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PAPER

Synthesis of SrFeO_{3-x}/g-C₃N₄ heterojunction with improved visible-light photocatalytic activities in chloramphenicol and crystal violet degradation

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Some solid magnetic photocatalysts containing ferrites are convenient to being separated from reaction solution by a magnet. This study reports the use of the photocatalyst SrFeO_{3-x}/g-C₃N₄ heterojunction for the photocatalytic degradation chloramphenicol (CAP) and crystal violet (CV) under visible irradiation. Herein, the novel heterojunctions of SrFeO_{3-x}/g-C₃N₄ are fabricated by sintering SrFeO_{3-x} with g-C₃N₄. The preparation and characterization of SrFeO_{3-x}/g-C₃N₄ photocatalyst is the first report demonstrating the systematic synthetic study of SrFeO_{3-x}/g-C₃N₄ using sintering method. Their photocatalytic activities are evaluated by degrading CAP and CV in aqueous solution induced by visible light. The intermediates formed in the degradation CAP processes are separated and identified by HPLC-ESI-MS technique. The quenching effects of different scavengers and EPR display that the reactive O₂^{•-} and [•]OH play the major roles and h⁺ plays the minor role in the CAP degradation. The possible degradation pathways are proposed and discussed in this research. The study is useful to the synthesis of SrFeO_{3-x}/g-C₃N₄ and the degradation of the CAP and CV at future applications to environmental pollution and control.

PAPER

1. Introduction

Pharmaceutical industry produces a wide variety of products, among which the pharmaceuticals receive extensive concern because of a wide usage in the world. The existence of pharmaceuticals in the aquatic environment and their possible effects on living organisms are giving rise to growing concern. Many of these samples have been detected from wastewater as well as surface and/or ground waters. These compounds are emanated from industrial discharges, hospital, and domestic sewage.¹⁻³

Recently, a number of antibiotics have been detected worldwide in soil, surface water, wastewaters and even drinking water.¹ The residues of antibiotics in environments may cause potential risks to public health. CAP is widely used in the treatment of serious infections, even if recent research revealed serious side effects of CAP on the haemopoietic system, which sometimes accompanied by leucopenia and thrombocytopenia and aplastic anemia.⁴ As a consequence, it has been banned for the use in foodstuffs of animal origin in the European Union⁵ and United States⁶. However, it is sometimes used topically for eye infections; nevertheless, the global problem of advancing bacterial resistance to newer drugs has led to a renewed interest in its use.⁵ Furthermore, in low-income countries, chloramphenicol is still widely used because it is exceedingly inexpensive and readily available.

CAP as a representative antibiotic is applied to inhibiting Gram-positive and Gram-negative bacteria and its residual parts with metabolites from the excrement of human and animals get into the surface water and ground water after the sewage treatment.⁴ As a consequence, researchers have been making efforts to find out the ways of inactivating or eliminating the residual parts of CAP. Badawy *et al.*⁷ investigated the removal of CAP by Fenton-biological treatment processes. Radiation induced degradation of CAP was studied by Lin *et al.*⁸ and Csay *et al.*⁹ Recently, much attention has been paid to separate the source of the refractory or toxic effluent and treat it by advanced oxidation processes (AOPs) using homogeneous or heterogeneous catalysts.^{10,11} Degradation of CAP using TiO₂ as catalyst has been studied by several researchers.^{10,12} However, the previous works are based on the efficiencies and kinetics by changing the parameters and does not consider the various degradation products formed and mechanisms on photocatalytic degradation of CAP.

Triphenylmethane (TPM) dyes are extensively used in the cosmetic, paper, food and leather industries as coloring agents

for plastics, oils, fats, waxes, and varnishes.¹³ The thyroid peroxidase-catalyzed oxidation of TPM dyes in living organisms is of great concern because the oxidation reactions can produce various *N*-dealkylated aromatic amines with structures similar to those of carcinogenic aromatic amines.¹⁴ Recent reports have indicated that TPM dyes can serve as targetable sensitizers in the photodecomposition of specific cells or cellular components.¹⁴ In recent years, photocatalytic processes have been successfully used to degrade TPM dye pollutants.¹⁵⁻¹⁶ In most cases, the reaction kinetics, efficiency, and mechanisms have been well documented.

Recently, an effective and simple strategy to improve the photocatalytic activity of a photocatalyst is the incorporation of a heterostructure, because heterojunctions have great potential for tuning the desired electronic properties of photocatalysts and efficiently separating the photogenerated electron-hole pairs.¹⁷⁻²⁰

In the search for robust and stable visible-light-driven semiconductor photocatalysts, a polymeric semiconductor, graphitic carbon nitride (g-C₃N₄), has recently attracted tremendous attention.^{21,22} The heptazine ring structure and high condensation degree enable metal-free g-C₃N₄ to possess many advantages such as good physicochemical stability, as well as an appealing electronic structure combined with a medium-band gap (2.7 eV).²³ These unique properties make g-C₃N₄ a promising candidate for visible light photocatalytic applications utilizing solar energy.

It is believed that there is a close relationship between the size, morphology and the properties of photocatalysts. Therefore, photocatalysts with hierarchical architectures are expected to exhibit enhanced photocatalytic performance.²⁴⁻²⁷ Recently, TiO₂/g-C₃N₄,²⁸ ZnWO₄/g-C₃N₄,²⁹ BiOCl/g-C₃N₄,³⁰ Zn₂GeO₄/g-C₃N₄,³¹ BiOBr/g-C₃N₄,³² CdS/g-C₃N₄,³³ AgVO₃/g-C₃N₄,³⁴ BiOI/g-C₃N₄,³⁵ BiOBr_{0.2}I_{0.8}/g-C₃N₄³⁶ and magnetic MFe₂O₄/graphene³⁷ composites have been synthesized in order to improve the photocatalytic activity of the materials.

Some solid magnetic photocatalysts containing ferrites are handy to be separated from reaction solution by a magnet.³⁸ However, no work compared to g-C₃N₄ based on a SrFeO_{3-x} has been reported. It is expected that functionalizing graphitic carbon nitride nanosheets with SrFeO_{3-x} can not only combine both the advantages of SrFeO_{3-x} and graphitic carbon nitride nanosheets but may also result in new properties. The preparation and characterization of SrFeO_{3-x}/g-C₃N₄ photocatalyst is the first report demonstrating the systematic synthetic study of SrFeO_{3-x}/g-C₃N₄ using sintering method. The photocatalytic activities of SrFeO_{3-x}/g-C₃N₄ are evaluated by measuring the degradation efficiencies of CAP, exhibiting

excellent activity under visible-light irradiation. Besides, the intermediates in the photocatalytic process are separated, identified, and characterized using HPLC-PDA-ESI-MS to propose the CAP-decomposition mechanism.

2. Experiment

2.1 Materials

Chloramphenicol and sodium azide (Sigma), phenol (Shimakyu), *p*-benzoquinone (Alfa aesar), ammonium oxalate (Osaka), and isopropanol (Merck) were purchased and used without further purification. Reagent-grade sodium hydroxide, nitric acid, ammonium acetate, and HPLC-grade methanol were obtained from Merck.

2.2 Instruments and analytical methods

The field-emission transmission electron microscopy (FE-TEM) images, selected area electron diffraction (SAED) patterns, high resolution transmission electron microscopy (HRTEM) images, and energy-dispersive X-ray spectra (EDS) were obtained using a JEOL-2010 with an accelerating voltage of 200 kV. The Al-K α radiation was generated at 15 kV. The thermo-gravimetric and differential thermal analysis (TG-DTA; Seiko TG/TGA 300) was carried out in a flow of air (10 mL/min) at a heating rate of 10°C/min. The X-ray diffraction (XRD) patterns were recorded on a MAC Science MXP18 equipped with Cu-K α radiation, operating at 40 kV and 80 mA. Field emission scanning electron microscopy-electron dispersive X-ray spectroscopy (FE-SEM-EDS) measurements were carried out using a JEOL JSM-7401F at an acceleration voltage of 15 kV. High resolution X-ray photoelectron spectroscopy (HRXPS) measurements were carried out using an ULVAC-PHI. The Ultra-violet photoelectron spectroscopy (UPS) measurements were performed using a ULVAC-PHI XPS, PHI Quantera SXM. Photoluminescence (PL) measurements were carried out on Hitachi F-7000. UV-vis diffuse reflectance spectra were recorded on a Scinco SA-13.1 spectrophotometer at room temperature. The Brunauer-Emmett-Teller (BET) specific surface areas of the samples (S_{BET}) were measured with an automated system (Micrometrics Gemini) using nitrogen gas as the adsorbate at liquid nitrogen temperature. The magnetization curves and hysteresis loop of the sample were characterized with a model 4HF vibrating sample magnetometer (ADI) with a maximum field of 18 kOe at room temperature. The HPLC-PDA-ESI-MS system consisted of a Waters 1525 binary pump, 2998 photodiode array detector, and 717 plus autosampler, a ZQ2000 micromass detector.

2.3 Synthesis of g-C₃N₄/SrFeO_{3-x}

Under atmosphere conditions, the g-C₃N₄ powder was synthesized by directing calcining melamine in a muffle furnace. In a typical synthesis run, 5 g melamine was placed in a semi-closed alumina crucible with a cover. The crucible

was heated to 520 °C for 4 h with a heating rate of 10°C/min. After cooling to room temperature, g-C₃N₄ was produced in a powder form.³⁹ SrFeO_{3-x} was fabricated through sintering method with Fe₂O₃ and SrCO₃ at 1000 °C, for 24 h. Herein, the novel heterojunctions of SrFeO_{3-x}/g-C₃N₄ were synthesized by sintering SrFeO_{3-x} with g-C₃N₄ at 400-600 °C, 1-3h.

