Research Article

Photoreduction of CO₂ to CH₄ over Efficient Z-Scheme c-Fe₂O₃/g-C₃N₄ Composites

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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 CO₂ conversion into valuable compounds, such as CH₄ and CH₃OH, 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-C₃N₄, 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
2. Experimental

2.1. Materials. Melamine (C₃H₆N₆), iron (II) sulfate heptahydrate (FeSO₄·7H₂O), 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-C₃N₄ and γ-Fe₂O₃/g-C₃N₄ Composite. Carbon graphitic nitride, g-C₃N₄, was synthesized by calcination of melamine at 550°C for 3 hours under the nitrogen atmosphere.

A series of x%γ-Fe₂O₃/g-C₃N₄ composites was prepared by the precipitation-impregnation method. First, 1 g of g-C₃N₄, 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 FeSO₄·7H₂O 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-C₃N₄. The latter was filtered and washed by deionized water and dried at 70°C. Four Z-scheme γ-Fe₂O₃/g-C₃N₄ photocatalysts, denoted as xFeCN, with x equal to 5, 10, 15, or 20 wt.% of γ-Fe₂O₃ were obtained.

2.3. Characterization. All composites were characterized by X-ray diffraction (XRD, model Bruker D8), Fourier transform infrared (FTIR, model 8101M Shimazu), X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific MultiLab 2000), UV-vis diffuse reflectance spectroscopy (UV-DRS, model Jasco 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 quark window (Figure 1). The high purity (99.999%) CO₂ 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-C₃N₄ and xFeCN photocatalysts. The formation of g-C₃N₄ by melamine calcination was confirmed by the presence of peaks at 2θ of 13.2 and 27.3° (JCPDS 87–1526). For the composite photocatalysts, the characteristic peaks of γ-Fe₂O₃ appeared in all patterns with 2θ at 30.2, 35.7, 43.2, 53.8, 57.2, and 62.9° (JCPDS 004-075). The peak intensity of the γ-Fe₂O₃ phase is proportional to its content in the composite materials.
Figure 2(b) shows the FTIR spectra of all fresh photocatalysts. All these materials have similar characteristic signals of g-C₃N₄ structure. The peak at 804 and 887 cm⁻¹ is attributed to the heptazine stretching mode [37], while those at 1203–1630 cm⁻¹ correspond to stretching vibrations of C=N and C–N bonds of the heterocycle [38, 39]. For the broad band from 3000 to 3500 cm⁻¹, the signals were ascribed to the vibration of NH₂ and NH functional groups of g-C₃N₄ and the OH group of absorbed water [40]. In addition, the weak signals observed at 586 cm⁻¹ originated from the Fe–O bond vibrations [41]. These results confirmed the formation of the two expected crystalline phases of g-C₃N₄ and γ-Fe₂O₃ 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 γ-Fe₂O₃ (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 eV corresponding to Fe³⁺2p½ and Fe³⁺2p½, respectively. These two peaks are characteristics of the Fe³⁺ oxidation state as observed on the XPS spectrum of Fe₂O₃ oxide [42, 43]. Besides, two satellite peaks can be detected at positions 718.2 and 731.0 eV. With the C1s spectrum (Figure 3(e)), there are three peaks at 284.9, 286.5, and 288.5 eV. The first peak at 284.9 eV is assigned to C–C/C=C bonds, the second to the carbon of the C–NH₂ group, and the third to bonded C in the heptazine structure (N–C=N) [44, 45]. In the N1s spectrum (Figure 3(d)), the peak deconvolution shows the presence of 3 peaks at 399.0, 400.3, and 401.2 eV, which correspond to Sp² bonded N in triazine ring (C–N=C), the tertiary nitrogen N-(C)₃ group in the heptazine structure, and N in the C–N–H group, respectively [39, 40]. For the oxygen element (Figure 3(c)), the peak deconvolution of O1s indicates the existence of three components: lattice oxygen of Fe–O bond (529.7 eV), oxygen of surface hydroxyl–OH (531.0 eV), and the one of adsorbed water H₂O (533.3 eV) [43]. Hence, the results of XPS, XRD, and IR proved that γ-Fe₂O₃/g-C₃N₄ composites were successfully synthesized.

