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ARTICLE TYPE

# Photocatalytic and photoelectrochemical studies of Visible-light active $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites

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Nanocrystalline hematite iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) were prepared and used as precursors to synthesise  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts of various compositions by wet impregnation method. The synthesized photocatalysts were characterized by x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), UV-vis diffuse reflection spectroscopy (DRS) and photoluminescence spectroscopy (PL). The efficiency of the photocatalysts was evaluated by photoelectrochemical measurements and photodegradation of direct red 81 (DR81) as a target textile pollutant under visible light irradiation. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composites exhibited remarkably improved visible-light induced photocatalytic activity. The composite photocatalysts with optimal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> content with the highest photocatalytic activity was found to be 2%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub>. The synergistic enhancement in the photocatalytic degradation of composite photocatalysts might be due to an increase in the visible-light absorption efficiency and rapid photoinduced charge separation. A possible photocatalytic mechanism has been proposed for the photocatalytic activity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts.

## 1. Introduction

Semiconductor photocatalysis has received considerable attention in the areas of environmental remediation and energy storage, as it uses abundantly available solar energy.<sup>1</sup> The essential requirements of a photocatalyst is that it should be stable, inexpensive and capable of harvesting light in the visible region.<sup>2</sup> The main factor that lowers the efficiency of a photocatalyst is the recombination rate of photo-generated electron-hole pairs.<sup>3,4</sup> Therefore, enormous effort has been made on the development of an efficient catalytic material for harvesting solar energy for photocatalytic degradation. Over the past few decades, various semiconductor materials such as metal oxides,<sup>5,6</sup> sulphides<sup>7,8</sup> and oxynitrides<sup>9</sup> have been identified as efficient photocatalysts for the degradation of toxic pollutants in water. Among the semiconductor materials, TiO<sub>2</sub> is the most widely used one because of its excellent catalytic activity, non-toxicity and stability. However, what greatly limits its practical application is its poor absorption in the visible region of the solar spectrum.<sup>10</sup>

More recently, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) material has been widely used as a metal-free visible light active photocatalyst. g-C<sub>3</sub>N<sub>4</sub> has been extensively explored for the photocatalytic evolution of H<sub>2</sub> and O<sub>2</sub>,<sup>11</sup> photodegradation of organic pollutants,<sup>12</sup> biomedical applications<sup>13</sup> and photocatalytic organic synthesis.<sup>14</sup> Nevertheless, a relatively low photocatalytic efficiency of pure g-C<sub>3</sub>N<sub>4</sub> still limits its practical application due to the high recombination rate of photo-generated electron-hole pairs.<sup>1</sup> To resolve this problem and improve its photocatalytic

performance, several methods have been developed, viz., doping of metals,<sup>15</sup> combining with other semiconductor material to form a composite photocatalyst<sup>16</sup> and sensitizing with organic dyes.<sup>17</sup> The combination of two semiconductors with different energy level may form an ideal system to cause a rapid charge separation and reduced recombination rate of photoinduced electron-hole pairs.<sup>18</sup> Very recently, remarkable progress has been made in the synthesis of composite photocatalysts. For example, g-C<sub>3</sub>N<sub>4</sub>-Fe<sub>3</sub>O<sub>4</sub>,<sup>2</sup> SiO<sub>2</sub>/carbon nitride,<sup>3</sup> Ag<sub>2</sub>O-g-C<sub>3</sub>N<sub>4</sub>,<sup>15</sup> Ni(OH)<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub>,<sup>19</sup> g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub>,<sup>20</sup> Co<sub>3</sub>O<sub>4</sub>-g-C<sub>3</sub>N<sub>4</sub><sup>21</sup> and PANI-g-C<sub>3</sub>N<sub>4</sub><sup>22</sup> have been shown to exhibit high visible light photocatalytic activities than pure g-C<sub>3</sub>N<sub>4</sub>.

Ye et al.<sup>23</sup> synthesised Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> from the precursor, melamine. In the present investigation, we have synthesised  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposite photocatalyst by a simple and low-cost method. Urea was chosen as a precursor for the synthesis of g-C<sub>3</sub>N<sub>4</sub> because it is a low-cost raw material.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was synthesized using citrate route.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is an emerging material due to its superior properties such as high electrical conductivity and magnetic activity.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has high absorption (around 43%) in the red region of visible light in solar spectrum.<sup>25</sup> These properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> makes it as a good candidate for coupling with g-C<sub>3</sub>N<sub>4</sub> and improving its catalytic activities for the photodegradation of aqueous organic pollutants. Direct red 81 (DR81) was chosen for this study due to its harmful nature. DR81 is commonly used in the textile, leather, plastics and cosmetics industries to colour their products. These industries produce large volume of colored dye effluents which are toxic, non-biodegradable and cause a significant damage to the environment.

A series of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composites with different mole percent of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were successfully synthesized and their visible light photocatalytic performances were evaluated for the photodegradation of DR81. A possible photocatalytic degradation mechanism has been proposed.