2.4 Photocatalytic and active species experiments

The CAP (or CV) irradiation experiments were carried out on stirred aqueous solution contained in a 100-mL flask; the aqueous suspension of CAP (or CV) (100 mL, 10 ppm) and the amount of catalyst powder were placed in a Pyrex flask. The pH of the suspension was adjusted by adding either NaOH or HNO₃ solution. Dark experiments were performed in order to examine the adsorption/desorption equilibrium. 10 mg of the photocatalyst was mixed with 100mL CAP (or CV) aqueous solution with a known initial concentration, in a 100mL flask and the mixture shaken in an orbital shaker (100 rpm) at a constant temperature. The mixture was centrifuged at 3000 rpm in a centrifugation machine after batch sorption experiments so that the absorbance of CAP (or CV) could be determined at 296 nm by means of HPLC-PDA-ESI-MS. For visible light experiments a 422 nm cutoff filter was used. Irradiation was carried out using 150 W Xe arc lamps; the light intensity was fixed at 31.2 W/m², and the reaction vessel was placed 30 cm from the light source. At given irradiation time intervals, a 5-mL aliquot was collected and centrifuged to remove the catalyst. The supernatant was measured by HPLC-PDA-ESI-MS.

A series of quenchers were introduced to scavenge the relevant active species in order to evaluate the effect of the active species during the photocatalytic reaction. O₂^{•-}, [•]OH, h⁺, and ¹O₂ were studied by adding 1.0 mM benzoquinone (BQ, a quencher of O₂^{•-}),⁴⁰ 1.0 mM isopropanol (IPA, a quencher of [•]OH),⁴¹ 1.0 mM ammonium oxalate (AO, a quencher of h⁺),⁴² and 1.0 mM sodium azide (SA, a quencher of ¹O₂),⁴³ respectively. The method was similar to the former photocatalytic activity test.

3. Results and discussion

3.1 Characterization of SrFeO_{3-x}/g-C₃N₄ Composites

3.1.1 Phase structure

Figure 1 and Figure S1-S2 of ESI[†] show the XRD patterns of the as-prepared samples; the patterns clearly show the coexistence of different phases. All the samples as-prepared contain the SrFeO_{3-x} phase (JCPDS 34-0638) and g-C₃N₄ (JCPDS 87-1526), in addition to the SrCO₃ (JCPDS 74-1491), and Fe₂O₃ (JCPDS 73-2234) phases. The XRD patterns for 1wt%-500-2, 2wt%-500-2, and 4wt%-500-2 (**Figure 1**) are identical to those reported for the SrFeO_{3-x}/g-C₃N₄ binary phases; 8wt%-500-2, 10wt%-500-2, and 30wt%-500-2 are identical to those reported for the SrFeO_{3-x}/SrCO₃/g-C₃N₄

ternary phases; 50wt%-500-2, 70wt%-500-2, and 90wt%-500-2 (**Figure S1** of ESI[†]) are identical to those reported for the SrFeO_{3-x}/SrCO₃ binary phases; 4wt%-400-2 and 4wt%-450-2 are identical to those reported for the SrFeO_{3-x}/g-C₃N₄; 4wt%-550-2 is identical to those reported for the SrCO₃/g-C₃N₄; 4wt%-400-2, 4wt%-450-2, and 4wt%-500-2 are identical to those reported for the SrFeO_{3-x}/g-C₃N₄ binary phases; and, 4wt%-600-2 is identical to those reported for the SrCO₃/Fe₂O₃ (**Figure S2** of ESI[†]) binary phases. **Table 1** summarizes the results of the XRD measurements.

During the synthetic process, the nucleation and growth of SrFeO_{3-x} grains may preferentially occur on the surface of g-C₃N₄ sheets for the relatively lower nucleation energy of heterogeneous nucleation. The (110) peak of SrFeO_{3-x} in the heterojunctions was much wider than that of pure SrFeO_{3-x}, and gradually broadened and shifted with the increase of g-C₃N₄, suggesting a stepwise size decrease of SrFeO_{3-x} in the heterojunctions. This result implies that the crystallite growth of SrFeO_{3-x} along the c-axis would be attenuated after being deposited onto g-C₃N₄. In addition, remarkable shift in the (110) peak was observed, suggesting that there was impact on the size of the SrFeO_{3-x} in the two-dimensional plane of g-C₃N₄. When SrFeO_{3-x} coupled with g-C₃N₄, it can be found that the (1 1 0) peaks of SrFeO_{3-x} and the (0 0 2) peak of g-C₃N₄ shifted to 28.1 and 27.3. It implied that the coupling between SrFeO_{3-x} and g-C₃N₄ may be happened on SrFeO_{3-x}-(1 1 0) facets and g-C₃N₄-(0 0 2) facets. After facet coupling between SrFeO_{3-x}-(1 1 0) and g-C₃N₄-(0 0 2), the (1 1 0) facets of SrFeO_{3-x} were cover and interaction by g-C₃N₄. So, the intensity of g-C₃N₄-(0 0 2) peaks should be decreased and shifted. On the other hand, the half band width of g-C₃N₄-(0 0 2) peaks are larger than others, it also accelerate the disappearance of (0 0 2) peaks.

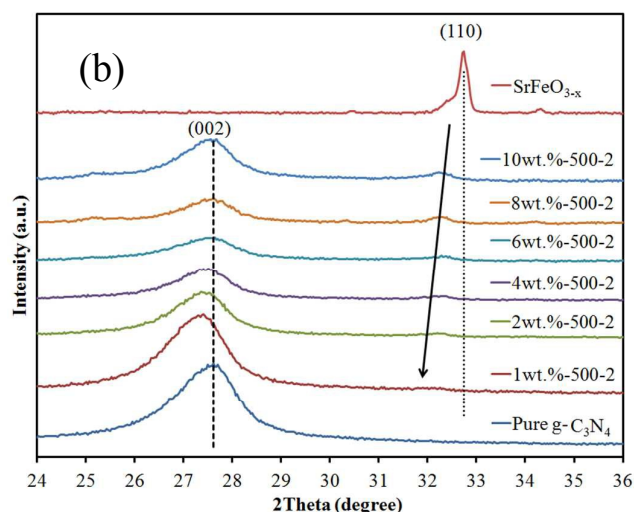
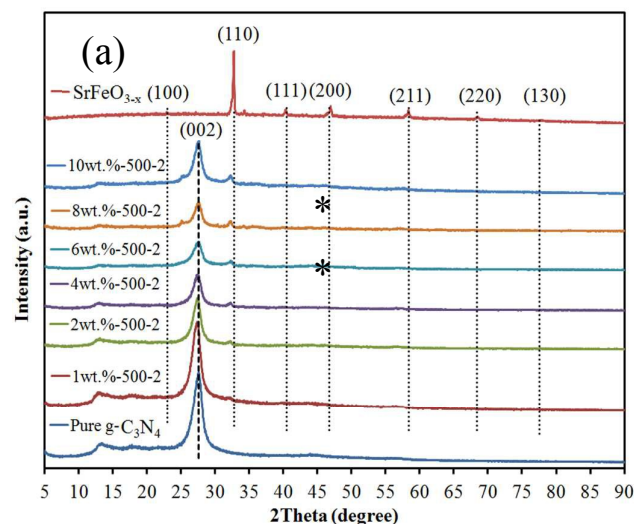


Figure 1. (a) XRD patterns of as-prepared samples under different weight percentage. (b) enlarged view. (Sintering temp = 500°C, time = 2 h; * Impurity phase SrCO₃)

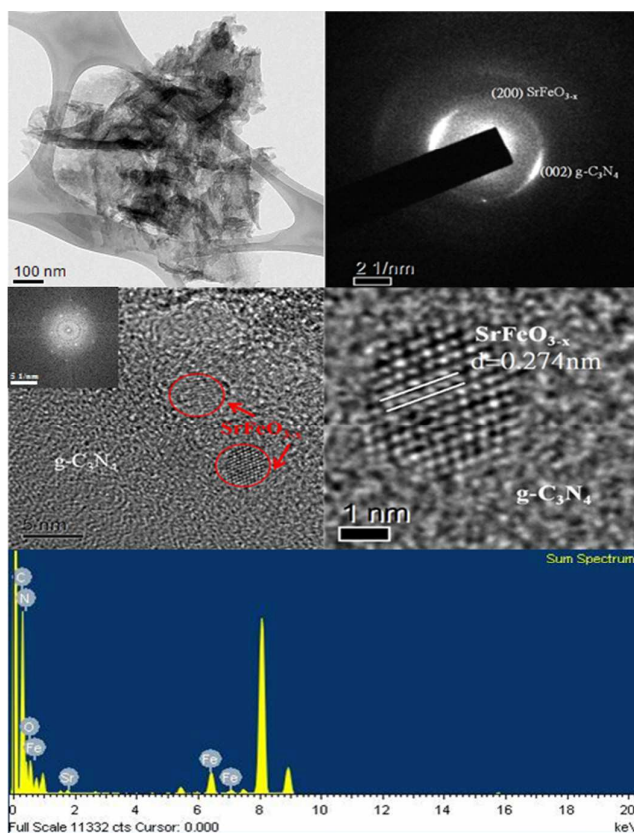


Figure 2. FE-TEM images and EDS of 4wt%-500-2 sample by the sinetring method.

Figure 2 displays that 4wt%-500-2 is composed of differently sized layers, consistent with the TEM observations. In addition, the EDS spectrum shows that the sample contains the elements of Fe, Sr, O, C, and N. The HRTEM image shows that two sets of different lattice images are found with a d-spacing of 0.274 nm, corresponding to the (200) plane of SrFeO_{3-x}, which is in good agreement with the XRD results.

The results suggest that the $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ phases have been produced in the composites, which are favorable for the separation of photoinduced carriers, yielding high photocatalytic activities.

Figure S2 of ESI[†] reveals the XRD patterns of the 4 wt% $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ samples calcined at different temperatures. The calcination temperature shows a great effect on the powder XRD patterns. When the calcination temperature is higher than 450 °C, the XRD peak of $\text{g-C}_3\text{N}_4$ decreases with the increase in calcination temperature and disappears at 600 °C. This result indicates that the heating process at high temperature decreases the $\text{g-C}_3\text{N}_4$ content, as confirmed by the TG-DTA experiment (**Figure 3**). In **Figure 3(a)**, the TG-DTA curves of the pure $\text{g-C}_3\text{N}_4$ exhibit only one sharp weight loss with one endothermic peak at 725 °C in the temperature range of room temperature to 1000 °C, which may be mainly attributed to the decomposition (or sublimation) of $\text{g-C}_3\text{N}_4$ since a large amount of $\text{g-C}_3\text{N}_4$ is oxidized. The TG-DTA curves of the physical mixture of $\text{g-C}_3\text{N}_4$ and SrFeO_{3-x} (4wt%-500-2) are highly different from those of pure $\text{g-C}_3\text{N}_4$.

