



# Photoreduction of CO<sub>2</sub> to CH<sub>4</sub> over Efficient Z-Scheme $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> Composites

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## Research Article

# Photoreduction of CO<sub>2</sub> to CH<sub>4</sub> over Efficient Z-Scheme $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> Composites

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A series of composite  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> (denoted as xFeCN with  $x$  equal 5, 10, 15, and 20 of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> percentage in weight) was prepared by calcination and precipitation-impregnation methods. X-ray diffraction (XRD), Fourier transform infrared (FTIR), and X-ray photoelectron spectrometry (XPS) characterizations indicated the successful synthesis of Z-scheme FeCN composites. A red shift of the light absorption region was revealed by UV-vis diffuse reflectance spectroscopy (UV-DRS). In addition, photoluminescence spectroscopy (PL) spectra showed an interface interaction of two phases Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> in the synthesized composites that improved the charge transfer capacity. The photocatalytic activity of these materials was studied in the photoreduction of CO<sub>2</sub> with H<sub>2</sub>O as the reductant in the gaseous phase. The composites exhibited excellent photoactivity compared to undoped g-C<sub>3</sub>N<sub>4</sub>. The CH<sub>4</sub> production rate over 10FeCN and 15FeCN composites ( $2.8 \times 10^{-2}$  and  $2.9 \times 10^{-2} \mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively) was *ca.* 7 times higher than that over pristine g-C<sub>3</sub>N<sub>4</sub> ( $0.4 \times 10^{-2} \mu\text{mol h}^{-1} \text{g}^{-1}$ ). This outstanding photocatalytic property of these composites was explained by the light absorption expansion and the prevention of photogenerated electron-hole pairs recombination due to its Z-scheme structure.

## 1. Introduction

Carbon dioxide from fossil energy consumption is the most important source of greenhouse gas emissions to the atmosphere, causing global warming [1, 2]. Carbon dioxide capture and storage (CCS) or utilization (CCU) has largely been studied during the last decades [3, 4]. Among them, photocatalytic CO<sub>2</sub> conversion into valuable compounds, such as CH<sub>4</sub> and CH<sub>3</sub>OH, is an attractive route [5–7]. Thus, many semiconductors have been investigated as photocatalysts with a particular focus on the development of photocatalytic heterojunction systems by combining various semiconductor materials to form different photocatalyst types such as type I, type II, or especially Z-scheme systems [8–12]. In the type I and type II photocatalysts, there occurs the photogenerated electrons transfer between conduction

bands and holes, one between valance bands of each component in a composite. While in the Z-scheme type, this transfer takes place between the conduction and valance band of two adjacent components. By this characteristic, the Z-scheme photocatalyst has the advantage of mobilizing the potential position of the conduction band or valance band of each semiconductor when they are simultaneously combined for targeted reaction. Thereby, Z-scheme photocatalysts are expected to have stronger redox properties, better charge transfer, and higher improved light absorption yield than those of other simple photocatalyst types.

Recently, graphitic carbon nitride, g-C<sub>3</sub>N<sub>4</sub>, a semiconductor, has attracted researchers as a potential photocatalyst thanks to its easy synthesis, low cost, and moderate bandgap energy of 2.7 eV, which allows the absorption of visible light [13, 14]. In particular, the conduction band (CB) position of

g-C<sub>3</sub>N<sub>4</sub> is quite negative (−1.14 eV), which is favorable for the photoreduction of CO<sub>2</sub> into almost valuable hydrocarbons such as CH<sub>4</sub>, HCOOH, CH<sub>3</sub>OH, and C<sub>2</sub>H<sub>5</sub>OH [15]. However, one of the major disadvantages of g-C<sub>3</sub>N<sub>4</sub> is the fast electron-hole pair recombination, the relative high bandgap energy to be able to absorb most of the visible light, occupying 44% solar spectra. To improve these drawbacks, one of the strategies is to combine g-C<sub>3</sub>N<sub>4</sub> with other semiconductors [16–20].

Among the semiconductors used as photocatalysts, iron oxide, Fe<sub>2</sub>O<sub>3</sub>, is an interesting candidate [21]. One of the outstanding features of this semiconductor is its low synthesis cost and relatively low band gap energy,  $E_g = 2.2$  eV, which allows broad absorption in the visible region of sunlight. Therefore, Fe<sub>2</sub>O<sub>3</sub> oxide has been extensively studied as a photocatalyst through the photodegradation of polluted organic compounds in water [22, 23]. However, for the photoreduction of CO<sub>2</sub>, the conduction band potential (CB) is positive (+1.58 eV). So, Fe<sub>2</sub>O<sub>3</sub> oxide is not able to reduce this molecule. Combining Fe<sub>2</sub>O<sub>3</sub> oxide with another semiconductor having enough negative conduction band potential is required to create an efficient photocatalyst for CO<sub>2</sub> photoreduction [24–29]. The improving photocatalytic activity by adding  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was also reported in some other works. In the research of Ding et al., for the photoreduction of CO<sub>2</sub> in liquid phase to CH<sub>3</sub>OH [30],  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> with the weight ratio  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: g-C<sub>3</sub>N<sub>4</sub> of 60:40 had the best photocatalytic activity with 2.9-fold than pristine g-C<sub>3</sub>N<sub>4</sub>. Duan and Mei [31] also reported the highest amount of CH<sub>3</sub>OH obtained on 15%Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> (>3.5 fold than pristine g-C<sub>3</sub>N<sub>4</sub>). For CO<sub>2</sub> photoreduction in the gas phase, Wong et al. [32] observed the CO formation on dendrite-structured  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> (27.2  $\mu\text{mol h}^{-1}\text{g}^{-1}$ ), which was about 2.2 times higher than the one on pure g-C<sub>3</sub>N<sub>4</sub> (10.3  $\mu\text{mol h}^{-1}\text{g}^{-1}$ ). On the same type of catalyst with urchin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> morphology, Yong Zhou et al. also recognized a CO production rate of 17.8  $\mu\text{mol g}^{-1}\text{h}^{-1}$ , 3 times higher than that of pristine g-C<sub>3</sub>N<sub>4</sub> (6.1  $\mu\text{mol g}^{-1}\text{h}^{-1}$ ) [33]. Besides, Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites also showed higher photoactivity than pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> in the photodegradation of organic pollutants (Direct Red 81, Rhodamin B, and tetracycline hydrochloride) [34–36]. These studies showed that the morphology of Fe<sub>2</sub>O<sub>3</sub> oxide seems to play an important role in the activity of catalyst. The different morphologies may change interface interaction between Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> phase, leading to the change in charge carrier, a key factor of photocatalysis.

