Generation of Hydrogen Gas Using CuCr$_2$O$_4$-g-C$_3$N$_4$ Nanocomposites under Illumination by Visible Light

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1. INTRODUCTION

In recent years, numerous investigations were accomplished regarding impressive generation of hydrogen gas as a clean source of energy, using photocatalysis methods. Water is considered one of the most important sources of hydrogen gas production that could be used to generate hydrogen gas with the aid of photocatalysis. Nevertheless, such a process is characterized by the production of a low yield of hydrogen gas owing to the large capability of reversible reaction to occur between the produced gases. Consequently, many efforts have been performed to find another adequate and efficient source for hydrogen production. Among the efficient hydrogen sources that exhibited powerful results in hydrogen gas production via photocatalysis are biomass-originated compounds like bio-oil, sugars, alcohols, etc.1−3

In the same context, glycerol was used as an efficient and economical source of hydrogen generation via the aid of photocatalysis owing to its great abundance. The first trials to generate hydrogen gas from the biomass-originated compounds by photocatalysis methods were achieved over metal oxide semiconductors (like titania) decorated with noble metals. Nevertheless, confined efficiency was attained using these photocatalysts under illumination by visible light. So, efforts were directed to explore alternatives for such systems, and it was concluded that graphitic carbon nitride (g-C$_3$N$_4$), an n-type semiconductor, exhibited excellent efficiency toward the photocatalytic generation of hydrogen gas owing to its admirable characteristics like finite band gap energy, a reasonable ability to absorb visible light, large stability, and excellent electronic characteristics.5

Numerous kinds of g-C$_3$N$_4$ semiconductors of improved characteristics (surface, electronic, and morphological) were attained experimentally by different methods where each experimental process produces a certain kind of g-C$_3$N$_4$ semiconductor. Although acceptable properties are possessed by the synthesized g-C$_3$N$_4$ semiconductor, its photocatalytic performance when subjected to visible light is still confined owing to the ease of recombination amid the photoinduced charges in addition to its rather limited surface area. Consequently, the creation of g-C$_3$N$_4$-containing compounds acquiring enhanced photonic efficiency was of great interest to many researchers, which was accomplished via various pathways such as mixing g-C$_3$N$_4$ with another semiconductor and decoration of g-C$_3$N$_4$ with noble metals.6,9,10

Construction of heterojunctions made of g-C$_3$N$_4$ mixed with another semiconductor and preparation of a g-C$_3$N$_4$ semiconductor of improved surface texture via selecting the suitable preparation method are the most advantageous pathways to attain upgraded photocatalytic characteristics of g-C$_3$N$_4$. 

ABSTRACT: In this research, nanocomposites made of CuCr$_2$O$_4$-g-C$_3$N$_4$ accommodating distinct contents of CuCr$_2$O$_4$ (1−4 wt %) nanoparticles (NPs) were endorsed for hydrogen gas production after illumination by visible light in the presence of aqueous glycerol solution. The ultrasonication-mixture method was applied to assure the homogeneous distribution of CuCr$_2$O$_4$ NPs over synthesized mesoporous g-C$_3$N$_4$. Such nanocomposites possess suppressed recombination between the photoinduced charges. High-resolution transmission electron microscopy and X-ray photoelectron spectroscopy examinations affirmed the formation of CuCr$_2$O$_4$-g-C$_3$N$_4$ heterojunctions. The separation between the induced charges and the photocatalytic performance with the CuCr$_2$O$_4$ NP amount were investigated. The CuCr$_2$O$_4$-g-C$_3$N$_4$ heterojunction of 3 wt % CuCr$_2$O$_4$ content was documented as the optimal heterojunction with the extent of ten and thirty times as those registered for pure CuCr$_2$O$_4$ and g-C$_3$N$_4$ specimens, respectively, under illumination by visible light. The photocatalytic performance acquired by the diverse synthesized specimens was assessed not only by their effectiveness to absorb light in the visible region but also by their potential to separate the photoinduced charges.