As shown in **Figure 3(b)**, two exothermic peaks at approximately 588 °C and 619 °C appear in the DTA curve of the sample, which may be due to the production of SrCO_3 and Fe_2O_3 . Correspondingly, two weight losses are observed in the TG curve. The total weight loss is 75 wt%, showing that $\text{g-C}_3\text{N}_4$ with SrFeO_{3-x} is eliminated for the production of SrCO_3 and Fe_2O_3 . The result of **Figure 3** clearly reveals that the added SrFeO_{3-x} is a photocatalyst which can absorb and activate the oxygen in the air and then oxidize the $\text{g-C}_3\text{N}_4$ at a relatively low temperature.³⁹ The high temperature can promote oxygen activation. Therefore, the decrease in $\text{g-C}_3\text{N}_4$ concentration is more evident in the sample sintered at a high temperature. When the mixture is calcined at 638 °C, nearly all of $\text{g-C}_3\text{N}_4$ is eliminated and SrCO_3 and Fe_2O_3 can be found. The results illustrate that at different reaction temperature, a series of changes happen in the products. The proposed processes for the formation of SrCO_3 and Fe_2O_3 are described in equations 1–4.

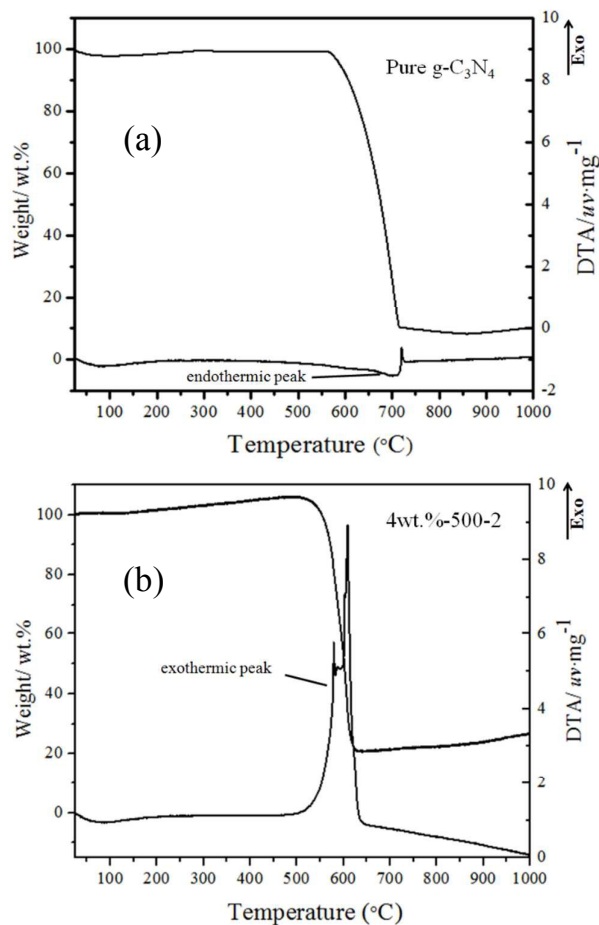
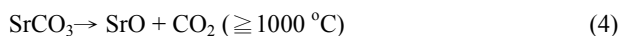
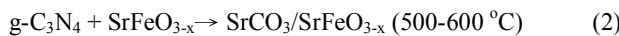
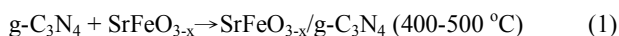


Figure 3. TG-DTA thermograms for heating (a) the pure $\text{g-C}_3\text{N}_4$ and (b) the precursor of 4 wt % $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$.

Figure 4 and **Figure S3** of ESI[†] reveal the FT-IR spectra of the SrFeO_{3-x} , $\text{g-C}_3\text{N}_4$, $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$, and SrCO_3 , and Fe_2O_3 composite photocatalysts. The peaks at 442 and 524 cm^{-1} in the SrFeO_{3-x} spectrum correspond to the Fe-O stretching and bending vibrations of the octahedral FeO_6 groups in the perovskite-type structure.⁴⁴ The infrared spectrum of a carboxylate group, CO_3^{2-} , displays the characteristically broadened absorption due to the asymmetric and symmetric stretching and bending vibrations at 1443 and 854 cm^{-1} (probably SrCO_3).⁴⁵ With the relation to pure $\text{g-C}_3\text{N}_4$, the peaks at 1251, 1325, 1419, 1571, and 1639 cm^{-1} correspond to the typical stretching modes of the CN heterocycles.⁴⁶ Additionally, the characteristic breathing mode of the triazine units at 810 cm^{-1} is observed.⁴⁷ The FT-IR spectra of $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ symbolize the overlap of the FT-IR spectra of $\text{g-C}_3\text{N}_4$ and SrCO_3 . With the decrease in the $\text{g-C}_3\text{N}_4$ concentration or the increase of the calcination temperature, the FT-IR peaks of $\text{g-C}_3\text{N}_4$ decrease. This result agrees with that of the XRD experiment.

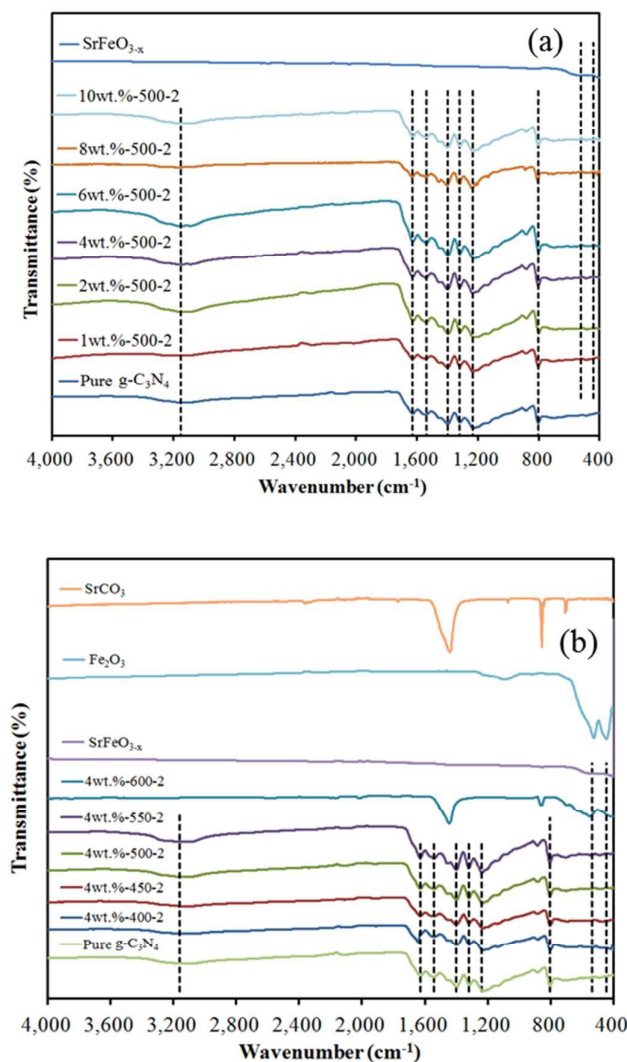


Figure 4. FT-IR spectra for SrFeO_{3-x}/g-C₃N₄ fabricated from different (a) weight percentage and (b) reaction temperature.

3.1.2 Morphological structure and composition

SrFeO_{3-x}/g-C₃N₄ is synthesized from g-C₃N₄ and SrFeO_{3-x} by sintering methods at different temperature and weight ratios. The surface morphologies of the as-prepared samples (Figures S4-S8 of ESI[†]) are measured by FE-SEM-EDS. Table 1 shows that as the weight ratio from 1 to 90 wt%, a gradual change in the atomic ratio of Sr and Fe happens, showing the production of a variety of compounds in the crystalline phase, including SrFeO_{3-x}/g-C₃N₄, SrFeO_{3-x}/SrCO₃/g-C₃N₄, and SrFeO_{3-x}/SrCO₃, and as the temperature from 400 to 600 °C, a gradual change in the crystal phases of the reflection peaks happens, showing the production of a variety of compounds in the crystalline phase, including SrFeO_{3-x}, g-C₃N₄, and SrCO₃, and Fe₂O₃. In Figure S5-S6, the FE-SEM image illustrates that the morphology of the samples prepared with different SrFeO_{3-x}/g-C₃N₄ weight percentage changing from irregular nanosheets to irregular microtubes, before changing to micro crystals. In Figure S7, the FE-SEM image displays that the morphology of the samples prepared with a same SrFeO_{3-x}/g-C₃N₄ weight

percentage at different temperature changing from irregular sheets to irregular microtubes, before changing to macro-crystals. In Figure S8, the FE-SEM image demonstrates that the morphology of the samples prepared with a same SrFeO_{3-x}/g-C₃N₄ weight percentage and temperature at different reaction time changing from irregular micro-crystals to irregular particle, before changing to macro-crystals. The SEM-EDS and TEM-EDS results demonstrate that the main elements within these samples are carbon, nitrogen, strontium, iron, and oxygen at Table 1. From Table 1, the strontium (or iron) atomic ratios (%) of the samples are within the range 0.06–21.67 (or 0.18–20.48), which corresponds to SrFeO_{3-x}/g-C₃N₄, SrFeO_{3-x}/SrCO₃/g-C₃N₄, SrFeO_{3-x}/SrCO₃, and SrCO₃/Fe₂O₃, compared to the stoichiometric ratio (Sr: Fe atomic ratio around 1), and could be selectively synthesized through a sintering method.

Table 1. Physical and chemical properties of SrFeO_{3-x}/g-C₃N₄ and crystalline phase changes of samples prepared under different reaction conditions.