## 2. Experimental section

### 2.1 Materials

Urea, sodium sulphate and methanol were purchased from SDFCL India. Ferric nitrate nanohydrate was purchased from Qualigens India. Citric acid was obtained from Rankem India. Direct red 81 and demineralised water used in the experiments was purchased from Sigma-Aldrich and nice chemicals India, respectively. All reagents were of analytical grade and used without further purification.

### 2.2 Synthesis of photocatalysts

Ferric nitrate nanohydrate and citric acid (1:3 mole ratio) was dissolved in deionised water. The resulting solution was continuously stirred and subsequently dried at 95 °C. The obtained precipitate was heated in air atmosphere at 450 °C for 2 hours to produce  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. g-C<sub>3</sub>N<sub>4</sub> powders were synthesized by urea loaded in an alumina crucible with a cover to prevent sublimation of precursors and heated to 520 °C for 2 hours at a heating ramp of 15 °C/min and the furnace was cooled to room temperature naturally. The yellow colour product was collected and ground into a powder.

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposite photocatalysts were prepared as follows: 0.5 g of g-C<sub>3</sub>N<sub>4</sub> and calculated amount of as-prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were added into 40 mL of methanol in a beaker. Then the beaker was placed in an ultrasonic bath for 15 min. The mixed solution was magnetically stirred at 80 °C. The obtained product after volatilization of the methanol was sintered at 300 °C for 30 min.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composite with different mole ratios 1%, 2% and 3% of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were prepared and are denoted in this manuscript as FOCN-1, FOCN-2 and FOCN-3, respectively.

### 2.3 Characterization of photocatalysts

The synthesized photocatalysts were characterized by powder x-ray diffraction (XRD) method using a powder x-ray diffractometer (Mini Flex II, Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 0.154 nm) at a scan speed of 3°/min. The phase purity was ascertained using x-ray diffraction. The crystalline size was analyzed using Scherrer's equation,  $d = 0.9\lambda / B \cos\theta$ , where  $d$  is the crystallite size,  $\lambda$  is the wavelength of x-ray radiation,  $B$  is the full width half maximum value (FWHM) in radian and  $\theta$  is the diffraction angle. The micro-strain ( $\epsilon$ ) of the photocatalysts were estimated using the  $\epsilon = B/4 \tan\theta$  equation. Fourier transform infrared (FT-IR) spectra were recorded (KBr pellets) with a wavenumber ranging from 4000-400 cm<sup>-1</sup> using an FT-IR (JASCO 460 plus) instrument. The morphology of the products was examined by scanning electron microscopy (SEM) VEGA3TESCAN model. UV-vis diffuse reflectance spectra of the samples were recorded using a Shimadzu 2100 UV-vis

spectrophotometer in the range of 200-800 nm. BaSO<sub>4</sub> was used as the reference. Photoluminescence (PL) measurements were recorded at room temperature using Jobin Yvon Fluorolog-3-11 spectrofluorometer. Radiation source was 450 W xenon lamp.

### 2.4 Photocatalytic activity

The photocatalytic activity of synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites were studied by the photodegradation of direct red 81 (DR81) under visible light irradiation generated by a 100 W tungsten-halogen lamp. In each experiment, calculated amount of photocatalyst was mixed with 75 mL of 5x10<sup>-5</sup> M solution of DR81. Prior to irradiation, the suspensions were magnetically stirred in the dark for 120 min to obtain the equilibrium adsorption of DR81 onto the catalyst. During irradiation 4 mL of aliquots were collected at fixed time intervals and filtered through a 0.45  $\mu$ m membrane syringe filter (Pall Corporation) to remove the photocatalyst particles. The concentration of DR81 was monitored using a UV-vis spectrophotometer at 509 nm.

### 2.5 Photoelectrochemical studies

Photoelectrochemical measurements were performed on a CHI608E electrochemical workstation in a conventional three electrode configuration with a Pt-wire as counter electrode and Ag/AgCl (in saturated KCl) as a reference electrode. A 250 W Xe arc lamp (OSRAM, Germany) was used as the light source. A 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The working electrode was prepared as follows: the 50 mg of photocatalyst was ground with 150  $\mu$ L of PEG (Mol.Wt 400) and 125  $\mu$ L of ethanol to make slurry. The slurry was spread on a 2.5x2.5 cm<sup>2</sup> fluorine-doped tin oxide (FTO) glass substrate with an active area of about 1x1 cm<sup>2</sup> by doctor-blade method using scotch tape as spacer. It was dried in air and then annealed at 350 °C for 45 min.