Received: December 20, 2020
Accepted: January 27, 2021
Published: February 3, 2021
which, by their roles, increase the capability of the photocatalyst to absorb visible light. Briefly, improvement of the surface texture of g-C₃N₄ could be attained via either preparing g-C₃N₄ of a mesoporous structure utilizing an adequate template or via exfoliating. On the other hand, the progression of heterojunctions of boosted photocatalytic performance could be realized via mixing g-C₃N₄ with another semiconductor.

The basic principle of the latter method depends mainly on suppressing the recombination amid the photoinduced charges as well as enhancing the charges’ speed. g-C₃N₄ could be mixed with various materials like phosphides, selenides, oxides, and sulfides as adequate semiconductors to construct heterojunctions of advanced photocatalytic performance.

On the other hand, owing to the admirable properties possessed by CuCr₂O₄ such as confined band gap energy (1.40 eV), it was used as a successful semiconductor of p-type for diverse photocatalytic applications like supercapacitors, ceramic pigments, photocatalytic decomposition of some pollutants, some selective conversion reactions, and photocatalytic hydrogen generation. Consequently, the construction of heterojunctions made of g-C₃N₄ nanosheets decorated with diverse CuCr₂O₄ proportions is expected to introduce an advanced photocatalyst that is capable of absorbing a large quantity of visible light when illuminated, separating effectively the induced charges and enhancing the photocatalytic reaction rate.

In this investigation, novel CuCr₂O₄-g-C₃N₄ nanocomposites were synthesized via decoration g-C₃N₄ with diverse proportions of CuCr₂O₄ aiming to boost visible-light absorption and to accomplish enhanced photocatalytic generation of hydrogen gas from aqueous glycerol solution. Various techniques were applied to characterize and identify the synthesized specimens. Crystallinity and phase structure of the prepared samples were explored by X-ray diffraction (XRD), energy dispersive X-rays (EDX), and Fourier transform infrared spectroscopy (FTIR) analyses. Meanwhile, the surface area of the synthesized specimens was measured by applying the Brunauer—Emmett—Teller (BET) formula. The morphology and microstructure of the prepared specimens were explored by transmission electron microscopy (TEM) investigation. Chemical states of the diverse specimens were assessed by X-ray photoelectron spectroscopy (XPS) evaluations. UV—vis diffuse reflectance spectroscopy (UV—vis DRS) was performed to discover the optical characteristics of the synthesized specimens in addition to the estimation of the band gap values. On the other hand, the separation between the photoinduced charges was estimated by photoluminescence (PL) evaluation. The photocatalytic performance of the synthesized photocatalysts toward photocatalytic hydrogen gas production from glycerol was assessed.

2. MATERIALS AND EXPERIMENTAL ROUTINE

2.1. Materials. All chemicals and reagents were delivered from Sigma-Aldrich, and they were utilized in this examination without subsequent treatment. The main materials involved in this research were urea, chromium nitrate(III) nonhydrate, copper nitrate trihydrate, and dicyandiamide. On the other hand, a nonionic surfactant triblock copolymer (Pluronic L-64) with a molecular weight of 2900 g/mol was utilized as a template. Furthermore, the following materials were utilized as reagents: cyclohexane, absolute ethyl alcohol, acetic acid, hydrochloric acid, and formic acid.

2.2. Construction of Mesoporous CuCr₂O₄. This section describes the construction of mesoporous CuCr₂O₄ NPs with Pluronic L-64 as a nonionic surfactant. Initially, a mixture of absolute ethyl alcohol (30 mL) and Pluronic L-64 (0.4 g) was stirred for 1 h to assure homogeneous distribution of the template. Then, 5.5 and 15.4 g of copper nitrate trihydrate and chromium nitrate nonhydrate, accordingly, were introduced to the surfactant solution accompanied by prolonged stirring. After that, 2.5 and 0.8 mL of acetic acid and hydrochloric acid were therefore added to the previously attained system. The produced sol was kept at a temperature of 40 °C in a humidity of about 60%. Finally, the dried sol was maintained at 65 °C for 12 h to attain extra drying followed by heating for 3 h at 550 °C in air, and so, the mesoporous CuCr₂O₄ NPs were produced.