Photocatalysts	EDS of atomic ratio (%)					XRD pattern
	C	N	Sr	Fe	O	
g-C ₃ N ₄	36.49	63.51	--	--	--	g-C ₃ N ₄
SrFeO _{3-x}	--	--	16.04	19.39	64.56	SrFeO _{3-x}
1wt%-500-2	37.37	58.92	0.06	0.18	3.47	SrFeO _{3-x} /g-C ₃ N ₄
2wt%-500-2	36.79	61.54	0.11	0.23	1.33	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-500-2	34.44	60.52	0.16	0.25	4.63	SrFeO _{3-x} /g-C ₃ N ₄
6wt%-500-2	38.04	60.21	0.37	0.47	1.61	SrFeO _{3-x} /g-C ₃ N ₄
8wt%-500-2	48.84	46.23	0.56	0.62	4.75	SrFeO _{3-x} /g-C ₃ N ₄ /SrCO ₃
10wt%-500-2	34.97	62.39	1.32	1.82	2.41	SrFeO _{3-x} /g-C ₃ N ₄ /SrCO ₃
30wt%-500-2	41.43	24.68	7.87	7.24	18.79	SrFeO _{3-x} /g-C ₃ N ₄ /SrCO ₃
50wt%-500-2	29.06	11.55	10.92	10.13	38.34	SrFeO _{3-x} /SrCO ₃
70wt%-500-2	20.82	5.90	16.30	17.10	38.87	SrFeO _{3-x} /SrCO ₃
90wt%-500-2	9.90	2.34	21.67	20.48	45.61	SrFeO _{3-x} /SrCO ₃
4wt%-400-2	37.31	58.12	0.17	0.27	4.24	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-450-2	35.69	59.88	0.10	0.17	4.16	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-500-2	34.44	60.52	0.16	0.25	4.63	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-550-2	33.15	17.61	4.50	4.78	39.96	Fe ₂ O ₃ /g-C ₃ N ₄ /SrCO ₃
4wt%-600-2	17.22	0.86	15.04	14.74	62.14	Fe ₂ O ₃ /SrCO ₃
4wt%-500-1	41.01	52.20	0.40	0.78	5.61	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-500-1.5	44.25	49.74	0.54	0.44	5.03	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-500-2	34.44	60.52	0.16	0.25	4.63	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-500-2.5	40.12	53.16	0.26	0.40	6.04	SrFeO _{3-x} /g-C ₃ N ₄
4wt%-500-3	40.43	52.58	0.54	0.34	6.11	SrFeO _{3-x} /g-C ₃ N ₄

3.1.3 X-ray photoelectron spectroscopy analysis

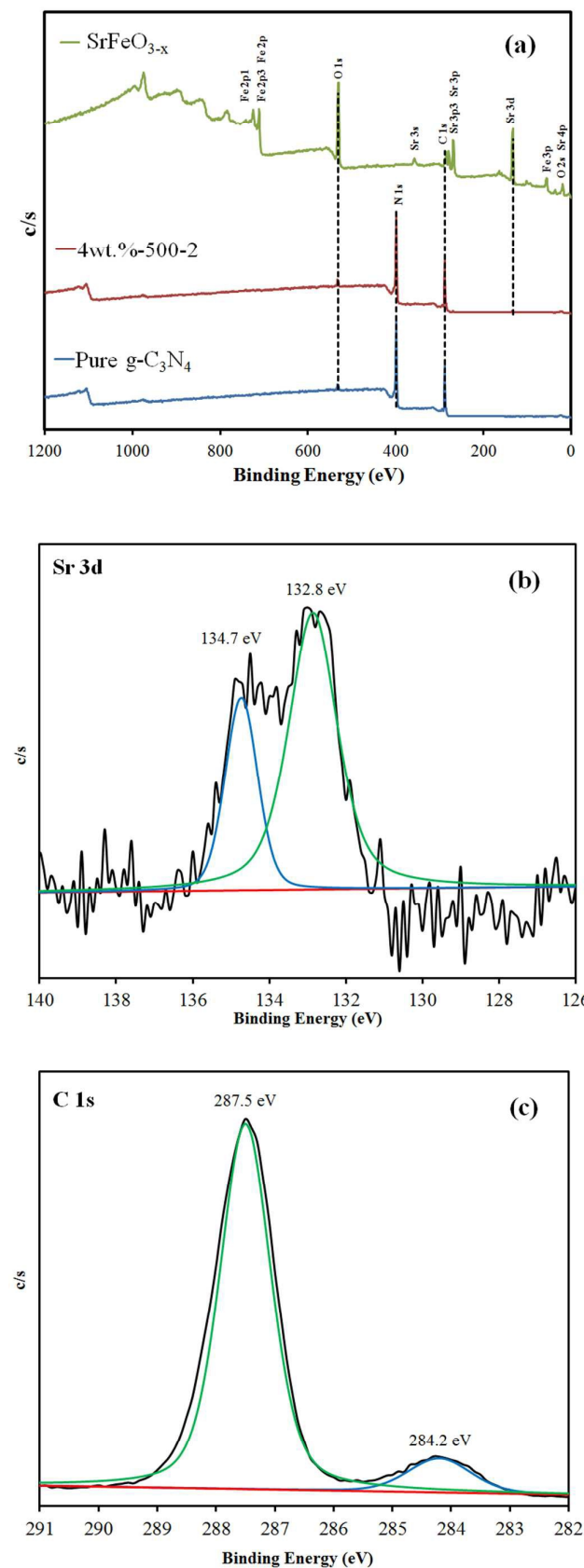
XPS is used for measuring the purity of the prepared samples; the spectra are shown in Figure 5. Figure 5 presents the C 1s, N 1s, Sr 3d, Fe 2p, and O 1s XPS spectra of the SrFeO_{3-x}/g-C₃N₄ samples. Observation of the transition peaks involving the C 1s, N 1s, Sr 3d, Fe 2p, and O 1s orbitals identifies that the catalysts are composed of C, N, Sr, Fe, and O. The structure details about backbone C and N elements in g-C₃N₄ are further researched by their corresponding high resolution spectra. Figure 5(b) shows the high resolution C 1s spectrum of the SrFeO_{3-x}/g-C₃N₄ heterojunction. There are mainly two carbon species displayed in the C 1s spectra: one (284.2 eV) is sp² C-C bonds, and the other (287.5 eV) is sp²-hybridized carbon in N-containing aromatic ring (N-C=N). The latter is indicated as the major carbon species in polymeric g-C₃N₄.⁴⁸

In **Figure 5(c)**, three peaks are deconvoluted for N 1s spectra. The highest peak centering at 398.0 eV is assigned as the sp^2 -hybridized nitrogen involved in triazine rings ($C-N=C$), whereas the peak at 400.3 eV corresponds to the tertiary nitrogen $N-(C)_3$ groups. Both of them, together with sp^2 -hybridized carbon ($N-C=N$, 287.5 eV), compose the heptazine heterocyclic ring units, constructing the basic substructure units of $g-C_3N_4$ polymers. The weak peak at 403.6 eV is characterized to charging effects or positive charge localization in heterocycles.⁴⁹ In **Figure 5(d)**, the Sr 3d core-level spectra of the samples are satisfactorily assigned to one doublet, attributing that Sr ions are located in same environments. As judged from the BE of the most intense Sr 3d_{5/2} peak, it would show that the component at 132.4–132.9 eV comes from Sr ions incorporated into the perovskite structure, whereas that observed at 133.8 eV, which is dominant, can be fitted to $SrFeO_{3-x}$.⁵⁰ It is reported that the Fe 2p peaks at binding energies of 711.2 and 725.0 eV with a satellite signal at 719.0 eV are the characteristics of Fe^{3+} , while the peaks at binding energies of 709.9 and 723.4 eV with a satellite signal at 715.5 eV are the characteristics of Fe^{2+} .⁵¹ To the best of our knowledge, the principal features of the Fe 2p-spectra are two maxima reflecting the Fe 2p_{3/2} and Fe 2p_{1/2} electron levels. **Figure 5(e)** shows the XPS spectra of Fe 2p and the deconvoluted peaks. Extraordinary broad peak assigned to 2p_{3/2} core levels is observed. The peak of high spin Fe^{3+} ions is broadened significantly compared to Fe^0 and low spin Fe^{2+} state. This broadening is explained by the electrostatic interaction and spin orbit coupling between the 2p core hole and unpaired 3d electrons of the iron ions and crystal field splitting of the 3d orbital into t_{2g} and e_g level.⁵² By fitting the peaks for the valence state of Fe ions, the ratio of Fe^{2+}/Fe^{3+} in the $SrFeO_{3-x}$ is calculated as 1:3.5, which is similar to the previous report.⁵³ The asymmetric O 1s peak shown in **Figure 5(f)** can be split by using the XPS peak-fitting program. The peak at 532.2 eV is assigned to the external $-OH$ group or the water molecule adsorbed on the surface, and the other O 1s peak appearing at 530.8 eV corresponds to lattice oxygen atoms in the $SrFeO_{3-x}$.⁵⁴

3.1.4 Optical absorption properties

As shown in **Figure S9-S10** and **Table S1** of ESI[†], the absorption edge of the pure $g-C_3N_4$ is at about 464.4 nm, which originates from its band gap of ~ 2.67 eV and is consistent with the reported results.⁵⁵ As for the as-prepared $SrFeO_{3-x}$ sample, it clearly exhibits a wide and strong light absorption in the whole UV–vis range of 200–800 nm, which is related to its excellent photocatalytic activity.^{56,57} After the introduction of $SrFeO_{3-x}$ particles on the surface of $g-C_3N_4$, the absorption intensity of these composites is stepwisely strengthened with increasing $SrFeO_{3-x}$ mass ratios. The E_g value of $SrFeO_{3-x}/g-C_3N_4$ is determined from a plot of $(ah\nu)^{1/2}$ vs energy ($h\nu$), which is calculated as 2.54–2.67 eV (**Table S1**). The results suggest that the fabrication of the heterostructured $SrFeO_{3-x}/g-C_3N_4$ can greatly improve the

optical absorption property and increase the utilized efficiency of solar light, which are favorable for the enhancement of the photocatalytic activity.



