CoAl$_2$O$_4$–g-C$_3$N$_4$ Nanocomposite Photocatalysts for Powerful Visible-Light-Driven Hydrogen Production

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ABSTRACT: There is no doubt that the rate of hydrogen production via the water splitting reaction is profoundly affected to a remarkable degree based on the isolation of photogenerated electrons from holes. The precipitation of any cocatalysts on the substrate surfaces (including semiconductor materials) provides significant hindrance to such reincorporation. In this regard, a graphite-like structure in the form of mesoporous g-C$_3$N$_4$ formed in the presence of a template of mesoporous silica has been synthesized via the known combustion method. Hence, the resulting g-C$_3$N$_4$ nanosheets were decorated with varying amounts of mesoporous CoAl$_2$O$_4$ nanoparticles (1.0–4.0%). The efficiencies of the photocatalytic H$_2$ production by CoAl$_2$O$_4$-doped g-C$_3$N$_4$ nanocomposites were studied and compared with those of pure CoAl$_2$O$_4$ and g-C$_3$N$_4$. Visible light irradiation was carried out in the presence of glycerol as a scavenger. The photocatalyst also showed 5 times higher photocatalytic stability than that of CoAl$_2$O$_4$ or g-C$_3$N$_4$. The presence of CoAl$_2$O$_4$ (polymeric metal-free semiconductor with a band gap energy of approximately 2.7 eV, enabling it to absorb the visible light) was able to enhance the photocatalytic activity of the g-C$_3$N$_4$ surface. The 3.0% CoAl$_2$O$_4$–g-C$_3$N$_4$ nanocomposite had the optimum concentration. This photocatalyst showed extremely high photocatalytic activities that were up to 22 and 45 times greater than those of CoAl$_2$O$_4$ and g-C$_3$N$_4$, respectively. This photocatalyst also showed 5 times higher photocatalytic stability than that of CoAl$_2$O$_4$ or g-C$_3$N$_4$. The presence of CoAl$_2$O$_4$ nanoparticles as a cocatalyst increased both the efficiency and productivity of the CoAl$_2$O$_4$–g-C$_3$N$_4$ photocatalyst. This outcome was attributed to the mesostructures being efficient charge separation carriers with narrow band gaps and high surface areas, which were due to the presence of CoAl$_2$O$_4$.

1. INTRODUCTION

Currently, fossil fuels have been used to yield approximately 80% of energy used in the world; hence, an increasing number of environmental problems and crises have been declared. To overcome these problems, many ecofriendly sources of renewable energy have been classified as important for potential evolution and progress. Starting from this point, many researchers have developed the use of another type of fuel, that is, hydrogen produced from water splitting photocatalytic systems. These cells used are functional designs used to obtain clean energy. 1–3 In the past decade, a photoelectrochemical water splitting process for the production of hydrogen and oxygen in the presence of TiO$_2$ was reported by Fujishima and Honda. 4 This type of conversion involves the transformation of solar energy to another form of energy, chemical energy. This conversion can be carried out using different photocatalysts and constitutes an efficient and appropriate solution to overcome the most obvious energy and environmental problems.

In addition, two-dimensional semiconductor photocatalysts have received considerable attention as a result of the photocatalytic response that they exhibit to visible light. 5,6 Among these materials, graphitic carbon nitride, g-C$_3$N$_4$, is a polymeric metal-free semiconductor with a band gap energy ($E_g$) of approximately 2.7 eV, enabling it to absorb the visible light. It also exhibits many other characteristics, including nontoxicity, excellent stability, low cost, and versatile structural properties. 7,8 The drawbacks of g-C$_3$N$_4$ nanosheets have been widely reported in various studies. 7–9 Metal or nonmetal doping, semiconductor coupling, and construction of porous structures are some of the solutions used to avoid these drawbacks. 10–13 However, these proposed structures still suffer from a significant number of disadvantages, including the fast recombination of electron–hole pairs and insufficient absorption of visible light. Pristine g-C$_3$N$_4$ still displays a considerably limited performance with respect to photocatalytic activity. 14 Heterostructures containing g-C$_3$N$_4$ have been calcified to produce the best g-C$_3$N$_4$ compositions in the photocatalysis field, which noticeably promoted photocatalytic achievements among all previously known types. This outcome may result from the development of charge carrier separation, which occurs with each of the catalysts g-C$_3$N$_4$/Ag$_2$MoO$_4$, g-C$_3$N$_4$/Bi$_2$O$_3$, g-C$_3$N$_4$/perovskite oxide, and g-C$_3$N$_4$/TiO$_2$. 14–15 Combined