## 3. Results and Discussion

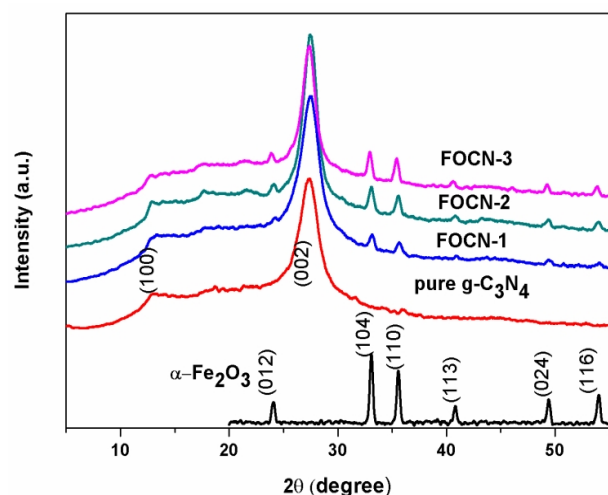
### 3.1 X-ray diffraction studies

The X-ray diffraction (XRD) patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites are shown in Fig. 1. The diffraction peaks of iron oxide synthesized from citrate precursor route at  $2\theta = 24.1^\circ, 33.1^\circ, 36.0^\circ, 40.8^\circ, 49.4^\circ$  and  $54.0^\circ$  are in good agreement with the corresponding (012), (104), (110), (113) (024) and (116) diffraction planes of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS 80-2377).<sup>26</sup> g-C<sub>3</sub>N<sub>4</sub> shows two distinct diffraction peaks observed at  $2\theta = 13.06^\circ$  and  $27.42^\circ$  which are indexed as (100) and (002) diffraction planes of graphitic carbon nitride material (JCPDS 87-1526). These diffraction peaks are in good agreement with earlier report by Ge et al.<sup>22</sup> The high intensity peak at  $27.8^\circ$  is a characteristic inter layer stacking peak of aromatic systems and the weak peak at  $13.2^\circ$  corresponds to the inter-layer structural packing of the tri-s-triazine pores.<sup>27</sup> The XRD patterns of as-synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts consists of both  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> phases, the peak intensities in the composite sample is increased with mass content of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and

it confirms the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composite material.<sup>20, 28</sup> The calculated crystalline size and micro-strain of the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposite materials are summarized in Table 1. It can be seen that the average crystalline size of the synthesised  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> is around 4 to 5 nm and when compare with other composite materials, it is clear that the FOCN-2 showed the lower micro-strain value. The low micro-strain of FOCN-2 indicates the well crystalline nature of FOCN-2 composites.

**Table 1** Crystalline size and micro-strain of the as-synthesized photocatalysts.

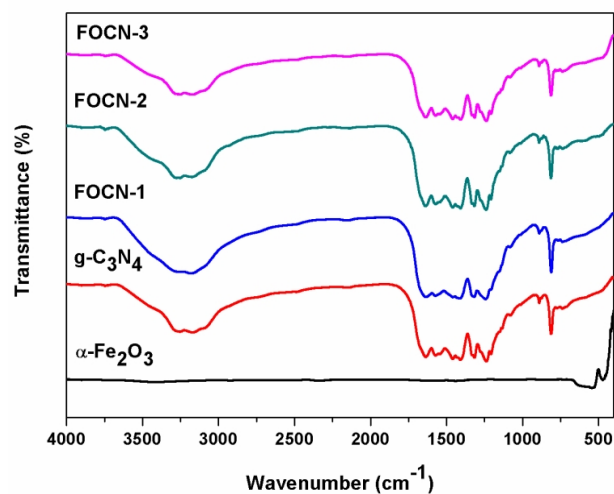
Sample	FWHM	Crystalline size (nm)	Micro-strain
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.276	30.02	0.001089
g-C <sub>3</sub> N <sub>4</sub>	1.902	4.29	0.004418
FOCN-1	1.853	4.41	0.003761
FOCN-2	1.467	5.56	0.002839
FOCN-3	1.408	5.80	0.003178



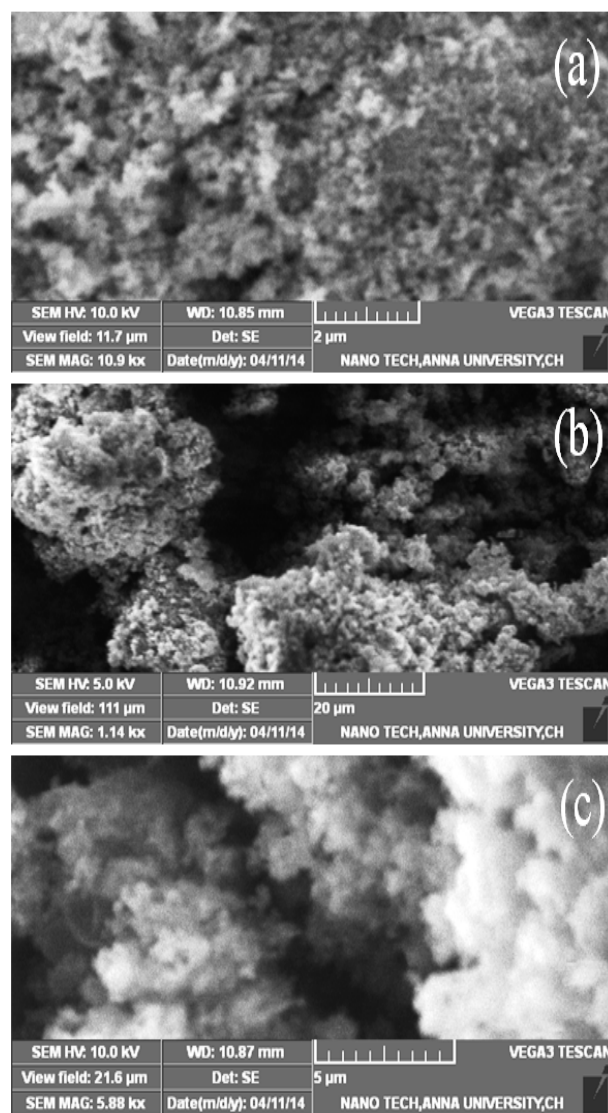
**Fig. 1** XRD patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> photocatalysts.