Based on the analysis above, in this study, we have synthesized Z-scheme  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts for CH<sub>4</sub> production from CO<sub>2</sub> photoreduction in the gas phase. This new Z-scheme material could take advantage of the low bandgap energy of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> oxide and the rather negative conduction band potential of g-C<sub>3</sub>N<sub>4</sub> as well.

## 2. Experimental

**2.1. Materials.** Melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>), iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), and sodium hydroxide (NaOH) with analytical purity were purchased from

Sigma-Aldrich. Deionized water was used as solvent for all preparations.

**2.2. Synthesis of g-C<sub>3</sub>N<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> Composite.** Carbon graphitic nitride, g-C<sub>3</sub>N<sub>4</sub>, was synthesized by calcination of melamine at 550°C for 3 hours under the nitrogen atmosphere.

A series of x% $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites was prepared by the precipitation-impregnation method. First, 1 g of g-C<sub>3</sub>N<sub>4</sub>, which were synthesized from melamine calcination, was added in a 100 ml solution of 0.1 M NaOH. The mixture was covered by paraffin paper, stirred, and kept at 60°C for 2 hours. Then, a calculated amount of FeSO<sub>4</sub>·7H<sub>2</sub>O was slowly added in the solution above, and the pH was adjusted to 10 with 0.1 M NaOH solution, leading to the formation of a composite material of iron oxide precipitate and g-C<sub>3</sub>N<sub>4</sub>. The latter was filtered and washed by deionized water and dried at 70°C. Four Z-scheme  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts, denoted as xFeCN, with x equal to 5, 10, 15, or 20 wt.% of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were obtained.

**2.3. Characterization.** All composites were characterized by X-ray diffraction (XRD, model Bruker D8), Fourier transform infrared (FTIR, model 8101M Shimadzu), X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific MultiLab 2000), UV-vis diffuse reflectance spectroscopy (UV-DRS, model Jaco V-530), photoluminescence spectroscopy (PL, model Horiba FluoroMax-4), transmission electron microscopy (TEM, JEM 1400, Plus Jeon), and scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS, Hitachi TM4000 Tabletop Microscope).

**2.4. Photocatalytic Procedure.** In a typical test, 100 mg of catalyst was added in 15 mL deionized water in a beaker with a 5 cm diameter. The solvent in the mixture was completely evaporated in an oven at 70°C to well disperse the photocatalyst on the bottom of the beaker. After that, the catalyst-containing beaker was placed in a closed stainless reactor equipped with a quartz window (Figure 1). The high purity (99,999%) CO<sub>2</sub> flow of 500 ml/minute bubbled in a closed stainless contains deionized water kept at 25°C before entering the stainless reactor for 30 minutes. Then, a 150W Xenon lamp (Newport model 67005) was switched on for 18 h.

## 3. Results and Discussion

Figure 2(a) shows the XRD patterns of the fresh g-C<sub>3</sub>N<sub>4</sub> and xFeCN photocatalysts. The formation of g-C<sub>3</sub>N<sub>4</sub> by melamine calcination was confirmed by the presence of peaks at  $2\theta$  of 13.2 and 27.3° (JCPDS 87–1526). For the composite photocatalysts, the characteristic peaks of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> appeared in all patterns with  $2\theta$  at 30.2, 35.7, 43.2, 53.8, 57.2, and 62.9° (JCPDS 004–075). The peak intensity of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase is proportional to its content in the composite materials.

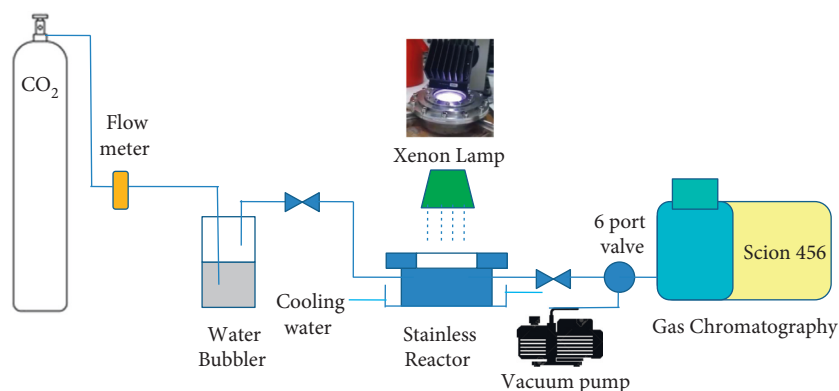


FIGURE 1: Scheme of the photocatalytic reactor used in this work.