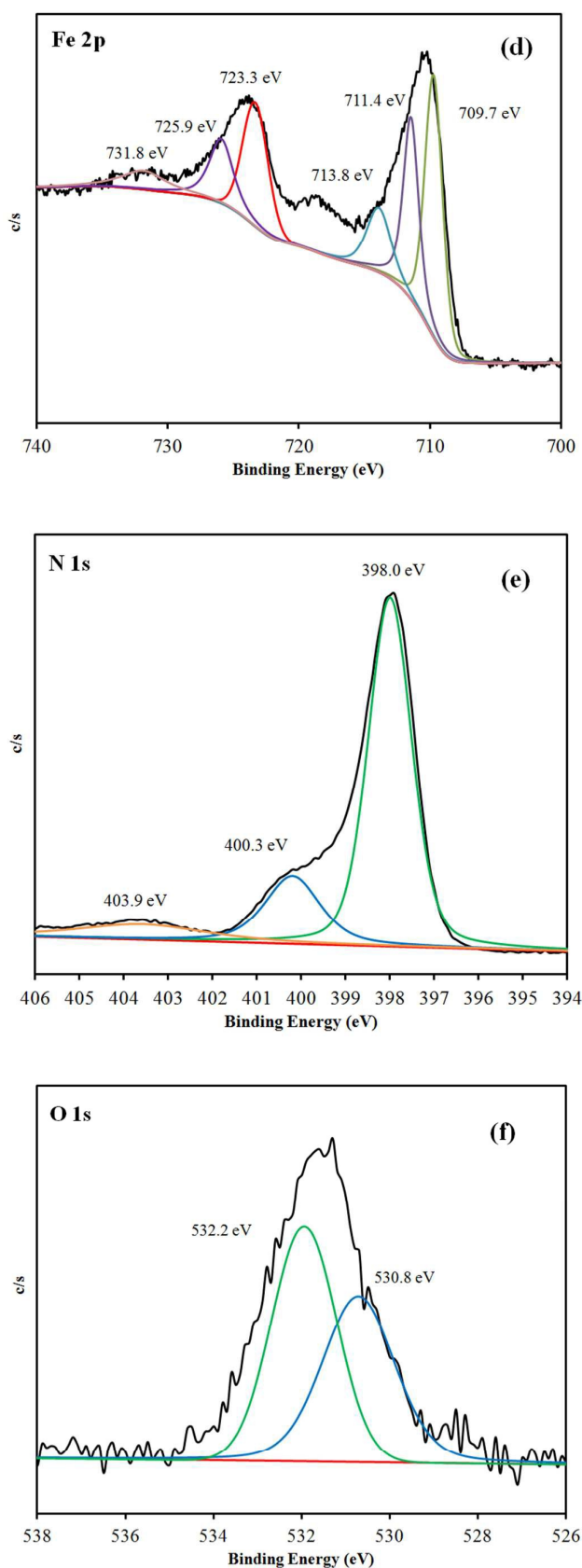


Figure 5. High resolution XPS spectra of the SrFeO_{3-x} , $\text{g-C}_3\text{N}_4$, and $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ composite: (a) Total survey, (b) C 1s, (c) N 1s, (d) Sr 3d, (e) Fe 2p, and (f) O 1s.

3.1.5 Magnetism

Some solid magnetic photocatalysts containing ferrites are convenient to be separated from the reaction solution by a magnet.⁵⁸ Magnetic hysteresis measurement for $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ heterojunction is carried out in applied magnetic field at room temperature, with the field sweeping from -15 to 15 kOe. The hysteresis loop (**Figure 6**) of the sample does not reach saturation up to the maximally applied magnetic field. The magnetization measurement of the sample exhibits a hysteretic feature with the remanent magnetization (M_r) and coercivity (H_c) being determined to be 0.116 emu/g and 1892 Oe, respectively, suggesting that the $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ heterojunction exhibits ferromagnetic behaviors at room temperature. This suggests that $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ photocatalyst can be easily separated from the solution phase using an external magnet.

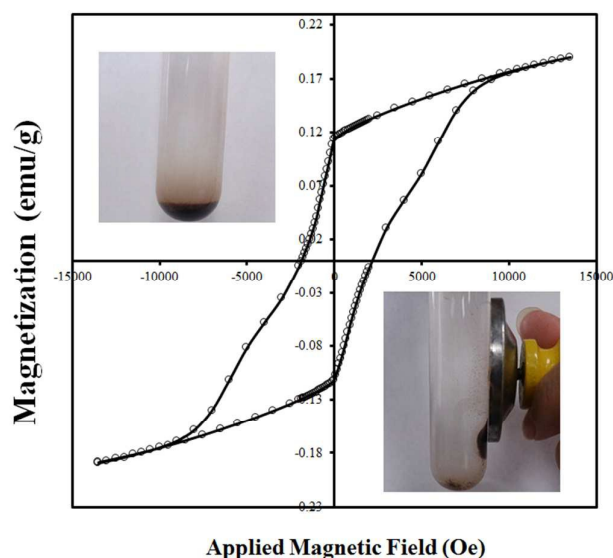


Figure 6. Hysteresis loop of 4 wt%-500-2 sample measured at 298 K.

3.1.6 Adsorption-desorption isotherm

Figures S11-S12 of ESI[†] show the nitrogen adsorption-desorption isotherm curves of SrFeO_{3-x} , $\text{g-C}_3\text{N}_4$, and 4wt% $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$. The isotherms of all the samples are close to Type IV with a hysteresis loop at a high relative pressure between 0.6 and 1.0.⁵⁸ The shape of the hysteresis loop is close to Type H3, suggesting the existence of slit-like pores generally formed by the aggregation of plate-like particles, which is consistent with the self-assembled nanoplate-like morphology of samples. This result is consistent with the FE-SEM results, showing that self-assembled nanosheets or nanoplates result in the formation of 3D hierarchical architectures.

3.2 Photocatalytic Activity

3.2.1 UV-vis spectra

The changes in the UV-vis spectra during the photodegradation of CAP and CV in aqueous dispersions of 4wt% $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ under visible-light irradiation are

illustrated in **Figure 7(a)(c)**. After visible-light irradiation for 96 h, ca. 91.3% of the CAP is decomposed; and, after irradiation for 12 h, ca. 99.9% of the CV is degraded. During visible light irradiation, the characteristic absorption band of the CAP around 278 nm decreases rapidly, but no new absorption band appears even in ultraviolet range ($340 \text{ nm} > \lambda > 200 \text{ nm}$), indicating that there might be the cleavage of phenyl structure of the CAP.⁵⁹ During visible light irradiation, the characteristic absorption band of the CV dye around 588 nm decreases rapidly with slight hypsochromic shifts (555 nm), but no new absorption band appears even in ultraviolet range ($\lambda > 200 \text{ nm}$), indicating that there might be the formation of a series of *N*-de-methylated intermediates and cleavage of the whole conjugated chromophore structure of the CV dye. Further irradiation causes the decrease of absorption band at 555 nm, but no further wavelength shift is observed, inferring that the band at 555 nm is that of the full *N*-de-methylated product of the CV dye.

3.2.2 Degradation efficiency

The degradation efficiency as a function of reaction time is illustrated in **Figure 7(b)(d)** and **Figure S13-S14** of ESI[†]; the removal efficiency is significantly enhanced in the presence of 4wt% SrFeO_{3-x}/g-C₃N₄. After irradiation for 24 h, 4wt% SrFeO_{3-x}/g-C₃N₄ exhibits a superior photocatalytic performance, with a CAP (or CV) removal efficiency up to 97 (or 95)%. To further understand the reaction kinetics of CV degradation, the apparent pseudo-first-order model expressed by $\ln(C_0/C) = kt$ equation is applied in the experiments.⁶⁰ Via the first-order linear fit of the data shown in **Figure 7(a)**, the *k* value of 4wt% SrFeO_{3-x}/g-C₃N₄ is obtained as the maximum degradation rate of $9.97 \times 10^{-1} \text{ h}^{-1}$ using the first-order linear fit of the data, which is much higher than that of the other composites; the 4wt% SrFeO_{3-x}/g-C₃N₄ composite is a much more effective photocatalyst than the others synthesized in this study. **Figures 7(c)** shows the photocatalytic efficiency of SrFeO_{3-x}/g-C₃N₄ composites and mechanically mixed SrFeO_{3-x} with g-C₃N₄ samples. The photocatalytic efficiency of SrFeO_{3-x}/g-C₃N₄ composites significantly increases compared with that of the mechanically mixed sample (SrFeO_{3-x}+g-C₃N₄). Degradation of CAP using TiO₂/g-C₃N₄ composite as catalyst has been studied by several researchers.^{10,12} The disappearance of the organic molecule follows approximately a pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. It was observed that, with P-25 TiO₂ as photocatalyst, quantitative degradation of the organic molecule occurs after 4 h of illumination. However, the previous works are based on the efficiencies and kinetics by changing the parameters and does not consider the various degradation products formed and mechanisms on photocatalytic degradation of CAP. The photocatalytic activity of SrFeO_{3-x}/g-C₃N₄ composites reaches the maximum rate constant of $9.97 \times 10^{-1} \text{ h}^{-1}$, 4.8 times higher than that of g-C₃N₄, 2.0 times higher than that of TiO₂.

3.2.3 Brunauer-Emmett-Teller (*S*_{BET})

The 4wt% SrFeO_{3-x}/g-C₃N₄ composite has larger *S*_{BET} and pore volume (**Table S1** of ESI[†]). However, the result of **Table S1** shows that the 8wt% SrFeO_{3-x}/g-C₃N₄ sample—which shows the highest *S*_{BET}—does not represent the highest photocatalytic activity among the samples, suggesting that the changes in the photocatalytic activity is resulted from both the *S*_{BET} and SrFeO_{3-x}/g-C₃N₄ composites (or heterojunctions). Therefore, the 4wt% SrFeO_{3-x}/g-C₃N₄ composite shows the best photocatalytic activity. Thus, the SrFeO_{3-x}/g-C₃N₄ composites (or heterojunctions) may also play a role in enhancing the photocatalytic activity.

3.2.4 Ion chromatography

The concentrations of Cl⁻, NO₃⁻ and NO₂⁻ were confirmed using ion chromatography (IC), based on their retention times. An alternative approach for tracking the progress of irradiation time with/without photocatalyst is to monitor the Cl⁻, NO₃⁻ and NO₂⁻ formed in the solution (**Figure S15** of ESI[†]). IC analysis showed an increase in the Cl⁻, NO₃⁻ and NO₂⁻ concentrations at various irradiation times as the photocatalytic and photolysis method progressed. These results indicated initially that Cl⁻, NO₃⁻ and NO₂⁻ were gradually produced by irradiation as the time gradually increased. The higher the irradiation time was, the higher the Cl⁻, NO₃⁻ and NO₂⁻ content of the products was. Finally, these ions in the products were fully formatted, resulting in the degradation of CAP under irradiation conditions.

