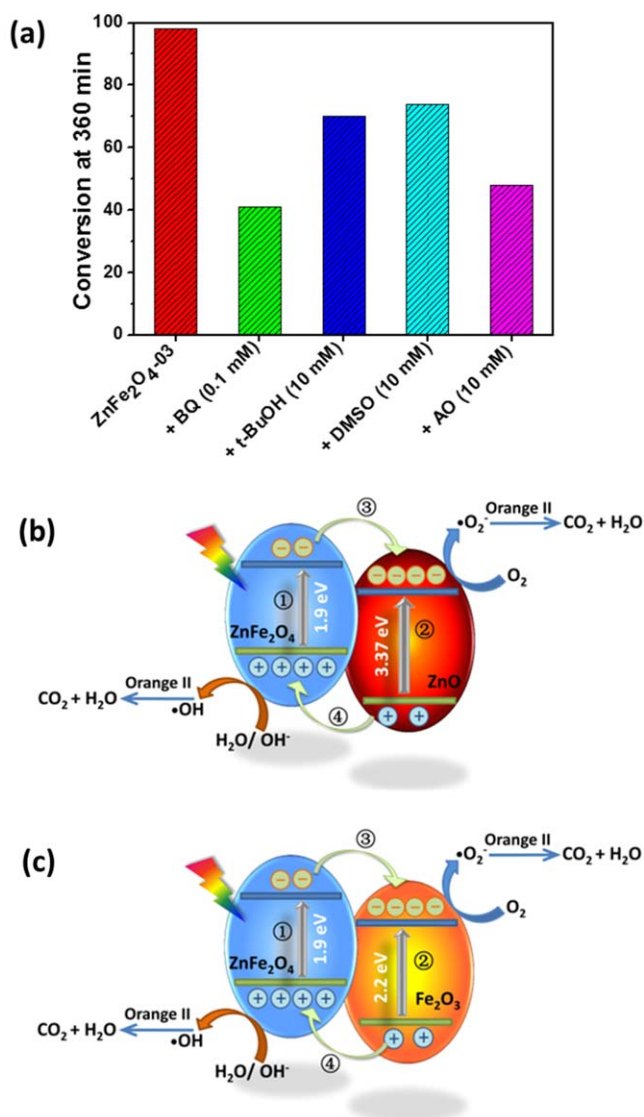


Figure 13. Photocatalytic mechanism of ZnFe₂O₄ related photocatalytic films under irradiation.

photodegradation of Orange II for multiple runs. It should be noted that film-formed photocatalysts are easier for photodegradation cycling test, they will not require any post-filtration after each usage. Results depicted in figure 11 show that after four reuses, the decomposition of Orange II remains above 90%, which demonstrates the high stability of the Fe₂O₃/ZnO heterostructured film. In addition, SEM shows that the morphology of the ZnFe₂O₄ film was not altered after its reuse (figure S6). Moreover, the XRD and Raman spectrum shown in figure S7 demonstrated the chemical stability of SPPS-deposited ZnFe₂O₄ samples.

Influence of the irradiation sources on photocatalytic performance

The photodegradation performance for Orange II decomposition driven by visible-light was also investigated. Based on the photocatalytic results obtained under UV light irradiation, ZnFe₂O₄-03, ZnFe₂O₄-A and ZnFe₂O₄-B samples

were selected for these tests (figures 12(a)–(c)). For the three ZnFe₂O₄ films, a decrease of the Orange II UV–visible absorption signal at 485 nm peak was observed upon illumination. The ZnFe₂O₄-A film exhibits the highest activity and a marked decrease of the characteristic peak of the dye (from about 0.3 to 0.015) was observed after 360 min of irradiation, indicating 95.3% degradation efficiency. For comparison, no photodegradation was observed using pure ZnO films under visible light irradiation due to the wide bandgap of this material. ZnFe₂O₄-B and ZnFe₂O₄-03 films exhibit lower photocatalytic activity under visible light irradiation (28.4% and 24.8% degradation after 360 min irradiation, respectively). The kinetics of the photodegradation under visible light irradiation was also investigated using a pseudo-first-order model. The $\ln(C_0/C_t)$ versus t plots are given in figure S7. The highest k_{app} value (0.009 min⁻¹) was determined for the ZnFe₂O₄-A sample, which highlights the potential of zinc ferrite-based films deposited via the SPPS for photocatalytic applications under visible light illumination.

Mechanism of ZnFe₂O₄ related photocatalytic films

To investigate the photocatalytic mechanism of ZnFe₂O₄-based films, trapping experiments were conducted to determine the active species involved in the photodegradation process. *Tert*-butanol (*t*-BuOH), *p*-benzoquinone (BQ), DMSO and ammonium oxalate (AO) were used to trap hydroxyl •OH radicals, superoxide O₂^{•-} radicals, electrons and holes, respectively (figure 13(a)). The photodegradation efficiency of Orange II markedly decreased upon adding BQ and AO, indicating that O₂^{•-} radicals and holes are the main active species involved in the process. Hydroxyl radicals and electrons are also involved but to a much weaker extent.