### 3.2 FT-IR studies

Fourier transform infrared (FT-IR) spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites are shown in Fig. 2. In the FT-IR spectrum of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, absorption bands at 473 cm<sup>-1</sup> and 544 cm<sup>-1</sup> are assigned to Fe-O stretching and bending vibration modes, respectively.<sup>29</sup> In the spectrum of g-C<sub>3</sub>N<sub>4</sub>, the broad band at 3100-3300 cm<sup>-1</sup> can be assigned to the stretching modes of N-H bonds of primary (-NH<sub>2</sub>) and secondary (=N-H) amines suggesting the hydrogenation of some nitrogen atoms in the g-C<sub>3</sub>N<sub>4</sub>.<sup>30</sup> The strong bands at 1200-1680 cm<sup>-1</sup> are attributed to the stretching vibration modes of C-N heterocycles. The peaks at 1638 cm<sup>-1</sup> and 1235 cm<sup>-1</sup> are attributed to the stretching vibration modes of C=N and C-N, respectively.<sup>31</sup> The absorption peaks at 812 cm<sup>-1</sup> corresponds to the characteristic ring breath of the triazine units. Further, the characteristic peaks of both  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> are appeared in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> composite.



**Fig. 2** FT-IR transmittance spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> photocatalysts.



**Fig. 3** Typical SEM photographs of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (b) g-C<sub>3</sub>N<sub>4</sub> and (c) FOCN-2.



The absorption peak intensity of g-C<sub>3</sub>N<sub>4</sub> is decreased slightly while increasing the mole percent of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the composite photocatalyst. The FT-IR results clearly indicate the coexistence of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> in the composite photocatalysts.

### 3.3 SEM and TEM studies

The typical SEM photographs of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and FOCN-2 photocatalysts are presented in Fig. 3(a), (b) and (c), respectively. The SEM micrograph of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles shows an aggregation of nanoparticles. The g-C<sub>3</sub>N<sub>4</sub> shows the aggregated particles containing a large number of irregular smaller crystals. The morphology of FOCN-2 composites clearly shows that the narrower particle distribution on the porous structure of g-C<sub>3</sub>N<sub>4</sub>. The observed larger SEM particle sizes may be attributed to the larger cluster size which formed due to larger surface area of the smaller crystallites. A surface morphology where the composite particles are tightly packed is a benefit for the efficient charge carrier formation.<sup>20</sup> Further, the morphology and particle size of FOCN-2 were explored by TEM and the corresponding images are shown in Fig. 3(d) and (e). TEM images show fine dispersion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the surface of the g-C<sub>3</sub>N<sub>4</sub> and the particle size of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is found to be about 20 nm. Also, the TEM images of composite particles show some agglomeration.

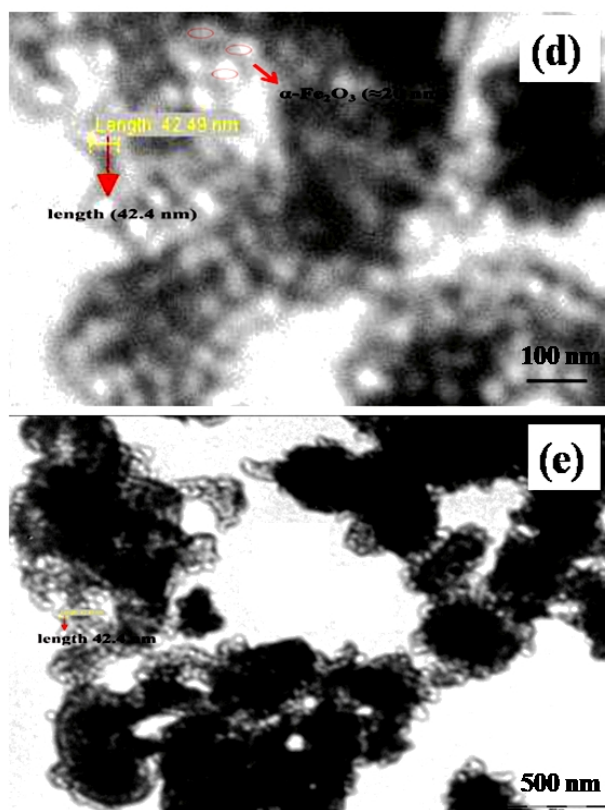


Fig. 3(d-e) TEM images of FOCN-2 photocatalyst particles.