3.2.5 Photoluminescence

As is known, the photocatalysts are excited to generate electron–hole pairs directly after the illumination in the photocatalytic process. Moreover, the photocatalytic efficiency mainly depends on the recombination rate or the lifetime of the photo-generated electron–hole pairs. The faster recombination occurs, the less time is for the chemical reactions. Therefore, PL spectra are utilized for investigating the recombination rate of the photogenerated electron–hole pairs.⁴⁷ To investigate the separation capacity of the photogenerated carriers in the heterostructures, the PL spectra of g-C₃N₄, SrFeO_{3-x}, and 2-6wt% SrFeO_{3-x}/g-C₃N₄ are measured; the results are shown in **Figure 8**. A strong emission peak around 483 nm appears for the as-prepared samples, which could have been derived from the direct electron–hole recombination of band transitions. However, the characteristic emission peak around the lowest intensity 483 nm for the 4wt% SrFeO_{3-x}/g-C₃N₄ indicates that the recombination of photogenerated charge carriers is greatly inhibited. The efficient separation of charge could increase the lifetime of charge carriers and enhance the efficiency of interfacial charge transfer to the adsorbed substrates, thus improving the photocatalytic activity.⁶¹ The lowest relative PL intensities of 4wt% SrFeO_{3-x}/g-C₃N₄ composites, as shown in **Figures 8**, suggest that they possess the lowest

recombination rate of electron-hole pairs, resulting in their higher photocatalytic activity, as shown in **Figure 7**.

3.2.6 Durability of photocatalyst

It can be assumed that the enhanced photocatalytic activities of SrFeO_{3-x}/g-C₃N₄ material could be ascribed to a synergistic effect, including high BET surface area, the formation of the heterojunction, layered structure, and the low energy band structure. In the absence of photocatalysts, CV could not be degraded under visible-light irradiation; the superior photocatalytic ability of 4wt% SrFeO_{3-x}/g-C₃N₄ may be ascribed to its efficient utilization of visible light and high separation efficiency of the electron-hole pairs within its composites.

The durability of the 4wt% SrFeO_{3-x}/g-C₃N₄ composite is evaluated by recycling the used catalyst. After each cycle, the catalyst is collected by centrifugation. No apparent loss is observed in the photocatalytic activity when CV is removed in the 3rd cycle; even during the sixth run, the decline in the photocatalytic activity is 5% (**Figure 9(a)**). The used 4wt% SrFeO_{3-x}/g-C₃N₄ is also examined by XRD and no detectable difference is observed between the as-prepared and the used samples (**Figure 9(b)**); hence, the 4wt% SrFeO_{3-x}/g-C₃N₄ composite has good photostability.

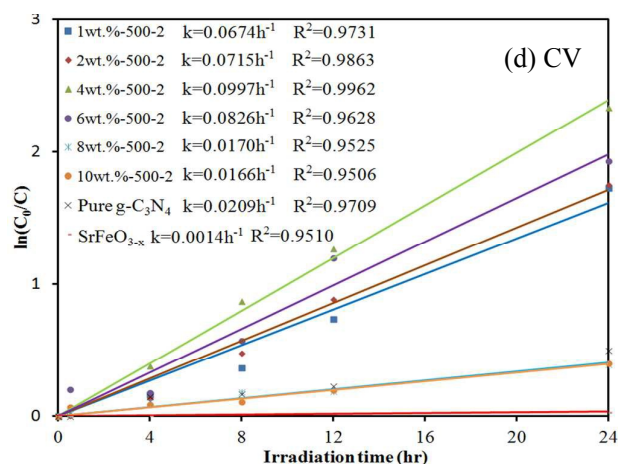
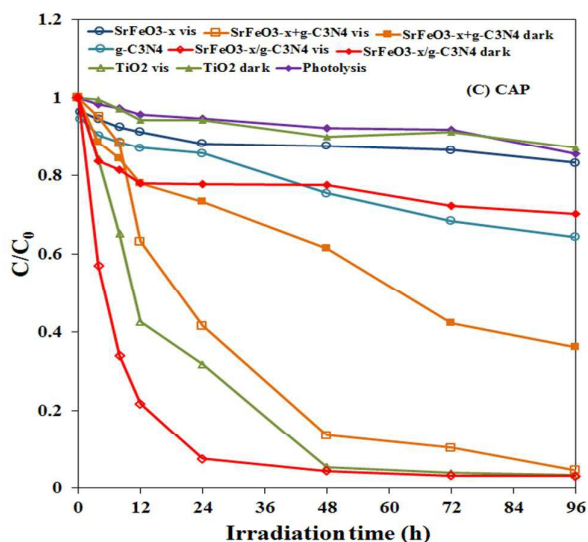
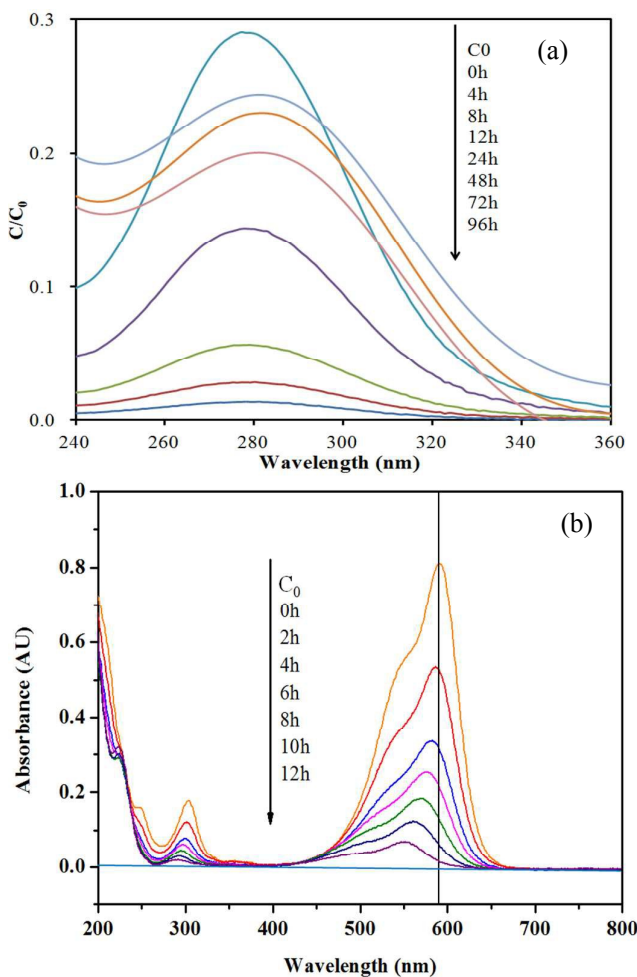


Figure 7. Temporal UV-vis adsorption spectral changes during the photocatalytic degradation of (a) CAP and (b) CV and photocatalytic degradation of (a) CAP and (b) CV as a function of irradiation time over aqueous SrFeO_{3-x}/g-C₃N₄ under visible light irradiation.

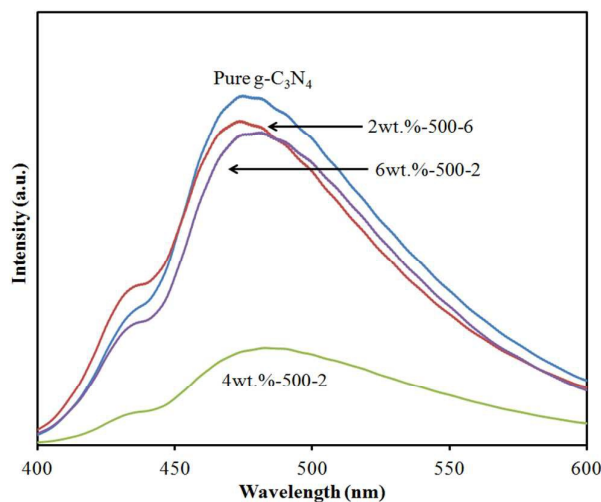


Figure 8. Photoluminescence spectra of 2wt.%-500-2, 4wt.%-500-2, 6wt.%-500-2, and g-C₃N₄.

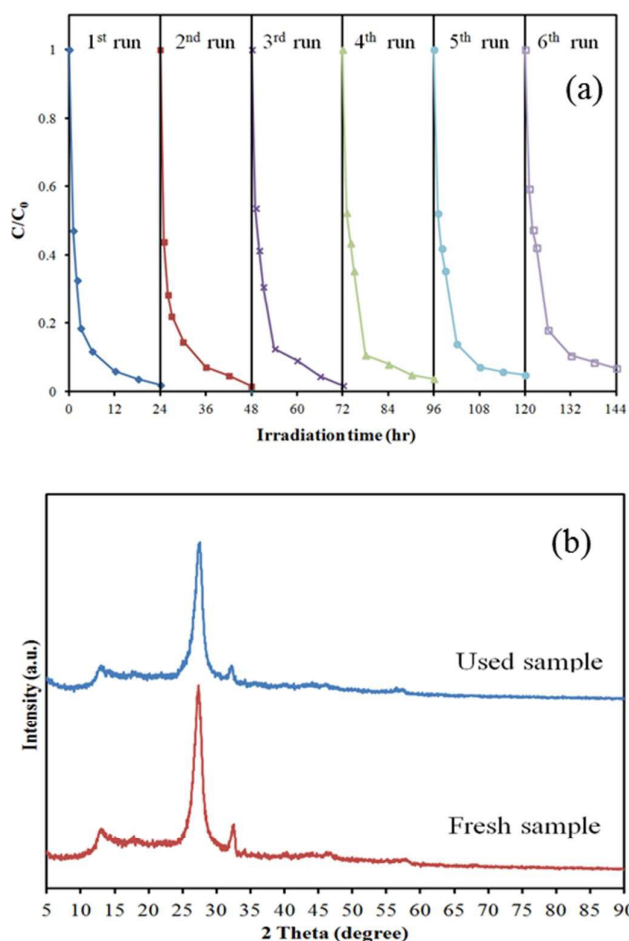


Figure 9. (a) Cycling runs and (b) XRD patterns acquired before and after the photocatalytic degradation of CAP in the presence of $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$.