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semiconductors containing CoAl2O4 have been utilized for photocatalytic decomposition. CoAl2O4 also has a narrow band gap of 1.80 eV and exhibits a strong response to visible light.20–30 To the best of our knowledge, hydrogen production using CoAl2O4–g-C3N4 photocatalysts has not been reported. In this regard, heterostructure-based CoAl2O4 and mesoporous g-C3N4 for the formation of CoAl2O4–g-C3N4 were synthesized by simple sol–gel procedures. The chemical structures of the resulting products were confirmed using various techniques. The photocatalytic activities were evaluated for hydrogen production under visible light. Finally, a likely hydrogen production mechanism for the mesoporous CoAl2O4–g-C3N4 heterostructured nanocomposites was also proposed.

2. EXPERIMENTAL SECTION

2.1. Materials. EO106-PO70EO106 surfactant was used as a triblock copolymer with an average MW of 12,600 g/mol (F-127). Co(NO3)2·6H2O, Al(NO3)3·9H2O, acetic acid, hydrochloric acid, and ethanol were all purchased from Sigma-Aldrich.

2.2. Preparation of Mesoporous CoAl2O4. A sol–gel procedure was used to prepare mesoporous CoAl2O4 using a structure-directing agent, namely, the F127 triblock copolymer. The required material was synthesized using molar ratios on the order of 1:0.02:50:2.25:3.75 for CoAl2O4/F127/C2H5OH/HCl/CH3COOH, respectively. For example, a solution of 1.6 g of F127 in 30 mL of ethanol was stirred for 60 min. Next, 0.74 mL of HCl and 2.3 mL of CH3COOH were added to the previous solution, and magnetic stirring was continued for 30 min. Co and Al precursors were weighed out in a 1:2 ratio and added to the F127–CH3COOH mesophase with additional stirring for 60 min. A humidity chamber (40%) was used to hold the prepared mesophase at 40 °C for 12 h to reduce the amount of ethanol, leading to the formation of a gel. Further aging at 65 °C for 24 h was carried out in the resulting gel. Finally, the samples were calcined at 600 °C for 24 h and then cooled at a rate of 2 °C/min in order to eliminate the F127 surfactant and obtain the mesoporous CoAl2O4 as a final product.

2.3. Synthesis of Mesoporous g-C3N4. Urea and dicyandiamide were purchased from Sigma-Aldrich. High-surface-area mesoporous silica (HMS) (~500–1000 m² g⁻¹) was used to prepare g-C3N4 with a large surface area. Furthermore, pyrolysis of dicyandiamide and urea in air was performed. The detailed HMS preparation was easily executed as reported in the literature.31 Approximately 50 mL of distilled water and 1 g of HMS were dispersed for 30 min. A mixture of dicyandiamide (3 g) and urea (5 g) was carefully added to the abovementioned solution. Continuous stirring at 80 °C was done to enhance the dissolution of both components. The sample was dried overnight at approximately 80 °C to remove the excess water. Calcination was performed at 550 °C for 4 h. Next, the obtained material was immersed in a solution of NH4HF2 (2 M, 50 mL) with vigorous stirring for 24 h to drive out the HMS template. To release any contaminants adsorbed by the produced g-C3N4 nanoparticles, they were easily cleaned by washing several times with water. Thereafter, the synthesized pure material was dried by heating for 12 h at 100 °C.

2.4. Synthesis of Mesoporous CoAl2O4–g-C3N4 Nanocomposites. A water exfoliation method was used to synthesize CoAl2O4–g-C3N4 nanocomposites. The samples were synthesized as follows: 0.2 g of the as-prepared g-C3N4 was mixed with the required amount of mesoporous CoAl2O4 and the mixture was then sonicated in 400 mL of deionized water for 3 h at a power of 40 kHz. This procedure allowed the formation of thin-layered CoAl2O4–g-C3N4 products. A centrifugation process was used to collect the final products with the general abbreviation xCoAl2O4–g-C3N4, where the nominal molar content of CoAl2O4 was represented by “x” in this formulation (x = 1, 2, 3, and 4%).