Based on these results, the possible mechanism underlying the photocatalytic degradation of ZnFe₂O₄ related photocatalytic films is schematically illustrated in figures 13(b) and (c). Firstly, the ZnO/ZnFe₂O₄ films exhibit higher photodegradation efficiency than the reference ZnO sample, which could be ascribed to the heterojunction between p-type ZnFe₂O₄ and n-type ZnO. For ZnO/ZnFe₂O₄ films (such as ZnFe₂O₄-03, ZnFe₂O₄-A and ZnFe₂O₄-B samples), the mechanism is depicted in figure 13(b). Under UV light, the electrons in the VB of ZnFe₂O₄ and ZnO materials are both promoted to the conduction band (CB) (steps ① and ②). Next, the electrons in the CB of ZnFe₂O₄ transfer to the CB of ZnO (step ③), and the holes migrate from ZnO to ZnFe₂O₄ (step ④). These processes promote the separation of electrons and holes and thus improve their use in photocatalytic reactions [57–60]. The electrons on the ZnO surface can react with adsorbed O₂ to produce O₂^{•-} radicals while holes on the ZnFe₂O₄ surface can directly oxidize the dye (Orange II → Orange II⁺) or water molecules to generate •OH radicals. Under visible light irradiation, ZnO cannot be photo-activated and only electrons transferred from ZnFe₂O₄ to ZnO and the holes in the VB of ZnFe₂O₄ should be considered [60].

For the Fe₂O₃/ZnFe₂O₄ film (including ZnFe₂O₄-01 sample), both Fe₂O₃ and ZnFe₂O₄ will be excited by UV and visible light due to the narrow bandgap of these materials

Table 2. Summary of the photodegradation performance from ZnFe₂O₄ related photocatalysts.

Photocatalysts	Catalysts form	Organic pollutant ^a	Irradiation source	k_{app} (min ⁻¹) or decomposition (%)	Reference
ZnFe ₂ O ₄ @ZnO	Nanoparticle	MB	UV	0.3	[20]
ZnO/ZnFe ₂ O ₄	Nanoparticle	IC	UV	0.624	[62]
Tannin/ZnFe ₂ O ₄	Nanoparticle	IC	UV	0.402	[62]
Tannin/ZnFe ₂ O ₄ /ZnO	Nanoparticle	IC	UV	1.026	[62]
Fe ₂ O ₃ /ZnO paper	Immobilized on paper	TCP	Solar	0.84	[63]
ZnFe ₂ O ₄	Nanoparticle	RhB	Visible	0.03	[59]
ZnO/ZnFe ₂ O ₄	Nanoparticle	RhB	Visible	0.444	[59]
Fe ₂ O ₃ /ZnFe ₂ O ₄	Nanoparticle	RhB	Visible	0.138	[59]
ZnFe ₂ O ₄ /graphene	Nanoparticle	RhB	Visible	22%, 2 h	[64]
ZnFe ₂ O ₄ /g-C ₃ N ₄ (0.01 M H ₂ O ₂)	Nanoparticle	Orange II	Visible	0.168	[65]
ZnFe ₂ O ₄ -A sample	Film	Orange II	UV	1.08, 100%, 4 h	This work
ZnFe ₂ O ₄ -A sample	Film	Orange II	Visible	0.54 95%, 6 h	This work

^a MB: Methylene Blue; IC: Indigo Carmine; TCP: Tetrachlorophenol; RhB: Rhodamine.

(figure 13(c)). However, both Fe₂O₃ and ZnFe₂O₄ suffer from high charge carriers recombination rate [51–54], resulting in a low-efficiency in steps ③ and ④. This explains the low-efficiency of ZnFe₂O₄-01 sample in photocatalytic reactions. The high recombination rate in Fe₂O₃/ZnFe₂O₄ compared to ZnO/ZnFe₂O₄ was also reported in previous work [61].

The photocatalytic degradation performance of ZnFe₂O₄ related catalysts described in the literature are listed in table 2. It should be highlighted the photocatalyst developed in this work are immobilized on the Al₂O₃ substrate and exhibit a lower surface area than nanoparticles. The data of table 2 demonstrate that the SPPS-deposited ZnO/ZnFe₂O₄ film usually exhibit similar and even better photodegradation efficiency than nanoparticle-formed catalysts both under UV and visible light irradiation, further indicating the high interest of SPPS-deposited spinel films for photodegradation applications.

Conclusions

In summary, SPPS was demonstrated to be a fast and efficient process to synthesize spinel zinc ferrite (ZnFe₂O₄) related photocatalytic films. By varying the Zn/Fe molar ratio salt in the precursor solutions or the spraying pattern, various compositions (Fe₂O₃, ZnO and ZnFe₂O₄ phases) were detected in the resultant films. The content in ZnO was found to be higher when increasing the Zn/Fe ratio in the feeding solution. Two optimized ZnFe₂O₄ films (ZnFe₂O₄-A and ZnFe₂O₄-B samples) were prepared with a high amount of ZnO and hierarchical NRs nanostructures, respectively. The evaluation of photocatalytic activity under UV light irradiation shows that a higher loading in ZnO in the films allows increasing the photodegradation performance. The ZnFe₂O₄-A sample exhibited the highest photocatalytic activity for the degradation of the Orange II dye (100% within 240 min under UV light irradiation). The ZnFe₂O₄-A sample exhibits also a high activity under visible light irradiation (95% decomposition of

the dye within 360 min). This study demonstrates that the SPPS route is a novel and promising method to synthesize and deposit binary metal oxides composite films including other spinel, perovskite or fluorite type mixed oxides, which could be applied for photocatalytic degradation and other functional applications.

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