3.3 Photodegradation Mechanisms of CAP

In general, three possible reaction mechanisms are proposed to be involved in the photodegradation of organics by a semiconductor, including (i) photocatalysis, (ii) photolysis, and (iii) dye photosensitization.⁶² In the photolysis process, a photoinduced electron on the induced organics directly reacts with O_2 to produce a singlet oxygen atom that acts as an oxidant for the pure organic's photolysis.⁶³ In the experiments, CAP degradation caused by photolysis under visible light in a blank experiment is not observable; CAP is a structure-stable dye and the decomposition by the photolysis mechanism is negligible.

As is known to all, various primary reactive species, such as HO^\bullet , h^+ , $\text{O}_2^{\bullet-}$, H^\bullet and $^1\text{O}_2$, could be generated during photocatalytic degradation processes in the UV-vis/semiconductor systems.^{17,18,64-66} In earlier study, CV photodegradation by $\text{BiO}_m\text{X}_n/\text{BiO}_p\text{X}_q$ ($X, Y = \text{Cl}, \text{Br}, \text{I}$) under visible light is dominated by $\text{O}_2^{\bullet-}$ oxidation being the main active species and $^\bullet\text{OH}$ and h^+ being the minor active species.¹⁶⁻¹⁸ Xiao *et al.* revealed that high-efficiency visible light driven bisphenol-A removal with BiOCl/BiOI could

attribute to effective separation and transfer of photoinduced charge carriers in BiOCl/BiOI with narrower band gap and more negative conduction band position, which favored the photogenerated holes.⁶³ Yu's group reported $^\bullet\text{OH}$ and h^+ being two main actives in the whole degradation process.⁶⁷ Shenawi-Khalil *et al.* reported that $^\bullet\text{OH}$ radical was generated by multistep reduction $\text{O}_2^{\bullet-}$.⁶⁸ The generation of $\text{O}_2^{\bullet-}$ could not only inhibit the recombination of photoinduced charge carriers, but also benefit the de-chlorination of chlorinated phenol derivative. The hydroxyl radical HO^\bullet might only be formatted via an $\text{e}^- \rightarrow \text{O}_2^{\bullet-} \rightarrow \text{H}_2\text{O}_2 \rightarrow ^\bullet\text{OH}$ route. Meanwhile, $^\bullet\text{OH}$ radical was formatted by multistep reduction $\text{O}_2^{\bullet-}$ in the system.¹⁷ Zhu *et al.* reported that photocatalytic experiments in the presence of N_2 and the radical scavenger suggested $\text{O}_2^{\bullet-}$ and $^\bullet\text{OH}$ being two main actives in the photocatalytic degradation process.⁶⁹ Dimitrijevic *et al.*⁶² proposed that the water, both dissociated on the surface of TiO_2 and in subsequent molecular layers, had a three-fold role of (i) stabilization of charges, preventing electron-hole recombination, (ii) an electron acceptor, the formation of H atoms in a reaction of photo-generated electrons with protons on the surface, $-\text{OH}_2^+$, and (iii) an electron donor, the reaction of water with photo-generated holes to give $^\bullet\text{OH}$ radicals. According to earlier studies,⁶⁷ the dominant active oxygen species generated in direct oxidation and photocatalytic reactions were $^1\text{O}_2$ and $^\bullet\text{OH}$ radical, respectively. Besides, in this visible light-induced semiconductor system, hydroxylated compounds were also identified for the photocatalytic degradation of CV.^{17,18} On the basis of the references presented above, it is proposed that the probability of forming $^\bullet\text{OH}$ should be much lower than that for $\text{O}_2^{\bullet-}$; however, $^\bullet\text{OH}$ is an extremely strong and nonselective oxidant, which leads to the partial or complete mineralization of several organic chemicals.

3.3.1 Electron paramagnetic resonance

From **Figure 10(a)-(b)**, not only the four characteristic peaks of DMPO- $^\bullet\text{OH}$ adducts (1:2:2:1 quartet pattern) are observed, but also the six characteristic peaks of the DMPO- $\text{O}_2^{\bullet-}$ adducts are observed under visible light irradiated 4wt% $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ dispersion. **Figure 10(a)(b)** indicates that no EPR signals are observed when the reaction is performed in the dark, while the signals with intensity corresponding to the characteristic peak of DMPO- $^\bullet\text{OH}$ and DMPO- $\text{O}_2^{\bullet-}$ adducts⁷⁰ are observed during the reaction process under visible light irradiation, and the intensity gradually increases with the prolonged reaction time, suggesting that $\text{O}_2^{\bullet-}$ and $^\bullet\text{OH}$ as major active species are formed in the presence of 4wt% $\text{SrFeO}_{3-x}/\text{g-C}_3\text{N}_4$ and oxygen under visible light irradiation.

3.3.2 Quenching effect

In order to evaluate the effect of the active species during the photocatalytic reaction, a series of quenchers are introduced to scavenge the relevant active species. As shown in **Figure 10(c)**, indicating that $^1\text{O}_2$ can be negligible,

whereas $O_2^{\cdot-}$, $\cdot OH$, and h^+ are important active species in the process of photocatalytic degradation for CAP. Therefore, the quenching effects of different scavengers and EPR display that the reactive $O_2^{\cdot-}$ and $\cdot OH$ play the major role and h^+ plays the minor role in the CAP of the photocatalytic degradation.

3.3.3 Scheme for electron-hole separation

The structure characterizations have proven that the $SrFeO_{3-x}/g-C_3N_4$ photocatalyst is a two-phase composite. Considering that the composite presents much higher photocatalytic activity than the component phase alone, it is reasonable that there might have synergetic effect between $SrFeO_{3-x}$ and $g-C_3N_4$. Actually, many researchers have noted the synergetic effect in composite systems consisting of two semiconductors in contact,^{71,72} and attributed the effect to the efficient charge transfer at the interface of two semiconductors, which would result in an effective photoexcited electron-hole separation and, consequently, enhance the photocatalytic activity. The driving force of charge transfer originates from the matching band potentials. Therefore, the suitable band potential is the precondition for the synergetic effect of composite photocatalysts. **Figure 11** shows the type-II heterostructure band alignment⁷² and valence-band (VB) XPS spectrum of $SrFeO_{3-x}$ and $g-C_3N_4$. In **Figure 11**, the position of CB and VB of semiconductor $g-C_3N_4$ is both higher than that of semiconductor $SrFeO_{3-x}$, and the steps in the CB and VB go in the same direction. The position of the valence band edge of $g-C_3N_4$ is located at about 1.50 eV, consistent with the result of Li *et al.*⁷³ For $SrFeO_{3-x}$, the VB edge is determined to be 2.05 eV. Therefore, it is obvious that the $SrFeO_{3-x}$ and $g-C_3N_4$ exhibit suitable band potential. The photoinduced electrons on the $g-C_3N_4$ particle surface can easily transfer to $SrFeO_{3-x}$ via the interfaces, while the holes on the $SrFeO_{3-x}$ surface can migrate to $g-C_3N_4$ in a similar manner. The charge transfer effectively retards the recombination of electron-hole pairs in the two semiconductors and, thereby improves the photocatalytic efficiency.

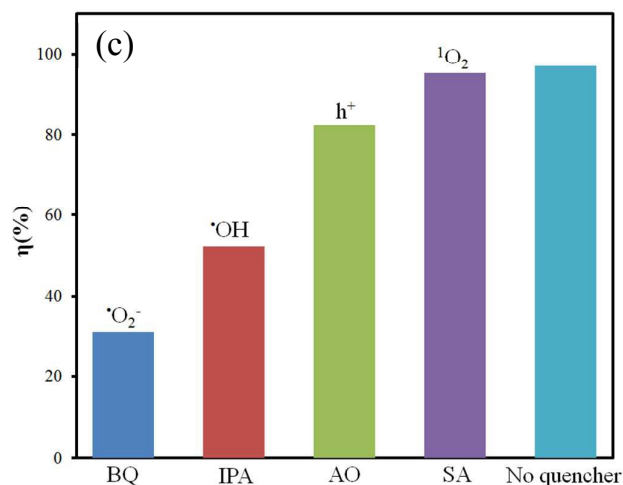
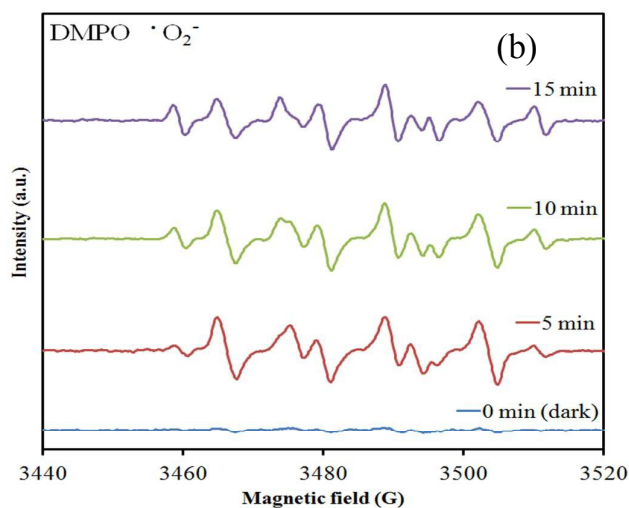
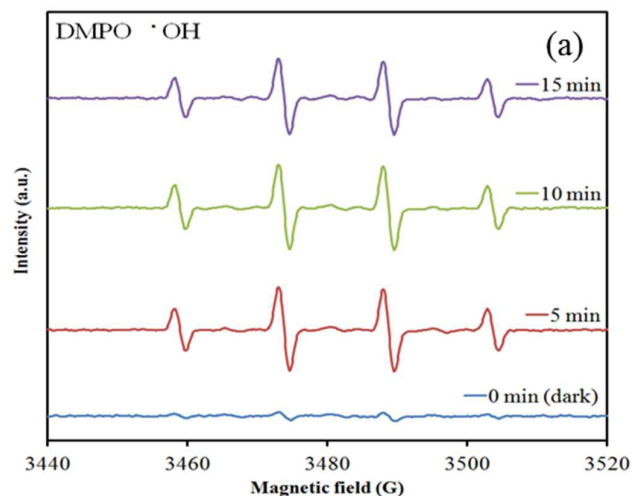


Figure 10. (a) (b) DMPO spintrapping EPR spectra for $DMPO-O_2^{\cdot-}$ and $DMPO-\cdot OH$ under visible light irradiation with $SrFeO_{3-x}/g-C_3N_4$ photocatalyst. (c) The dye concentration during photodegradation as a function of irradiation time observed in $SrFeO_{3-x}/g-C_3N_4$ photocatalyst under the addition of different scavengers of SA, IPA, AQ, and BQ.