2.3. Construction of the Mesoporous g-C₃N₄ Nanosheets. In this part, mesoporous g-C₃N₄ nanosheets were synthesized via the aid of the previously prepared MCM-41 hard template. The method of preparation of the mesoporous g-C₃N₄ nanosheets is principally dependent on the calcination of a mixture containing dicyandiamide and urea in the presence of MCM-41 for 4 h at 550 °C. Initially, deionized water (50 mL) was used to assure the homogeneous dispersion of the MCM-41 template (1 g) via the aid of sonication for 30 min. After that, 5 and 3 g of urea and dicyandiamide, accordingly, were introduced gradually to the previously obtained mixture accompanied with stirring for 3 h at 80 °C. Then, the previous mixture was heated at 80 °C to remove water completely. Finally, the system was burnt at 550 °C in air for 4 h. The MCM-41 template was removed from the product via leaching the previously produced powder by 2 M NH₄HF₂ (50 mL) accompanied with prolonged stirring overnight. Finally, the unreacted species were removed from the produced mesoporous g-C₃N₄ nanosheets after washing with deionized water followed by drying at 100 °C overnight to attain the pure mesoporous g-C₃N₄ nanosheets.

2.4. Construction of the Mesoporous CuCr₂O₄-g-C₃N₄ Heterojunctions. In this section, mesoporous CuCr₂O₄-g-C₃N₄ heterojunctions accommodating 1, 2, 3, and 4 wt % CuCr₂O₄ NPs were obtained via dispersing CuCr₂O₄ nanoparticles on the surface of g-C₃N₄ nanosheets. Initially, a mixture of C₆H₁₄ (10 mL) and ethanol (20 mL) was utilized to disperse CuCr₂O₄ NPs in the presence of MCM-41 for 4 h at 550 °C. Similarly, CuCr₂O₄-g-C₃N₄ heterojunctions were obtained after drying the previously obtained solid powder for 12 h at 110 °C. Similarly, CuCr₂O₄-g-C₃N₄ heterojunctions accommodating other portions of CuCr₂O₄ nanoparticles were produced.

2.5. Identification and Characterization of the Prepared Materials. Crystallinity and phase structure of the prepared specimens were explored by X-ray diffraction (XRD). XRD analysis was performed via a Bruker X-ray diffractometer with Cu Kα radiation. Fourier transform infrared spectroscopy (FTIR) analysis was performed using a PerkinElmer Fourier transform infrared spectrometer (FTIR) in the range of 400—4000 cm⁻¹. Meanwhile, N₂ adsorption—desorption isotherms of some selected specimens were attained by utilizing a Chromatech instrument ( Nova 2000).
series). Furthermore, the surface area of the synthesized specimens was measured by applying the Brunauer–Emmett–Teller (BET) formula from the obtained isotherms. The morphology and microstructure of the prepared specimens were explored by transmission electron microscopy (TEM) investigation using a TEM instrument (JEOL-JEM-1230). Chemical states of the diverse specimens were assessed by X-ray photoelectron spectroscopy (XPS) evaluations that were attained by the application of a Thermo Scientific K-ALPHA spectrometer. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was performed to discover the optical characteristics of the synthesized specimens in addition to the estimation of the band gap values derived from Tauc’s method. DRS was performed by utilizing a Jasco V-570 spectrophotometer (Japan). On the other hand, separation between the photo-induced charges was estimated by photoluminescence (PL) evaluation that was performed using a Shimadzu RF-5301 spectrophotometer (a Xe lamp as an excitation source). The transient photocurrent of the synthesized samples was evaluated using a Zahner Zennium electrochemical system.