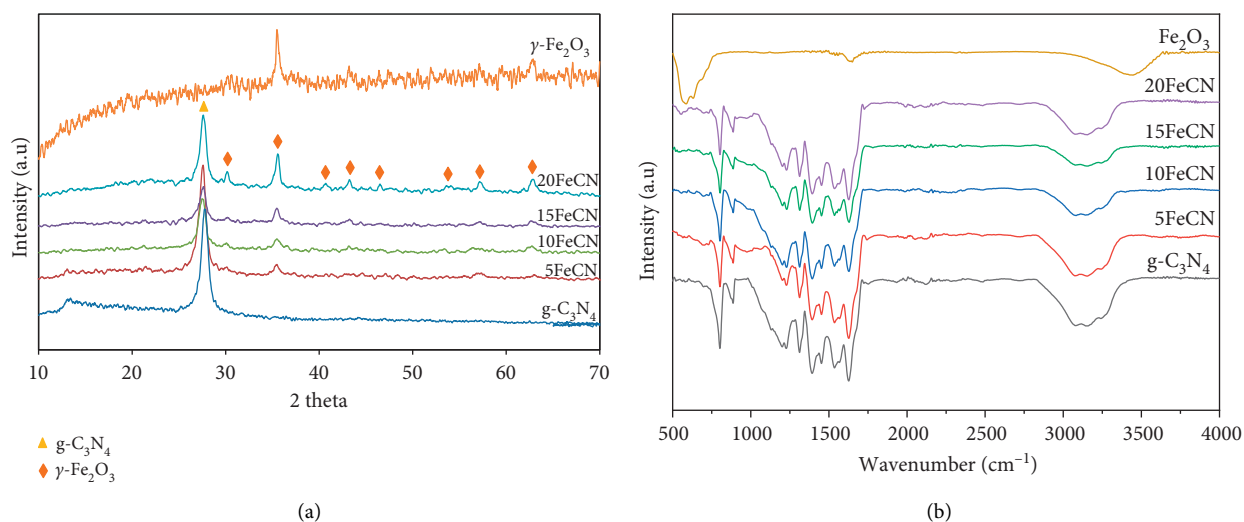
FIGURE 2: XRD patterns (a) and FTIR (b) spectra of  $g\text{-C}_3\text{N}_4$ ,  $x\text{FeCN}$  composites.

Figure 2(b) shows the FTIR spectra of all fresh photocatalysts. All these materials have similar characteristic signals of  $g\text{-C}_3\text{N}_4$  structure. The peak at  $804$  and  $887\text{ cm}^{-1}$  is attributed to the heptazine stretching mode [37], while those at  $1203\text{--}1630\text{ cm}^{-1}$  correspond to stretching vibrations of  $\text{C}=\text{N}$  and  $\text{C}-\text{N}$  bonds of the heterocycle [38, 39]. For the broad band from  $3000$  to  $3500\text{ cm}^{-1}$ , the signals were ascribed to the vibration of  $\text{NH}_2$  and  $\text{NH}$  functional groups of  $g\text{-C}_3\text{N}_4$  and the  $\text{OH}$  group of absorbed water [40]. In addition, the weak signals observed at  $586\text{ cm}^{-1}$  originated from the  $\text{Fe}-\text{O}$  bond vibrations [41]. These results confirmed the formation of the two expected crystalline phases of  $g\text{-C}_3\text{N}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  in the photocatalysts synthesized. In order to confirm the formation of composite materials between these two components, XPS analysis was performed for one photocatalyst containing 10 wt% of  $\gamma\text{-Fe}_2\text{O}_3$  (Figure 3). The general XPS spectrum (Figure 3(a)) shows the presence of Fe, O, C, and N on the surface of this photocatalyst. On the high-resolution Fe elemental spectrum (Figure 3(b)), there are two major peaks at the binding energy  $711.2$  and  $724.7\text{ eV}$  corresponding to  $\text{Fe}^{3+}2p_{3/2}$  and  $\text{Fe}^{3+}2p_{1/2}$ , respectively. These two peaks are characteristics of the  $\text{Fe}^{3+}$  oxidation state as observed on the XPS spectrum of  $\text{Fe}_2\text{O}_3$

oxide [42, 43]. Besides, two satellite peaks can be detected at positions  $718.2$  and  $731.0\text{ eV}$ . With the  $\text{C}1s$  spectrum (Figure 3(e)), there are three peaks at  $284.9$ ,  $286.5$ , and  $288.5\text{ eV}$ . The first peak at  $284.9\text{ eV}$  is assigned to  $\text{C}-\text{C}/\text{C}=\text{C}$  bonds, the second to the carbon of the  $\text{C}-\text{NH}_2$  group, and the third to bonded C in the heptazine structure ( $\text{N}-\text{C}=\text{N}$ ) [44, 45]. In the  $\text{N}1s$  spectrum (Figure 3(d)), the peak deconvolution shows the presence of 3 peaks at  $399.0$ ,  $400.3$ , and  $401.2\text{ eV}$ , which correspond to  $\text{Sp}^2$  bonded N in triazine ring ( $\text{C}-\text{N}=\text{C}$ ), the tertiary nitrogen  $\text{N}-(\text{C})_3$  group in the heptazine structure, and N in the  $\text{C}-\text{N}-\text{H}$  group, respectively [39, 40]. For the oxygen element (Figure 3(c)), the peak deconvolution of  $\text{O}1s$  indicates the existence of three components: lattice oxygen of  $\text{Fe}-\text{O}$  bond ( $529.7\text{ eV}$ ), oxygen of surface hydroxyl- $\text{OH}$  ( $531.0\text{ eV}$ ), and the one of adsorbed water  $\text{H}_2\text{O}$  ( $533.3\text{ eV}$ ) [43]. Hence, the results of XPS, XRD, and IR proved that  $\gamma\text{-Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4$  composites were successfully synthesized.