2.5. Characterization. A JEOL JEM-1230 transmission electron microscope was used to determine the images of the prepared samples at 200 kV. Phase identification of the prepared materials was carried out using a Bruker AXS D8 Endeavor X-ray diffractometer. A Nova 2000 series Chromatex apparatus was used to determine the texture properties of the prepared photocatalysts. A Shimadzu system (RF-5301, Japan) was applied for the determination of the photoluminescence (PL) spectra of the prepared photocatalysts. The photocurrent intensity of the prepared photocatalysts was determined using a Zahner Zennium electrochemical workstation. The Fourier transform infrared (FT-IR) spectrum was measured in a KBr dispersion in the range of 400–4000 cm⁻¹ using a PerkinElmer spectrometer. A V-570 spectrophotometer (Jasco, Japan) was used to obtain the UV–vis–NIR spectra. The band gap values were determined by UV–vis diffuse reflectance spectroscopy.

2.6. Photocatalytic Tests. A certain quantity of the photocatalyst was suspended in 450 mL of H2O in the presence of a glycerol scavenger (10% vol) prior to the production of...
hydrogen. The required experiments were carried out under normal conditions at room temperature and atmospheric pressure. To overcome the effect of lamp heating on the reaction, a cooler made from quartz was used. Before photocatalysis began, nitrogen gas was bubbled for 30 min to eliminate oxygen dissolved in water. The area above the photoreactor was fixed with a 500 W xenon lamp producing visible light. The photocatalytic process for H₂ production started when the lamp was switched on. An Agilent GC 7890A gas chromatograph with nitrogen carrier gas was used to examine the quantity of H₂ produced over separate periods of time throughout the photocatalytic process. Further reactions, as additional confirmations of the optimized parameters, were carried out without a lighting source and without the desired photocatalyst.

3. RESULTS AND DISCUSSION

3.1. Investigation of the Product Samples. The X-ray diffraction (XRD) patterns for the pure g-C₃N₄ and CoAl₂O₄−g-C₃N₄ nanocomposites are illustrated in Figure 1A. The XRD diffraction patterns for pure CoAl₂O₄ are illustrated in Figure 1A,B. All the diffraction patterns obtained confirm the suggested structures. g-C₃N₄ was indicated by the diffraction peak observed at 27.4° in Figure 1A, according to card number JCPDS 044-0160. On the other hand, the XRD diffractogram assigned to pure CoAl₂O₄ corresponded to that in card number JCPDS 044-0160, as all essential peaks have been mentioned. These peaks are attributed to the CoAl₂O₄ phase, as shown in Figure 1B. The diffractograms also show that the g-C₃N₄ peak intensities showed considerable decreases as the CoAl₂O₄ content increased (1.0−4.0%). All CoAl₂O₄−g-C₃N₄ diffractograms show that no additional peaks related to pure CoAl₂O₄ were still present, which is attributed to the strong CoAl₂O₄ adhesion to the surface of g-C₃N₄ nanosheets. Additionally, this result was attributed to the lower CoAl₂O₄ content present in each composition. The XRD diffraction patterns also showed no additional equivocal peaks in any samples. This observation provides good evidence for the formation of the heterojunction nanocomposite between CoAl₂O₄ and g-C₃N₄ nanosheets.

The FT-IR spectra of the prepared pure CoAl₂O₄, g-C₃N₄, and CoAl₂O₄−g-C₃N₄ samples are illustrated in Figure 2. The

![Figure 2](https://example.com/figure2.png)
the pore filling of C$_3$N$_4$ with homogeneously dispersed particles on the surface.

Figure 6 illustrates the UV−vis spectra of the pure CoAl$_2$O$_4$, g-C$_3$N$_4$, and CoAl$_2$O$_4$−g-C$_3$N$_4$ photocatalysts with varying CoAl$_2$O$_4$ contents. The results confirm the absorption of visible light by all samples. The presence of CoAl$_2$O$_4$ also enhanced the width of both the absorption bands and band edges (Figure 6). UV−vis spectra were also used to determine the band gaps in all
cases, and the outcomes are listed in Table 2. The calculated values of the band gaps of g-C$_3$N$_4$ were heavily affected by the loading percentage of CoAl$_2$O$_4$ in the nanocomposites. Consistently, the band gap was reduced as the integrated weight percentage of CoAl$_2$O$_4$ on the surface of the g-C$_3$N$_4$ nanosheets was increased.