In order to predict the light absorption ability, all composites and g-C₃N₄ 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 eV for
Figure 3: XPS survey of 10FeCN composite (a) and its XPS spectra of Fe2p (b), O1s (c), N1s (d), and C1s (e).
g-C₃N₄, 5FeCN, 10FeCN, 15FeCN, 20FeCN, and γ-Fe₂O₃, respectively. So, the increase of γ-Fe₂O₃ content led to a 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 γ-Fe₂O₃ 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-C₃N₄, γ-Fe₂O₃, and 10FeCN composites (Figure 5(a)). As observed, the intensity of PL spectrum of g-C₃N₄ is nearly twice in comparison with the one of 10FeCN. No signal was observed on PL spectra of Fe₂O₃ at activated wavelength. This result reflected that the presence of γ-Fe₂O₃ and its interface interaction with g-C₃N₄ 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 Fe₂O₃ phase were quite homogenously dispersed on the surface of g-C₃N₄. The elemental composition is given in Table 1. It is noted that the experimental composition is quite close.

The morphology of composite 10FeCN was characterized by TEM (Figure 6). It is obvious that the particle Fe₂O₃ is in cubic form with average size of 10 nm. Apart from γ-Fe₂O₃ particles dispersed on the g-C₃N₄ surface, it seems that some these particles were covered by g-C₃N₄ layer to form core-shell structure Fe₂O₃@g-C₃N₄.

The photocatalytic activity was evaluated through photoreduction of CO₂. 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 γ-Fe₂O₃. This is explained by the more positive value of its conduction band potential in comparison of that reduction potential of CO₂/CH₄ (−0.24 V) [2]. It was noted that the presence of γ-Fe₂O₃ remarkably impacted the CH₄ formation. A volcano-like evolution of methane formation as a function of γ-Fe₂O₃ is observed. Concretely, under the same operational conditions, the amount of CH₄ formed is 0.4 × 10⁻², 2.1 × 10⁻², 2.8 × 10⁻², 2.9 × 10⁻², and 1.0 × 10⁻² μmol g⁻¹ h⁻¹ for g-C₃N₄, 5FeCN, 10FeCN, 15FeCN, and 20FeCN, respectively. Hence, the maximum CH₄ formation quickly increased when rising the γ-Fe₂O₃ content and reached the maximum with 10FeCN and 15FeCN composites. However, at higher γ-Fe₂O₃ content, e.g., 20wt.% Fe₂O₃, CH₄ production dropped rapidly to 1.0 × 10⁻² μmol g⁻¹ h⁻¹. In comparison with the research on urchin-like Fe₂O₃/g-C₃N₄ and dendrite-structured Fe₂O₃/g-C₃N₄ catalysts for CO₂ photoreduction in the gas phase, CH₄ 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, γ-Fe₂O₃ and g-C₃N₄, to make new active photocatalysts. The small formed CH₄ 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-C₃N₄ under N₂ gas were carried out. No CH₄ amount was detected for these ones. In addition, the test was performed also on the mixture of 10% (wt) of γ-Fe₂O₃ with g-C₃N₄ (Figure 7(a)), and the CH₄ product is under detectable limit that could be evidence for the absence of phase interaction between γFe₂O₃ and g-C₃N₄ as well as the presence of γ-Fe₂O₃ hindering the illumination on g-C₃N₄.

Generally, the outstanding photoactivity of γ-Fe₂O₃/g-C₃N₄ composite materials compared to g-C₃N₄ is assigned to
Figure 5: PL spectra of g-C₃N₄, γ-Fe₂O₃, 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).
better light-harvesting ability and charge transfer than those of single phase of γ-Fe2O3 or g-C3N4. 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-Fe2O3 as observed in TEM images, about 10 nm of diameter, have improved the interface interaction of composite γ-Fe2O3/g-C3N4. The increase of γ-Fe2O3 quantity superior of 15% (wt) has led to the decrease of photoactivity. This is probably due to the strong sintering of γ-Fe2O3 nanoparticles, causing less interface interaction. Besides, the accumulation of γ-Fe2O3 nanoparticles could

### 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.](image)

![Figure 7: CH4 production on g-C3N4 and different xFeCN composites (a); proposed mechanism of CO2 photoreduction on Z-scheme structure of γ-Fe2O3/g-C3N4 (b).](image)
cover g-C₃N₄ surface and inhibits the irradiation on this phase. Hence, the γ-Fe₂O₃ quantity of 10% (wt) was the most suitable to obtain the highest photoactivity.