### 3.4 Optical absorption studies

The optical properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposite were investigated by UV-vis diffuse reflectance spectroscopy and are shown in Fig. 4. g-C<sub>3</sub>N<sub>4</sub> sample shows an absorption edge at 461 nm that corresponds to a band gap energy of 2.68 eV. This is in good agreement with the band gap energy reported in the literature.<sup>23</sup> Hence, it can act as a good photocatalyst under visible light irradiation. The absorption edge value for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is observed at 686 nm and the corresponding band gap is estimated to be about 1.80 eV. The absorption edges of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites samples are significantly increased with an increase in the content of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. That is a red shift in the absorption edge on increasing the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> loading and also the powder colour changed from yellowish to light grey. This result implies that the charge-transfer transition between the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> species occurs while adding  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to g-C<sub>3</sub>N<sub>4</sub>. This subsequently indicate that the composite samples could absorb a major portion of light in the visible region to produce electron-hole pairs and that may in-turn lead to high photocatalytic activity of the composite catalysts.

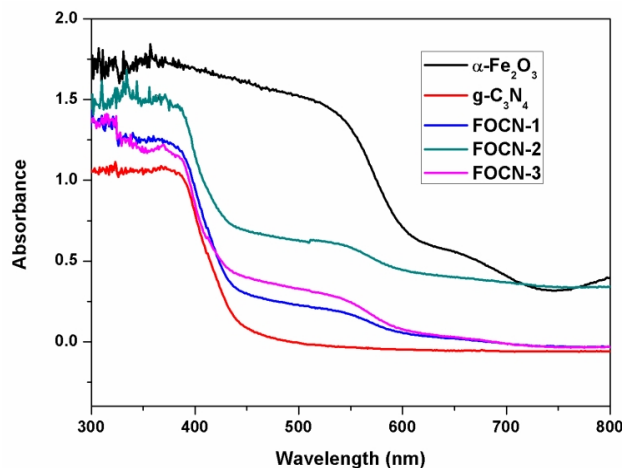
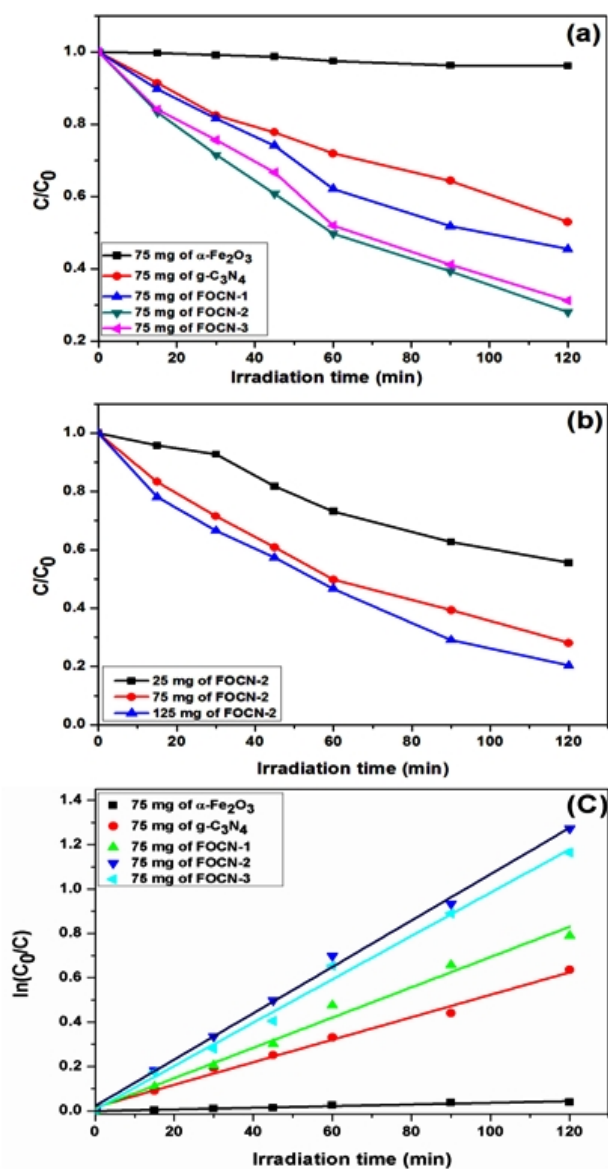


Fig. 4 UV-vis diffuse reflection spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> photocatalysts.