In order to predict the light absorption ability, all composites and  $g\text{-C}_3\text{N}_4$  were measured by the UV-DRS method. Figures 4(a) and 4(b) show the obtained results. From the Kubelka-Munk function, the obtained bandgap energy was of  $2.63$ ,  $2.54$ ,  $2.47$ ,  $2.25$ ,  $1.95$ , and  $1.80\text{ eV}$  for

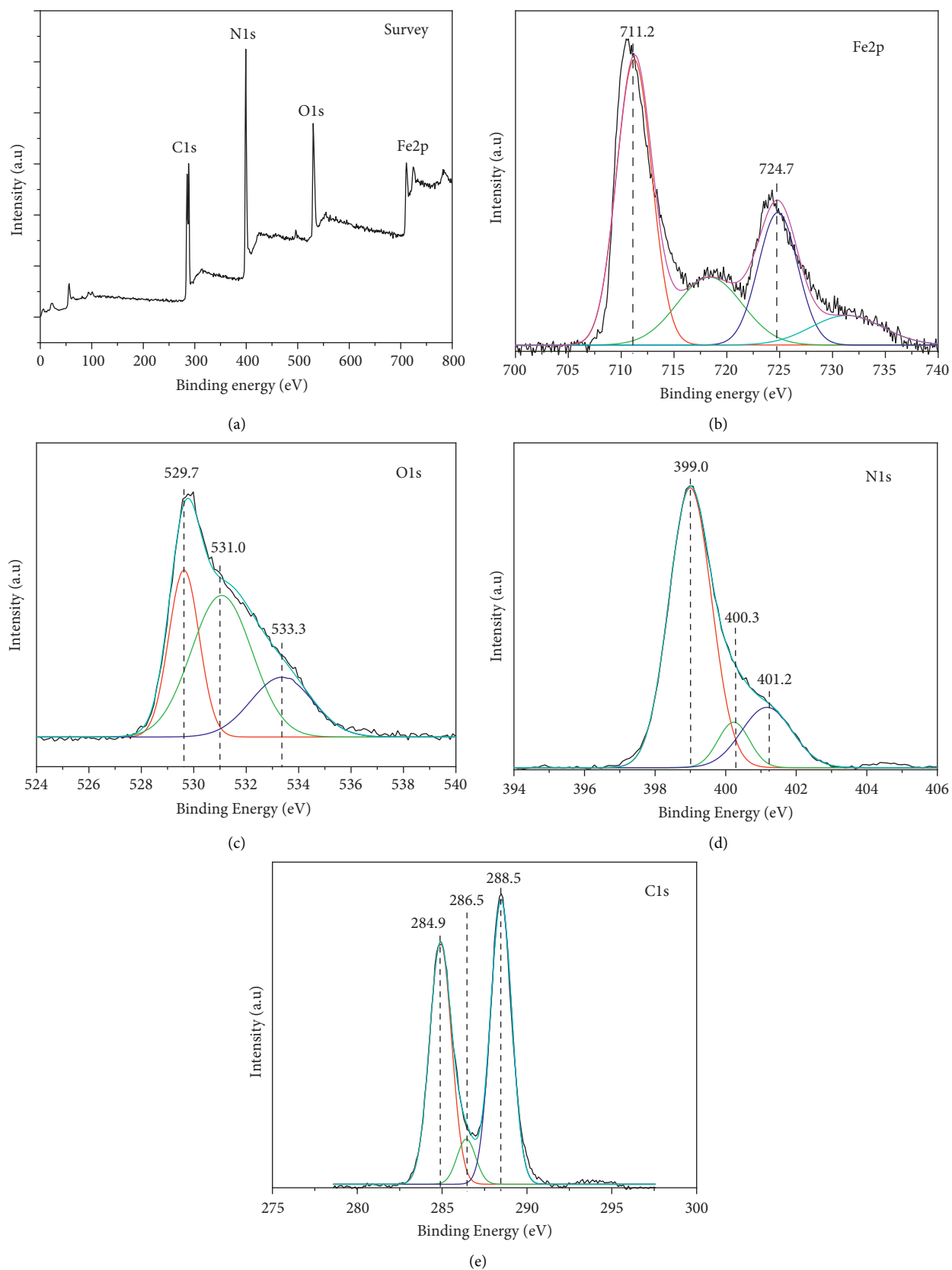


FIGURE 3: XPS survey of 10FeCN composite (a) and its XPS spectra of Fe2p (b), O1s (c), N1s (d), and C1s (e).