2.6. Photocatalytic Action Tests. The photocatalytic performance of the synthesized CuCr₂O₄–g-C₃N₄ photo-catalysts against photocatalytic hydrogen production in the presence of glycerol was assessed under illumination by visible light. In this test, a definite amount (50 mg) of the examined photocatalyst was dispersed in a 250 mL Pyrex reactor containing 200 mL of aqueous glycerol solution (10 vol%). The system was subjected to Argon gas bubbling to attain the desired stirring in addition to getting rid of the oxygen gas from the photocatalytic system. The system was left for a certain interval in the dark to permit the adsorption equilibrium to be reached. The photoreactor was then illuminated by visible light via light sourced from a Xe lamp (500 W) using a UV cutoff filter to assure the existence of radiation of a longer wavelength (>420 nm) only. The quantity of hydrogen gas produced at definite intervals (each 1 h) was estimated by utilizing a gas chromatograph (Agilent GC 7890A system) all over the reaction.

3. RESULTS AND DISCUSSION

3.1. Identification and Characterization of the Synthesized CuCr₂O₄–g-C₃N₄ Nanocomposites. Phase composition of the synthesized specimens was discovered from the interpretation of the X-ray diffraction patterns. Evidently, Figure 1 demonstrates X-ray diffraction patterns of the heterojunctions containing 0, 1, 2, 3, and 4 wt % CuCr₂O₄. The appearance of the peaks characterizing the (100) and (002) planes of C₃N₄ nanosheets at 2θ = 13.0 and 27.4°, respectively, in the X-ray diffraction patterns of pure g-C₃N₄ as well as of synthesized heterojunctions confirms the existence of pristine g-C₃N₄ within these specimens (JCPDS # 087-01526). The small proportions of the included CuCr₂O₄ NPs and/or their homogeneous distribution might be interpreted as the absence of the diffraction patterns of CuCr₂O₄ NPs within the X-ray diffractograms of the prepared heterojunctions. It could be derived from the data of Figure 1 that g-C₃N₄ retains its peaks’ position even after incorporation with CuCr₂O₄ NPs in the constructed heterojunctions, affirming that g-C₃N₄ conserves its graphitic layer arrangement. Nevertheless, exfoliation of g-C₃N₄ graphitic layers in the heterojunctions during sonication owing to the inclusion of CuCr₂O₄ NPs could be confirmed from the suppression of peak intensity assigned to the (002) plane of g-C₃N₄. The inset X-ray diffractogram of neat CuCr₂O₄ displays the peaks characterizing the planes assigned to the crystalline CuCr₂O₄ planes (JCPDS # 05-0657). FTIR spectral curves of the prepared specimens could provide extra knowledge about their phase composition (Figure 2). Neat g-C₃N₄ displays FTIR spectral bands at 808, 1639, 1567, 1407, 1319, 1240, and 3300 cm⁻¹. The occurrence of triazine units is declared from the existence of a spectral band at 808 cm⁻¹. Meanwhile, the presence of C=N–H and C=N heterocycles is asserted from the appearance of spectral bands at 1639, 1567, 1407, 1319, and 1240 cm⁻¹. The spectral peak at 3300 cm⁻¹ affirms the presence of the stretching vibration of −NH₂ or NH bonds. On the other hand, the spectral bands identifying pure g-C₃N₄ are retained in the FTIR spectral curves of the diverse synthesized CuCr₂O₄–g-C₃N₄ heterojunctions without the appearance of the bands assigned to CuCr₂O₄, confirming the conservation of the graphitic C=N lattice in the synthesized heterojunctions after incorporating g-C₃N₄ with CuCr₂O₄. Furthermore, the inclusion of higher contents of CuCr₂O₄ in the CuCr₂O₄–g-
C₃N₄ heterojunctions leads to the appearance of g-C₃N₄ spectral bands with declined intensities. This observation demonstrates that the functional groups (−NH₂, −NH−, and −N=−) of the g-C₃N₄ surface are affected owing to the inclusion of CuCr₂O₄ in such a way that permits the binding of the CuCr₂O₄ NPs on the g-C₃N₄ surface.³⁶,³⁷