### 3.5 Photocatalytic performance of the $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites

The photocatalytic efficiencies of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites were evaluated using DR81 as a model pollutant under visible irradiation. A blank experiment in the absence of catalyst was carried out for the dye alone ( $5 \times 10^{-5}$  M) under visible light irradiation for 2 hours. There was no significant change in absorbance of DR81 indicating the stable nature of the dye under visible light irradiation. Also, adsorption efficiency of DR81 on the photocatalyst was evaluated in the dark to identify the time taken to reach the adsorption-desorption equilibrium. It was found that the equilibrium between the catalyst and dye was established after 90 min of stirring (results not shown). The photocatalytic activities of g-C<sub>3</sub>N<sub>4</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> nanocomposites with different loading amount (1%, 2% and 3% mole content) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> are shown in Fig. 5(a). No significant



**Fig. 5** (a) Photocatalytic degradation of DR81 over  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$  and  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  photocatalysts under visible light irradiation, (b) Photocatalytic degradation of DR81 over FOCN-2 photocatalyst at different amounts; 0.5 g/L, 1.0 g/L and 1.25 g/L, (c) First-order kinetics plot for the photodegradation of DR81 over  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$  and  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  photocatalysts.

degradation was observed with  $\alpha\text{-Fe}_2\text{O}_3$  alone. Pradhan et al.<sup>25</sup> reported that though  $\alpha\text{-Fe}_2\text{O}_3$  has high absorption in the red region of visible spectrum (around 43 %), its efficiency for the photocatalytic performance is limited due to the charge carrier recombination. However, a significant decrease in the absorbance of the dye is observed when  $\text{g-C}_3\text{N}_4$  is used as a photocatalyst. This is due to the involvement of photo-generated produced electron and hole pairs in the degradation process. It can be seen that  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  composites exhibit much higher photodegradation activities than that of  $\text{g-C}_3\text{N}_4$  and the photocatalytic activity increases remarkably up to 2% increase the amount of  $\alpha\text{-Fe}_2\text{O}_3$ . It is noted that there exists a synergy in

the degradation rate when the composite material is used. This might be due to the higher absorption of light in the visible region. It can be noted that the photodegradation rate attained saturation on further increasing the content of  $\alpha\text{-Fe}_2\text{O}_3$ . The optimum photocatalytic activity of  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  is found to be at 2%  $\alpha\text{-Fe}_2\text{O}_3$  loading and therefore under the experimental conditions used.

The effect of catalyst amount on the photocatalytic degradation of DR81 was performed with the best composite by keeping other experimental parameters constant. Fig. 5(b) shows the photocatalytic activity of best performing sample FOCN-2 with different catalyst amounts of 0.5 g/L, 1.0 g/L and 1.25 g/L. It is seen from Fig. 5(b) that the photocatalytic degradation rate increases with an increase in catalyst loading and this may be due to increase in the number of available catalyst sites for light absorption which generates more electron-hole pairs for dye degradation and consequently enhances the degradation rate.

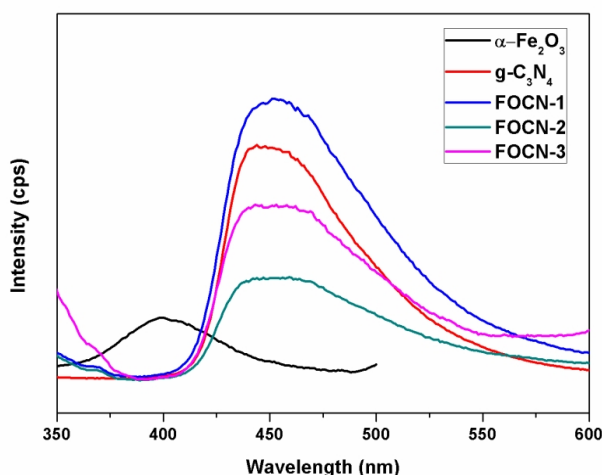
The experimental data were fitted by a first-order kinetic equation (1) to investigate the reaction kinetics of the DR81 photodegradation by  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$  and various  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  composite photocatalysts.

$$\ln C_0/C = kt \quad \text{-----} \quad (1)$$

where  $k$  is the first-order rate constant ( $\text{min}^{-1}$ ),  $t$  is the irradiation time (min),  $C_0$  and  $C$  is the initial concentration and concentration of DR81 at regular time intervals. It can be seen from the data shown in Figure 5(c) that the degradation process followed first order kinetics.

### 3.6 Photoluminescence studies

Photoluminescence (PL) spectral analysis is used to investigate the recombination processes of photoinduced electron-hole pairs in the composite materials. The PL spectra of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$  and  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  composite photocatalysts are shown in Fig. 6. The excitation wavelength for  $\alpha\text{-Fe}_2\text{O}_3$  was at 265 nm and 325 nm was used for  $\text{g-C}_3\text{N}_4$  and  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$ . The main emission band is centred at about 462 nm for  $\text{g-C}_3\text{N}_4$  and the peak position of composite photocatalysts in the PL spectra are similar to that of  $\text{g-C}_3\text{N}_4$  but the intensity of emission peaks is significantly decreased. This indicates that the recombination rate of photogenerated electron-hole pairs is very low for the composite photocatalysts.<sup>2,22</sup> It can be observed that there is no clear correlation between in the PL intensity and the incremental addition of  $\alpha\text{-Fe}_2\text{O}_3$  to  $\text{g-C}_3\text{N}_4$ . PL intensity trend is in the order, FOCN1>FOCN3>FOCN2. The observed PL trend supports the trend observed for the photocatalytic degradation efficiency. That is, FOCN-2 catalyst showed the weakest intensity, which supports the photocatalytic degradation results discussed in the previous section. Therefore, the FOCN-2 composite is the best composition for the photocatalytic degradation of DR81. However, the actual reason for the observed PL trend needs further investigation.