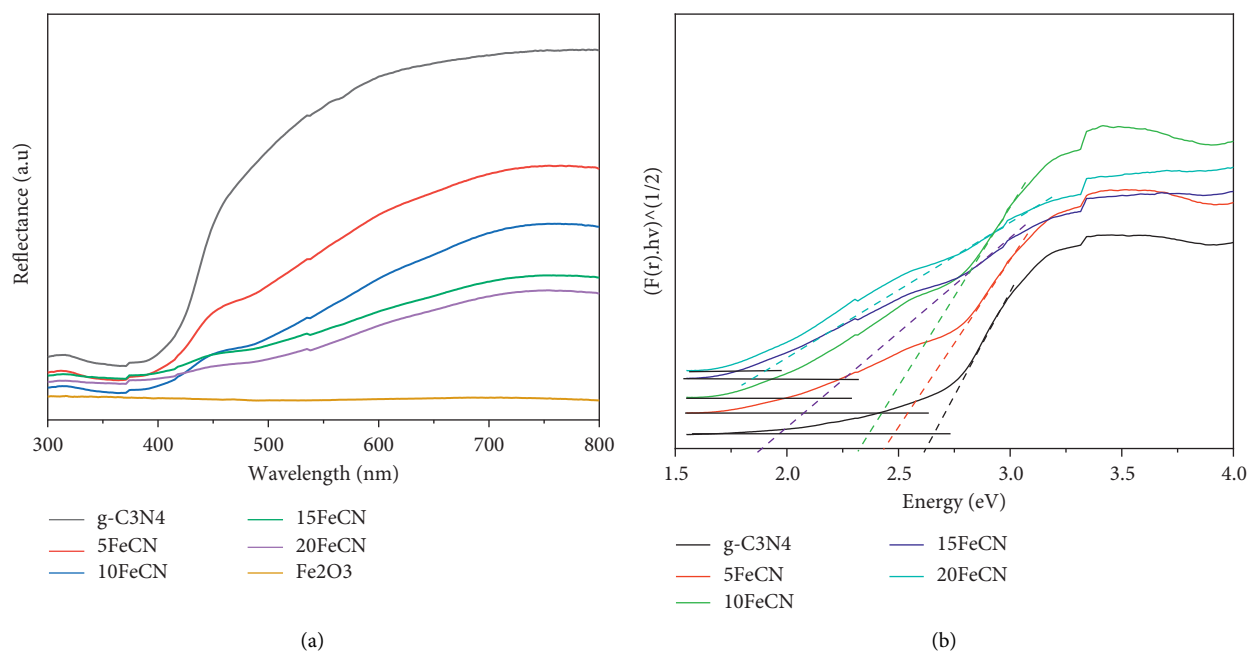


FIGURE 4: UV-DRS spectra (a) and Kubelka–Munk function (b) of xFeCN composites.

g-C<sub>3</sub>N<sub>4</sub>, 5FeCN, 10FeCN, 15FeCN, 20FeCN, and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, respectively. So, the increase of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> content led to decrease of the bandgap energy. In other words, it means that the light absorption region of catalysts shifted more in the visible light wavelength by increasing the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> content. Hence, the photocatalytic activity of composites is expected to be improved.

To estimate the recombination of electron-hole pair phenomena, the PL spectroscopy was carried out for g-C<sub>3</sub>N<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and 10FeCN composites (Figure 5(a)). As observed, the intensity of PL spectrum of g-C<sub>3</sub>N<sub>4</sub> is nearly twice in comparison with the one of 10FeCN. No signal was observed on PL spectra of Fe<sub>2</sub>O<sub>3</sub> at activated wavelength. This result reflected that the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and its interface interaction with g-C<sub>3</sub>N<sub>4</sub> seem to inhibit the photogenerated electron-hole pairs recombination, which could improve photoactivity.

Figures 5(b), 5(c), and 5(d) show the SEM image and different element distribution of the 10FeCN sample. It is obvious that Fe and O elements or Fe<sub>2</sub>O<sub>3</sub> phase were quite homogeneously dispersed on the surface of g-C<sub>3</sub>N<sub>4</sub>. The elemental composition is given in Table 1. It is noted that the experimental composition is quite.

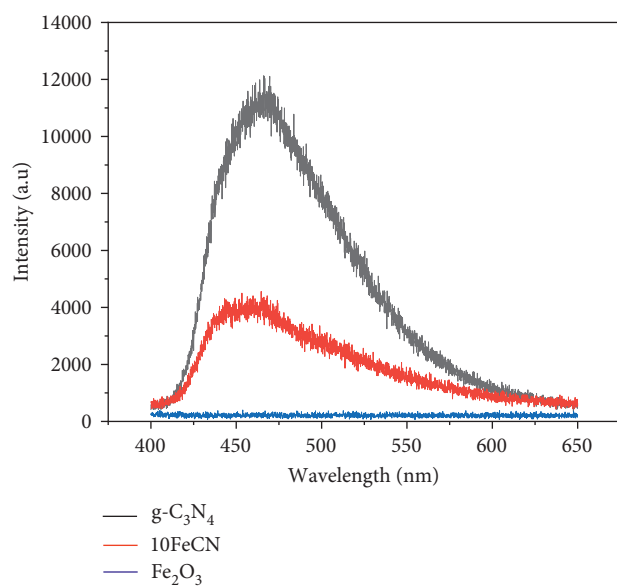
The morphology of composite 10FeCN was characterized by TEM (Figure 6). It is obvious that the particle Fe<sub>2</sub>O<sub>3</sub> is in cubic form with average size of 10 nm. Apart from  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles dispersed on the g-C<sub>3</sub>N<sub>4</sub> surface, it seems that some these particles were covered by g-C<sub>3</sub>N<sub>4</sub> layer to form core-shell structure Fe<sub>2</sub>O<sub>3</sub>@g-C<sub>3</sub>N<sub>4</sub>.