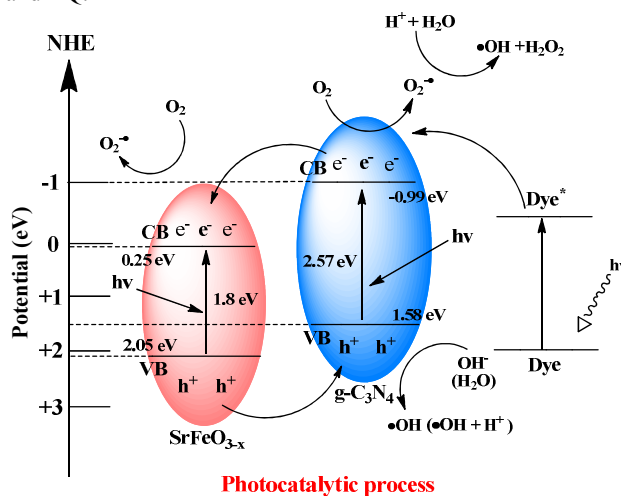


Figure 11. The band structure diagram of SrFeO_{3-x}/g-C₃N₄ and the possible charge separation processes.

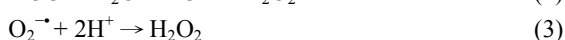
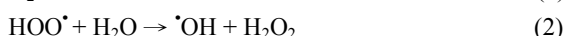
3.4 Photodegradation of CAP

3.4.1 Separation and identification of intermediates

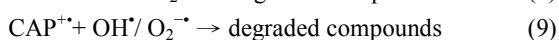
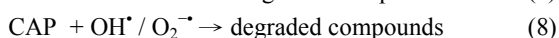
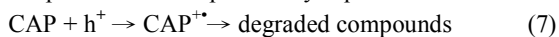
So as to get better understanding on the products and the mechanistic details of the photocatalytic degradation of CAP in aqueous g-C₃N₄/SrFeO_{3-x} suspensions under visible light irradiation, the technique of HPLC-PDA-ESI-MS is used for separating the photo-decomposed products and intermediates. According to chromatograms, the CAP and its related intermediates in **Figure 12** can be identified.

As shown in **Figure 12**, the ES⁻ mass spectral analyses confirm the components **1** (m/z = 150), **2** (m/z = 166), **3** (m/z = 291), **4** (m/z = 138), **5** (m/z = 321), **6** (m/z = 337), **7** (m/z = 154), **8** (m/z = 122), **10** (m/z = 127), and the ES⁺ mass spectral analyses confirm the components **5** (m/z = 323), **6** (m/z = 339), **8** (m/z = 124), **9** (m/z = 138), **11** (m/z = 181), **12** (m/z = 211), **13** (m/z = 241) in **Figure S16** of ESI[†] and **Table 2**. **Table 2** shows the λ_{max} of UV-visible spectra for peaks 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 being 286.5, 262.8, 316.3, 318.7, 274.6, 271.1, 355.8, 297.2, 286.5, 267.5, 287.7, respectively, and it corresponds to the TIC spectra by retention time. Based on the above experimental results, 12 intermediate products are identified.^{60,74} The intermediate product analyses and structures are depicted in **Tables 2 and Table S2** of ESI[†].

Fan *et al.* reported⁷⁵ that Pt-TiO₂ gathered less negative species on catalyst surfaces, which deteriorated reaction rates, than pure TiO₂ did in an acidic environment. The ·OH radical is subsequently produced. The ·OH radical is produced subsequently, as also shown in eqs.1-6.



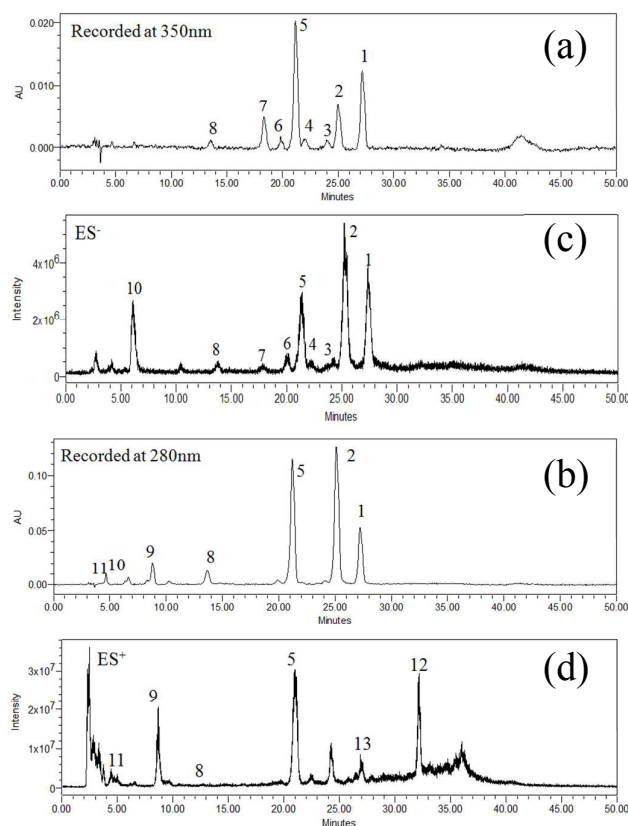
These cycles continuously happen when the system is exposed to visible-light irradiation;^{17,18} after several cycles of photo-oxidation, the degradation of CAP by the generated oxidant species can be expressed by Eqs.7-9:



On the basis of above experimental results, a detailed mechanism of degradation is illustrated in **Figure 13**.

Table 2. The degraded intermediates of CAP by photocatalytic degradation process.

Peak no.	MW	λ _{max} , nm	t _R (ES ⁻)	[M-H] ⁻	t _R (ES ⁺)	[M+H] ⁺
1	151	286.5	27.3	150	--	--
2	167	262.8	25.3	166	--	--
3	292	316.3	23.7	291	--	--
4	139	318.7	22.3	138	--	--
5(CAP)	322	274.6	21.4	321	21.5	323
6	338	271.1	20.2	337	20.1	339
7	155	355.8	17.9	154	--	--
8	123	297.2	13.8	122	13.8	124
9	137	286.5	--	--	09.0	138
10	128	267.5	05.6	127	--	--
11	180	287.7	--	--	05.6	181
12	210	--	--	--	27.5	211
13	240	--	--	--	32.6	241



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Figure 12. HPLC chromatogram, recorded at (a) 350nm, (b) 280nm, and (c) (d) total ion chromatogram of the degraded intermediates of CAP at different irradiation intervals with SrFeO_{3-x}/g-C₃N₄ photocatalyst.

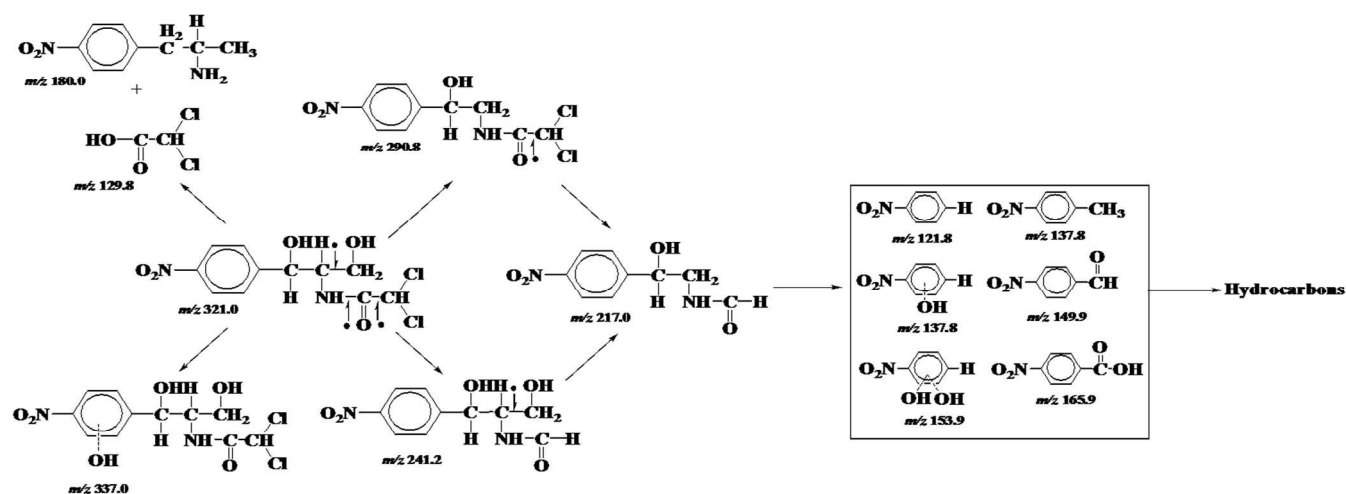


Figure 13. Proposed photodegradation mechanism of the CAP.

4. Conclusions

This is the first report on a series of SrFeO_{3-x}/g-C₃N₄ heterojunctions. The removal efficiency is significantly enhanced in the presence of 4wt% SrFeO_{3-x}/g-C₃N₄. The increased photocatalytic activities of SrFeO_{3-x}/g-C₃N₄ could be attributed to the formation of the heterojunction between SrFeO_{3-x} and g-C₃N₄, which effectively suppresses the recombination of photo-induced electron-hole pairs. It can be assumed that the enhanced photocatalytic activities of SrFeO_{3-x}/g-C₃N₄ materials could be ascribed to the formation of the heterojunction. O₂⁻ and [•]OH are main and h⁺ is minor active species in the whole process. The reaction mechanisms proposed in this study should offer some useful insight into the future development of technological applications.

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