**Fig. 6** Photoluminescence spectra of the as-synthesized pure  $\alpha$ - $\text{Fe}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$  and  $\alpha$ - $\text{Fe}_2\text{O}_3$ - $\text{g-C}_3\text{N}_4$  photocatalysts.

### 3.7 Photoelectrochemical studies

Photoelectrochemical study was carried out to give further support of the proposed photocatalytic activity of FOCN-2. The transient-photocurrent response of  $\text{g-C}_3\text{N}_4$  and FOCN-2 were recorded for light on-off cycles under visible light irradiation and the results are shown in Fig. 7(a). It is clear that FOCN-2 generates higher photocurrent than that of  $\text{g-C}_3\text{N}_4$ . The photocurrent enhancement of FOCN-2 indicated an enhanced charge carrier (electron and hole) separation. The observed high photocatalytic degradation in the presence of FOCN-2 may be attributed to the reduced recombination rate of charge carriers as supported from the transient photocurrent studies.

The reaction rate occurring on the surface of the electrode is reflected by the arc radius of the Nyquist impedance plots.<sup>32</sup> Electrochemical impedance study was performed for  $\text{g-C}_3\text{N}_4$  and FOCN-2 samples to know the interfacial electron transfer rate. The corresponding Nyquist plots with and without light illumination are shown in Fig. 7(b). It is found that the arc radius of FOCN-2 is smaller than that of  $\text{g-C}_3\text{N}_4$  indicating a more effective separation efficiency of photogenerated electron-hole pairs and a faster interfacial charge transfer. This shows a more favourable condition for enhanced photocatalytic activity of FOCN-2 composite.

### 3.8 Photocatalytic mechanism

A possible mechanism has been proposed for the synergistic effect of  $\alpha$ - $\text{Fe}_2\text{O}_3$ - $\text{g-C}_3\text{N}_4$  photocatalyst for the photocatalytic degradation of DR81 and a schematic diagram representing the series of possible photochemical events is illustrated in Fig. 8. Photocatalytic activity of  $\alpha$ - $\text{Fe}_2\text{O}_3$ - $\text{g-C}_3\text{N}_4$  composite is much higher than that of  $\text{g-C}_3\text{N}_4$ . The conduction band (CB) of  $\text{g-C}_3\text{N}_4$  is  $-1.12$  eV and the valance band is  $1.57$  eV.<sup>1</sup> Whereas by knowing the  $E_g$ , the conduction band (CB) and valance band (VB) potentials of  $\alpha$ - $\text{Fe}_2\text{O}_3$  are calculated using the Equation (2)<sup>33-35</sup>

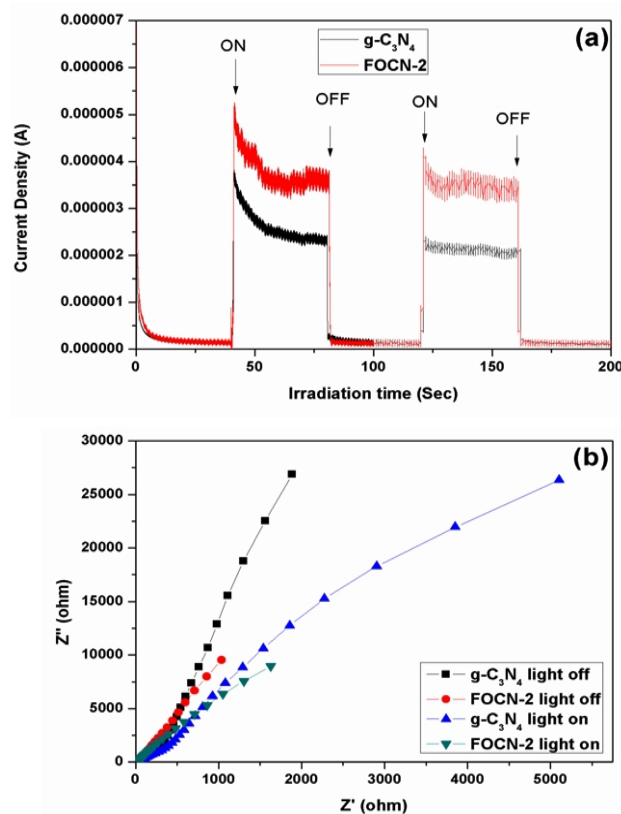
$$E_{VB} = X - E^e + 0.5E_g \quad \text{-----} \quad (2)$$

where  $E_{VB}$  is the valence band edge potential,  $X$  is the electronegativity of the semiconductor, for  $\alpha$ - $\text{Fe}_2\text{O}_3$  absolute electronegativity is 5.89,  $E^e$  is the energy of free electrons on the hydrogen scale ( $\sim 4.5$  eV).