From UV-DRS spectrum and Mulliken electronegativity theory, the valence band (VB) and conduction band (CB) of γ-Fe₂O₃ and g-C₃N₄ were calculated [30]. According to this theory, \( E_{CB} = X - E - 0.5E_p \), where \( E_{CB} \) is the conduction band edge energy. \( X \) is the electronegativity of the semiconductor (equal 5.825 eV for Fe₂O₃ and 4.72 eV for g-C₃N₄). \( E_p \) equal 4.5 eV, is the energy of free electrons with hydrogen scale, and \( E \) is the band gap energy of semiconductor. Basing on this equation and concrete value of each parameter, it is found that VB and CB of γ-Fe₂O₃ and g-C₃N₄ are +2.23, +0.43 eV and +1.53, −1.10 eV, respectively. Figure 7(b) shows a possible photoreduction mechanism of CO₂ photoreduction into CH₄. According to this Z-scheme composite, all the two phases, γ-Fe₂O₃ and g-C₃N₄, harvested the irradiated light and generated electron-hole pairs. The photogenerated electron located on CB of γ-Fe₂O₃ migrated and recombined with photogenerated holes located on the valence band (VB) of g-C₃N₄. 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:

\[
\begin{align*}
\gamma - \text{Fe}_2\text{O}_3 / g - \text{C}_3\text{N}_4 + h\nu &\rightarrow \gamma - \text{Fe}_2\text{O}_3 (h^+_{\text{VB}}) \\
&+ g - \text{C}_3\text{N}_4 (e^-_{\text{CB}}), \\
\text{CO}_2 + 8h^+ + 8e^-_{\text{CB}} \cdot (g - \text{C}_3\text{N}_4) &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \\
8\text{H}_2\text{O} + 8h^+_{\text{CB}}(\gamma - \text{Fe}_2\text{O}_3) &\rightarrow 8h^+ \cdot +8 \cdot \text{OH}, \\
&8 \cdot \text{OH} \rightarrow 4\text{H}_2\text{O} + 2\text{O}_2. \\
\end{align*}
\]

4. Conclusions

In this work, different Z-scheme photocatalysts, γ-Fe₂O₃/g-C₃N₄, were synthesized by simple methods of calcination and impregnation-precipitation. XRD, IR, and XPS characterization of these materials confirmed the formation of composite structure of these photocatalysts, wherein γ-Fe₂O₃ grew on g-C₃N₄ surface. SEM analysis highlighted a good distribution of Fe on the surface of g-C₃N₄ support. The UV-DRS and PL spectra of the photocatalyst containing 10 wt.% γ-Fe₂O₃exhibited interface interaction of the two phases of γ-Fe₂O₃ and g-C₃N₄.

The catalytic performance of these materials was evaluated through the CO₂ photoreduction in the gaseous phase. Methane was found as the main product, while no trace of CO was observed. According to CH₄ production, the photocatalytic activity followed the following order: 15FeCN (2.9×10⁻⁴ μmol g⁻¹ h⁻¹) > 10FeCN (2.8×10⁻⁵ μmol g⁻¹ h⁻¹) > 5FeCN (2.1×10⁻⁵ μmol g⁻¹ h⁻¹) > 20FeCN (1.0×10⁻⁵ μmol g⁻¹ h⁻¹) > g-C₃N₄ (0.4×10⁻⁵ μmol g⁻¹ h⁻¹).

Hence, 10FeCN and 15FeCN composites had the highest photoactivity, which is approximately 7 times higher than that on bulk g-C₃N₄. This could be explained by a synergy combination and interaction of the two phases γ-Fe₂O₃ and g-C₃N₄, 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 CO₂ reduction on the basis of γ-Fe₂O₃ and g-C₃N₄.

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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