The photocatalytic activity was evaluated through photoreduction of CO<sub>2</sub>. Figure 7(a) shows the obtained results. Methane was the main production of the reaction, while CO was not noticeable. No product was detected on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. This is explained by the more positive value of its conduction

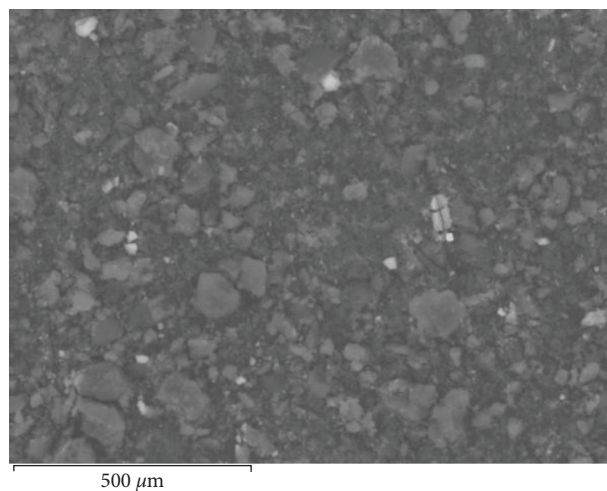
band potential in comparison of that reduction potential of CO<sub>2</sub>/CH<sub>4</sub> (−0.24 V) [2]. It was noted that the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> remarkably impacted the CH<sub>4</sub> formation. A volcano-like evolution of methane formation as a function of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is observed. Concretely, under the same operational conditions, the amount of CH<sub>4</sub> formed is  $0.4 \times 10^{-2}$ ,  $2.1 \times 10^{-2}$ ,  $2.8 \times 10^{-2}$ ,  $2.9 \times 10^{-2}$ , and  $1.0 \times 10^{-2} \mu\text{mol g}^{-1} \text{h}^{-1}$  for g-C<sub>3</sub>N<sub>4</sub>, 5FeCN, 10FeCN, 15FeCN, and 20FeCN, respectively. Hence, the maximum CH<sub>4</sub> formation quickly increased when rising the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> content and reached the maximum with 10FeCN and 15FeCN composites. Thus, compared to pristine g-C<sub>3</sub>N<sub>4</sub>, the produced amount of CH<sub>4</sub> over 10FeCN and 15FeCN composites was 7 fold. However, at higher  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> content, e.g., 20wt.% Fe<sub>2</sub>O<sub>3</sub>, CH<sub>4</sub> production dropped rapidly to  $1.0 \times 10^{-2} \mu\text{mol g}^{-1} \text{h}^{-1}$ . In comparison with the research on urchin-like Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> and dendrite-structured Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> catalysts for CO<sub>2</sub> photoreduction in the gas phase, CH<sub>4</sub> gas was the preferred product on this catalyst, instead of CO [32, 33]. Hence, the obtained results show interesting photocatalytic activity of the synthesized composite materials and also prove the good combination of two phases,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, to make new active photocatalysts. The small formed CH<sub>4</sub> amount was probably due to the low power of xenon lamp (only 150W). To justify these results, a blank test (without catalyst) and a test on g-C<sub>3</sub>N<sub>4</sub> under N<sub>2</sub> gas were carried out. No CH<sub>4</sub> amount was detected for these ones. In addition, the test was performed also on the mixture of 10% (wt) of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with g-C<sub>3</sub>N<sub>4</sub> (Figure 7(a)), and the CH<sub>4</sub> product is under detectable limit that could be evidence for the absence of phase interaction between  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> as well as the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> hindering the illumination on g-C<sub>3</sub>N<sub>4</sub>.

Generally, the outstanding photoactivity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite materials compared to g-C<sub>3</sub>N<sub>4</sub> is assigned to

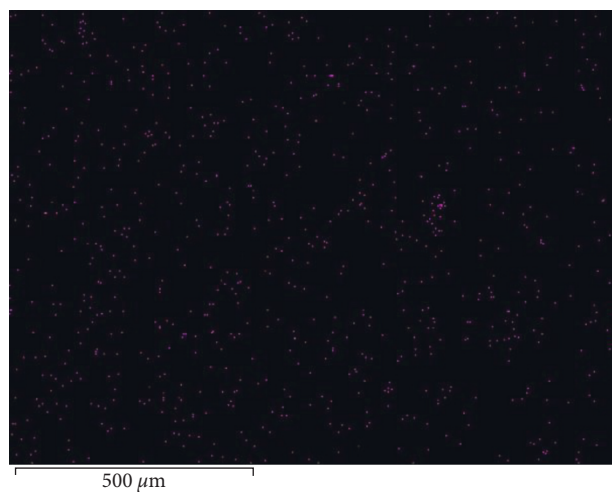




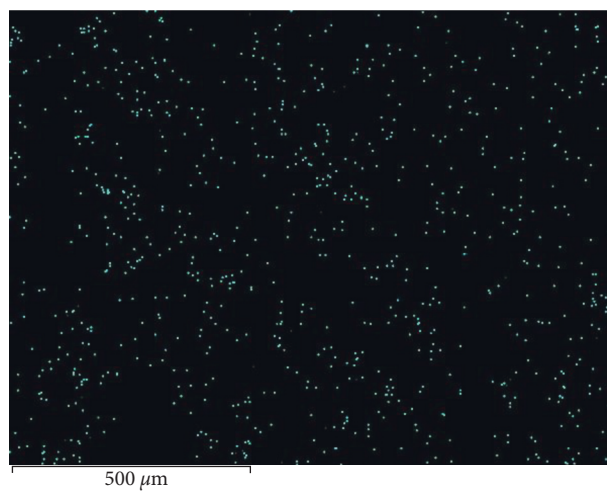
(a)