The obtained  $E_{VB}$  value using the above equation is  $0.49$  eV and from the  $E_{VB}$  value, we can determine the  $E_{CB}$  value using Equation (3).

$$E_{CB} = E_{VB} - E_g \quad \text{-----} \quad (3)$$

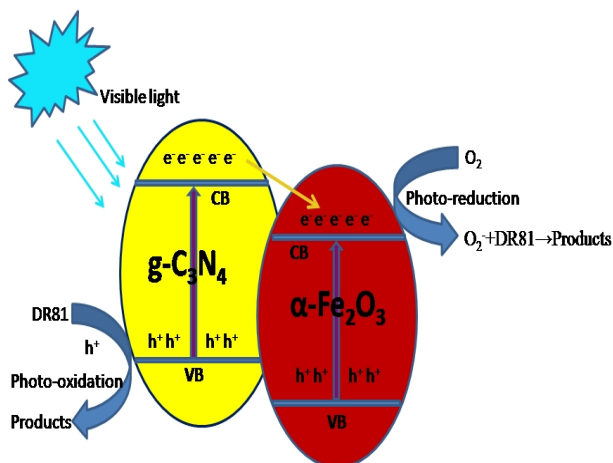
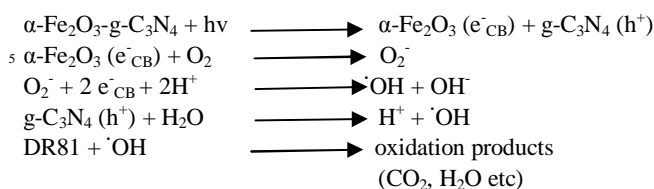
The calculated CB and VB edge potentials of  $\alpha$ - $\text{Fe}_2\text{O}_3$  are  $0.49$  and  $2.29$  eV, respectively.



**Fig. 7** (a) Transient-photocurrents of pure  $\text{g-C}_3\text{N}_4$  and FOCN-2 under visible light irradiation, (b) Nyquist plot of  $\text{g-C}_3\text{N}_4$  and FOCN-2 photocatalysts with and without visible light illumination.

The conduction band edge potential of  $\text{g-C}_3\text{N}_4$  is more negative than that of  $\alpha$ - $\text{Fe}_2\text{O}_3$ . Thus the photoinduced electrons transfer from  $\text{g-C}_3\text{N}_4$  into the CB of  $\alpha$ - $\text{Fe}_2\text{O}_3$ , while the holes are transferred to VB of  $\text{g-C}_3\text{N}_4$ . The recombination process of electron-hole pair is decreased and increases the charge separation, which leads to the more photocatalytic activity of  $\alpha$ - $\text{Fe}_2\text{O}_3$ - $\text{g-C}_3\text{N}_4$  composite.

The possible photocatalytic reactions are similar to those reported in the literature<sup>22,31</sup> as follows:



**Fig. 8** Schematic illustration of the mechanism of electron-hole separation and photocatalytic degradation of DR81 over  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  photocatalyst under visible light irradiation.

#### 4. Conclusion

In summary, nanocrystalline  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  phases were synthesized by simple and cost effective processes. Using these as precursors,  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  nanocomposite photocatalysts with different amounts of  $\alpha\text{-Fe}_2\text{O}_3$  were successfully synthesized by wet impregnation method. The interaction between the  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  in the composite and phase formation was confirmed by the FT-IR and XRD studies. The addition of  $\alpha\text{-Fe}_2\text{O}_3$  significantly affected the optical properties of the photocatalysts. The  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  composites exhibited the highest photocatalytic activity than  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  for the degradation of DR81 under visible light irradiation. The composite photocatalyst with 2 mol% of  $\alpha\text{-Fe}_2\text{O}_3$  was found to show the highest photocatalytic activity. The photoelectrochemical studies further confirmed the superior activity of the FOCN-2 photocatalyst. A possible photocatalytic mechanism has been proposed based on the photodegradation results. The reason for the high photocatalytic activity may be attributed by the increase of interfacial electron transfer process and decrease of the electron-hole recombination rate. The present investigation provides strong evidence that  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  nanocomposites are promising photocatalytic materials in efficient utilization of solar energy for the treatment of polluted wastewaters and also other environmental remediation processes.

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#### Notes and references

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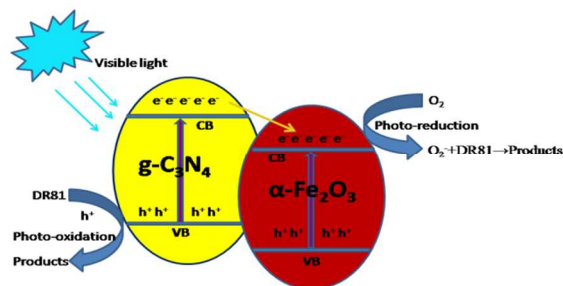
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## Photocatalytic and photoelectrochemical studies of Visible-light active $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$ nanocomposites

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Synergistic enhancement in photocatalytic degradation of  $\alpha\text{-Fe}_2\text{O}_3\text{-g-C}_3\text{N}_4$  due to an increase in visible-light absorption efficiency and rapid photoinduced charge separation.