3.2. Evolution of H$_2$ via Visible Light Irradiation with the Obtained Catalysts. The targeted CoAl$_2$O$_4$–g-C$_3$N$_4$ nanocomposite photocatalysts were examined and compared with pure CoAl$_2$O$_4$ and g-C$_3$N$_4$ for hydrogen production upon irradiation with visible light. The initial reaction conditions included a photocatalyst content of 1.2 g/L, a reaction solution volume of 450 mL, the presence of glycerol (10 vol %), a Xe lamp (500 W) light source, and 9 h of irradiation at room temperature. The effect of different CoAl$_2$O$_4$ loadings from 1.0 to 4.0 wt % in the CoAl$_2$O$_4$–g-C$_3$N$_4$ nanocomposite on the quantity of hydrogen produced was studied and compared with the volumes obtained with both pure CoAl$_2$O$_4$ and g-C$_3$N$_4$, as illustrated in Figure 7A. The results revealed that the quantities of hydrogen produced were 810 and 400 μmol g$^{-1}$ for CoAl$_2$O$_4$ nanoparticles and g-C$_3$N$_4$ nanosheets, respectively. The use of various weight percentages in the CoAl$_2$O$_4$–g-C$_3$N$_4$ samples (1.0, 2.0, 3.0, and 4.0 wt %) used for the generation of hydrogen resulted in 1912, 9450, 13050, and 13,095 μmol g$^{-1}$ of hydrogen, respectively. The values are greater than those in some published works and less than those in other published works.

Thus, the results obtained indicated that the addition of CoAl$_2$O$_4$ nanoparticles significantly increased the extent of charge carrier separation and the surface area and decreased the band gap energy. Therefore, the CoAl$_2$O$_4$ content in the original photocatalyst showed a direct and positive effect on the H$_2$ yield until a certain loading weight (3.0%) was reached. Above this weight percentage, there was no additional effect on the yield, which did not respond to the addition of any extra photocatalyst in the reaction mixture. The production of hydrogen was increased to 8775, 10,125, 13,050, and 13,095 μmol g$^{-1}$ as a result of the gradual increase in the content of photocatalyst from 0.4 to 2.0 g/L, as shown in Figure 7B. These results may have occurred because the total number of active sites over the 3.0% CoAl$_2$O$_4$–g-C$_3$N$_4$ photocatalyst surface showed a noticeable increase. The level of hydrogen production was at least 15,120 μmol g$^{-1}$ when the photocatalyst content was greater than 2.4 g/L. This result may be due to an effective reduction in light penetration during the illumination process in the presence of a higher particle content in the reaction solution.

The measurements of both PL and transient photocurrent responses emphasize the results obtained in this study. As seen in Figure 8A, the PL spectrum of g-C$_3$N$_4$ shows the highest PL emission intensity among all samples. However, upon increasing the content of CoAl$_2$O$_4$ nanoparticles adsorbed over the g-C$_3$N$_4$ nanosheet surface, the PL emission intensity noticeably decreased, as illustrated. The observed PL emission intensities decreased as follows: g-C$_3$N$_4$ > CoAl$_2$O$_4$ > 1.0% CoAl$_2$O$_4$–g-C$_3$N$_4$ > 2.0% CoAl$_2$O$_4$–g-C$_3$N$_4$ > 3.0% CoAl$_2$O$_4$–g-C$_3$N$_4$ ≈ 4.0% CoAl$_2$O$_4$–g-C$_3$N$_4$. The CoAl$_2$O$_4$ nanoparticles have a high PL emission intensity and show a lower band gap energy (1.80 eV). Therefore, CoAl$_2$O$_4$ displays a low photocatalytic activity, and the recombination rate of the charge carriers in the presence of CoAl$_2$O$_4$ is very high. However, the photocatalyst effectiveness remains clear and apparent from the standpoint of photocatalytic activity. The photocurrent transient responses are given in Figure 8B. The results indicate that a lower photocurrent density was observed for g-C$_3$N$_4$, while a substantial increase occurred as the content of CoAl$_2$O$_4$ increased.
deposited on the surface of g-C3N4 increased. The photocurrent densities of the designed nanocomposites increased in the following order: g-C3N4 < CoAl2O4 < 1.0% CoAl2O4−g-C3N4 < 2.0% CoAl2O4−g-C3N4 < 3.0% CoAl2O4−g-C3N4 ≈ 3.0% CoAl2O4−g-C3N4. These outcomes also show that the success of the photocatalytic process for the CoAl2O4−g-C3N4 nanocomposites coincides closely with, and is proportional to, the results of the PL measurements.