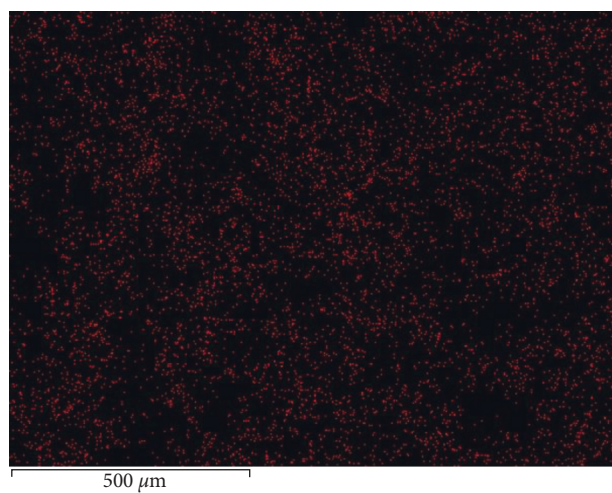
(b)



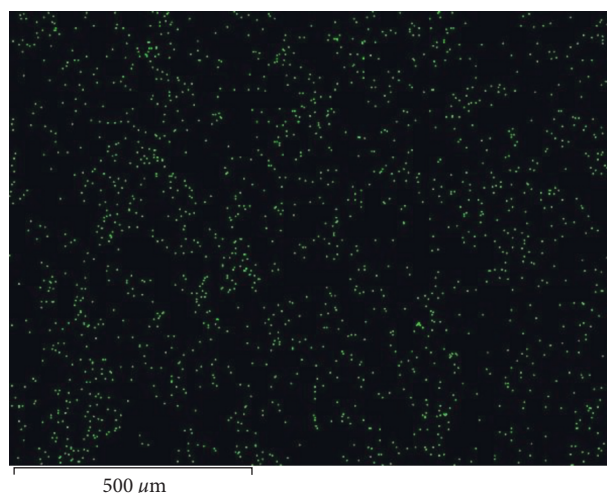
(c)



(d)



(e)



(f)

FIGURE 5: PL spectra of g-C<sub>3</sub>N<sub>4</sub>, γ-Fe<sub>2</sub>O<sub>3</sub>, and 10FeCN composite. (a) SEM mapping images of different elements in 10FeCN: SEM image (b), Fe distribution (c), O distribution (d), C distribution (e), and N distribution (f).

TABLE 1: Weight percentages of different elements in the composition of 10FeCN.

Element	Theoretical percent	Experimental percent
Fe	6.99	7.26
O	3.01	3.24
C	35.22	36.57
N	54.78	52.93

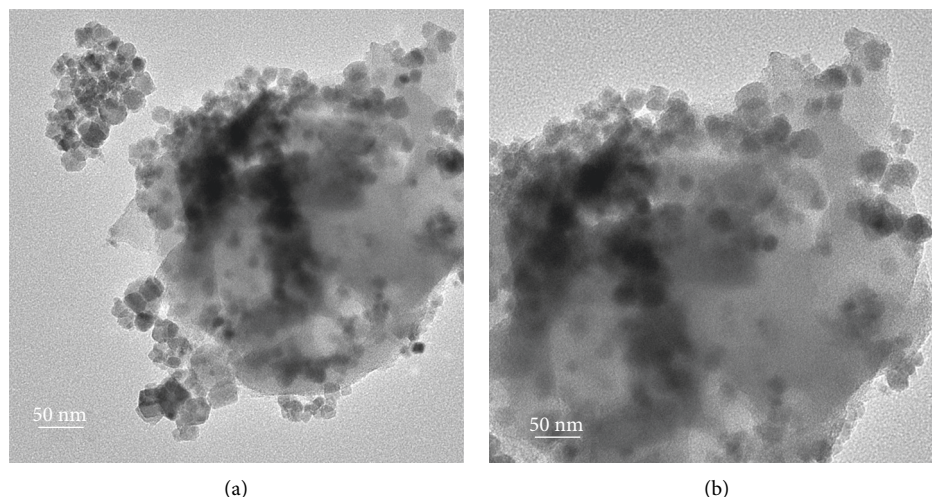
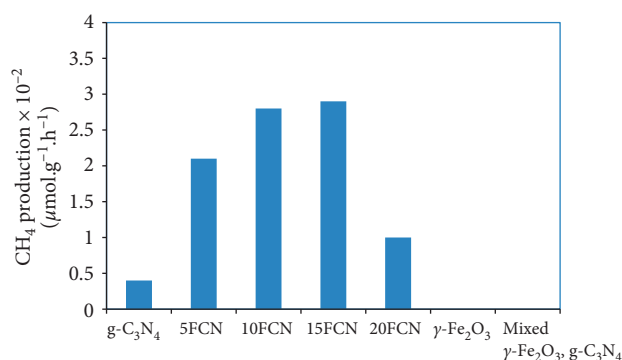
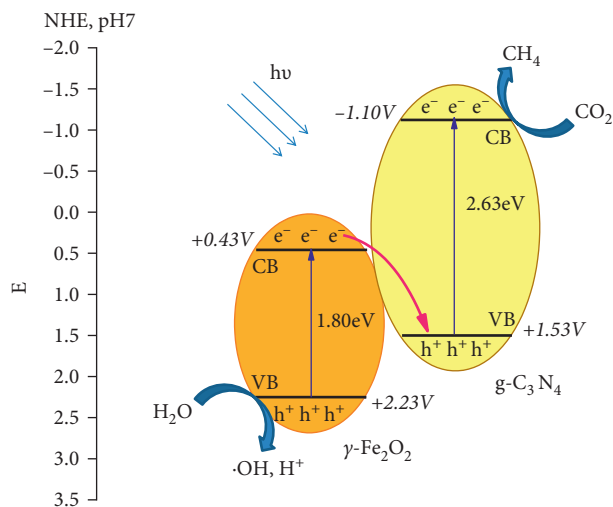


FIGURE 6: TEM images of 10FeCN.



(a)



(b)

FIGURE 7: CH<sub>4</sub> production on g-C<sub>3</sub>N<sub>4</sub> and different xFeCN composites (a); proposed mechanism of CO<sub>2</sub> photoreduction on Z-scheme structure of γ-Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> (b).

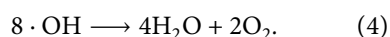
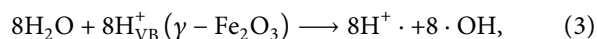
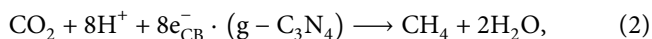
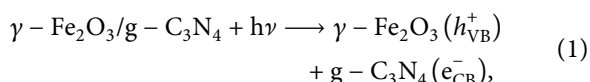
better light-harvesting ability and charge transfer than those of single phase of γ-Fe<sub>2</sub>O<sub>3</sub> or g-C<sub>3</sub>N<sub>4</sub>. It should be emphasized that the charge transfer process in the Z-scheme structure not only reduces photoelectron-hole pair recombination but also makes photocatalyst, the redox potential, stronger: CB potential more negative and VB potential more positive. In addition, it seems that the quite small size

particles of γ-Fe<sub>2</sub>O<sub>3</sub> as observed in TEM images, about 10 nm of diameter, have improved the interface interaction of composite γ-Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. The increase of γ-Fe<sub>2</sub>O<sub>3</sub> quantity superior of 15% (wt) has led to the decrease of photoactivity. This is probably due to the strong sintering of γ-Fe<sub>2</sub>O<sub>3</sub> nanoparticles, causing less interface interaction. Besides, the accumulation of γ-Fe<sub>2</sub>O<sub>3</sub> nanoparticles could



cover g-C<sub>3</sub>N<sub>4</sub> surface and inhibits the irradiation on this phase. Hence, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> quantity of 10% (wt) was the most suitable to obtain the highest photoactivity.

From UV-DRS spectrum and Mulliken electronegativity theory, the valance band (VB) and conduction band (CB) of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> were calculated [30]. According to this theory,  $E_{CB} = X - E_c - 0.5E_g$ , where  $E_{CB}$  is the conduction band edge energy,  $X$  is the electronegativity of the semiconductor (equal 5.825 eV for Fe<sub>2</sub>O<sub>3</sub> and 4.72 eV for g-C<sub>3</sub>N<sub>4</sub>),  $E_c$ , equal 4.5 eV, is the energy of free electrons with hydrogen scale, and  $E_g$  is the bandgap energy of semiconductor. Basing on this equation and concrete value of each parameter, it is found that VB and CB of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> are +2.23, +0.43 eV and +1.53, -1.10 eV, respectively. Figure 7(b) shows a possible photoreduction mechanism of CO<sub>2</sub> photoreduction into CH<sub>4</sub>. According to this Z-scheme composite, all the two phases,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, harvested the irradiated light and generated electron-hole pairs. The photogenerated electron located on CB of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> migrated and recombined with photogenerated holes located on the valance band (VB) of g-C<sub>3</sub>N<sub>4</sub>. This process allows broadening the light absorption region and also prevents recombination of photogenerated electron-hole pairs that both improved the photocatalytic activity. The details of this process are presented through the following equations:



## 4. Conclusions

In this work, different Z-scheme photocatalysts,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>, were synthesized by simple methods of calcination and impregnation-precipitation. XRD, IR, and XPS characterizations of these materials confirmed the formation of composite structure of these photocatalysts, wherein  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> grew on g-C<sub>3</sub>N<sub>4</sub> surface. SEM analysis highlighted a good distribution of Fe on the surface of g-C<sub>3</sub>N<sub>4</sub> support. The UV-DRS and PL spectra of the photocatalyst containing 10 wt.%  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> evidenced interface interaction of the two phases of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>.

The catalytic performance of these materials was evaluated through the CO<sub>2</sub> photoreduction in the gaseous phase. Methane was found as the main product, while no trace of CO was observed. According to CH<sub>4</sub> production, the photocatalytic activity followed the following order: 15FeCN ( $2.9 \times 10^{-2} \mu\text{mol g}^{-1} \text{h}^{-1}$ ) > 10FeCN ( $2.8 \times 10^{-2} \mu\text{mol g}^{-1} \text{h}^{-1}$ ) > 5FeCN ( $2.1 \times 10^{-2} \mu\text{mol g}^{-1} \text{h}^{-1}$ ) > 20FeCN ( $1.0 \times 10^{-2} \mu\text{mol g}^{-1} \text{h}^{-1}$ ) > g-C<sub>3</sub>N<sub>4</sub> ( $0.4 \times 10^{-2} \mu\text{mol g}^{-1} \text{h}^{-1}$ ). Hence, 10FeCN and 15FeCN composites had the highest photoactivity, which is approximately 7 times higher than that on bulk g-C<sub>3</sub>N<sub>4</sub>. This could be explained by a synergy

combination and interaction of the two phases  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, leading to the Z-scheme structure composites, which improved light absorption with red-shift light and also diminishes photogenerated electron-hole pairs recombination. These outstanding results are promising for the design of a low-cost and highly efficient photocatalyst for CO<sub>2</sub> reduction on the basis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>.

## Data Availability

The data used to support the findings of this study are included within the article.

## Conflicts of Interest

The authors declare that there are no conflicts of interest.

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