Figure 9 shows the photocatalytic reproducibility of reused photocatalysts. As previously mentioned, the 3.0% CoAl2O4−g-C3N4 photocatalyst contains the optimum composition and shows substantial recycling potential. CoAl2O4−g-C3N4 may be recycled five times without exhibiting any significant defects. The fifth round affords 99.7% of the hydrogen evolution efficiency observed in the first use. From the above results, the optimized photocatalyst, 3.0% CoAl2O4−g-C3N4, demonstrated high stability, representing a highly applicable and valuable photocatalyst for the evolution of hydrogen. The XRD, UV−vis, and PL characterizations of the photocatalysts used also confirmed that the photocatalysts are stable. Additionally, inductively coupled plasma analysis of the solution remaining after catalysis confirmed that there were no Co or Al ions present, which confirmed the stability of the photocatalyst.

### 3.3. Suggested Mechanism for the CoAl2O4−g-C3N4 Nanocomposite

The separation of photoelectrons and holes in g-C3N4 nanosheet-reinforced CoAl2O4 nanoparticles has been explained by using the proposed mechanism below (Scheme 1). The following equations have been used to calculate the band energy levels

\[ E_{CB} = X - 0.5E_g + E_0 \]  
\[ E_{VB} = E_g + E_{CB} \]

where the valence and conduction bands are designated \( E_{VB} \) and \( E_{CB} \), respectively; the band gap value is given as \( E_g \) and is determined from optical measurements; the absolute electronegativity of the semiconductor is represented as \( X \); and the normal hydrogen electrode versus the redox-level measurement on the absolute vacuum scale is given as \( E_0 \) (\( E_0 = -4.5 \text{ eV} \)). A narrow band gap value for g-C3N4 nanosheets has been previously reported. Hence, a lower energy is required to excite the system. As a result of the photocatalytic irradiation, the
photogenerated electrons from pure g-C3N4 originate from the valance band and are promoted to the conduction band. However, in the CoAl2O4−g-C3N4 nanocomposite, CoAl2O4 accepts the excited electrons, thereby realizing the desired charge carrier separation. The energy of the CoAl2O4 conduction band (+0.06 eV) exhibits a more positive value than that of g-C3N4 (−1.13 eV). Additionally, the distribution of CoAl2O4 nanoparticles across the g-C3N4 nanosheets in the nanocomposites provides a noticeable increase in the number of active sites on the CoAl2O4−g-C3N4 photocatalyst surface; the photocatalytic activity is enhanced and hydrogen production is considerably accelerated relative to either CoAl2O4 or g-C3N4.

In total, the gross efficiency of the hole-scavenging action is greatly increased because the reaction solution contains glycerol as a scavenger. Protons are readily produced by this process and can additionally react with charge carriers to create more H2. Therefore, according to Scheme 1, water splitting can occur at 1.23 eV according to ref 50, which lies within the band gap of g-C3N4. CO2 formation is an obvious product of hole transfer from p-type CoAl2O4 to the attached g-C3N4, exhibiting an energy of +1.57 eV. These holes could produce protons and CO2 from the obvious decomposition of glycerol, as seen in previous literature reports.51 With the assistance of the separated electrons in the CB of supported CoAl2O4, hydrogen generation is made possible by the combination of two protons with electrons.

4. CONCLUSIONS

It is easy to prepare g-C3N4 nanosheets via a combustion process using a template material of mesoporous silica. Various CoAl2O4 nanoparticle contents (1.0−4.0%) were used as adsorbents on the g-C3N4 nanosheets as a result of the preparation process. The g-C3N4 sheets were affected by the dispersion of CoAl2O4 on the surface of the nanocomposites. Prevention of electron−hole reincorporation was significantly enhanced by the decrease in the band gap energy. The photocatalyst CoAl2O4−g-C3N4 (3.0 wt %) produced 18,225 μmol g⁻¹ of hydrogen, the maximum amount produced by the catalysts prepared with various compositions. In addition, a maximum photocatalyst weight of up to 2.0 g/L was used, with irradiation carried out for 9 h at room temperature. The synergetic effect of CoAl2O4 and g-C3N4 enhances the production of hydrogen. The CoAl2O4−g-C3N4 composites produce a significantly greater amount of hydrogen than either the g-C3N4 sheets or pure CoAl2O4 nanoparticles. A highly efficient, stable product has been developed in the form of CoAl2O4−g-C3N4. A maximum of five repeated cycles was also studied, without any loss of hydrogen evolution in any of the cycles.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00872.

Comparison between the quantum efficiencies of different photocatalysts and our prepared photocatalyst (PDF)

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Notes
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