XPS of the Cu 2p, Cr 2p, O 1s, C 1s, and N 1s energy levels could be used to identify the valence as well as the chemical states within the specimen made of 3 wt % CuCr₂O₄-g-C₃N₄ heterojunctions (Figure 3). XPS of the Cu 2p energy level shows that Cu²⁺ ions are the main chemical states of the Cu element that could be affirmed from the existence of Cu 2p³/₂ and Cu 2p₁/₂ energy levels of the peaks at 932.3 and 952.2 eV (Figure 3A). In addition, the inclusion of a peak with declined intensity in between the previously mentioned energy levels confirms the presence of Cu as Cu²⁺ ions (XPS of Figure 3A).²²,³⁸ On the other hand, XPS of the O 1s energy level shows that oxygen anions are the main chemical states of the oxygen element in CuCr₂O₄ that could be affirmed from the existence of the O 1s energy level of the peak at 531.3 eV (Figure 3B).³⁹ Furthermore, the existence of the Cr metal in the form of Cr³⁺ oxidation state has been affirmed from the inclusion of the peaks at the binding energies of 576.5 and 586.4 eV that are connected with Cr 2p³/₂ and Cr 2p₁/₂ energy levels (Figure 3C).³⁸ Meanwhile, the description of XPS of the C 1s energy level concludes the existence of sp² hybridization of C≡C or CN₁ bonds owing to the appearance of the peak at 287.8 eV in addition to the existence of sp² hybridization of N−C≡N bonds owing to the occurrence of the peak at 286.0 eV. Also, the existence of a C−C bond is confirmed from the occurrence of the peak at 284.6 eV, accordingly (Figure 3D).³⁹−⁴¹ The occurrence of the peaks assigned to C−N bonds.
bonds with relatively lower intensities affirms the inclusion of CuCr$_2$O$_4$ NPs to the g-C$_3$N$_4$ structure. XPS of the N 1s energy level shows the existence of C–N=C and N=C/C–NH$_3$ groups within the structure of the heterojunction that could be affirmed from the existence of the peaks at 400.6 and 398.4 eV, accordingly along with little displacement in comparison to the same peaks for XPS of neat g-C$_3$N$_4$. Latter information supports that CuCr$_2$O$_4$ NPs are successfully incorporated to the g-C$_3$N$_4$ surface.

Knowledge about the microstructure and morphology of the prepared 3% CuCr$_2$O$_4$-g-C$_3$N$_4$ nanocomposites as well as those of the neat ingredients could be provided by interpreting the TEM images of the examined specimens (Figure 4A–C). The successful synthesis of the nanosheet structure of C$_3$N$_4$ of partial aggregation along with some extent of porosity, owing to the utilization of an MCM-41 hard template in the preparation step, is affirmed from the TEM image of Figure 4A. The development of irregular particles with the dimension of 12–16 nm is clear in the TEM image of neat CuCr$_2$O$_4$ (Figure 4B). These particulates are partially aggregated to form clusters of a dimension larger than 100 nm. Figure 4C clarifies the successful homogeneous distribution of the spherical CuCr$_2$O$_4$ NPs (6–8 nm) over the exfoliated g-C$_3$N$_4$ surface within the TEM image of the heterojunction containing 3 wt% CuCr$_2$O$_4$. Actually, the suppressed particle dimension possessed by the dispersed CuCr$_2$O$_4$ NPs within the nanocomposite when connected with that of the neat ones is assigned to the sonication technique applied in the preparation process. The HRTEM image of the 3 wt% CuCr$_2$O$_4$-g-C$_3$N$_4$ heterojunction could provide information about the lattice planes of its components (Figure 4D). The existence of the (002) lattice plane of g-C$_3$N$_4$ is affirmed from the appearance of its characteristic lattice spacing of 0.280 nm. On the other hand, the existence of the (111) lattice plane of CuCr$_2$O$_4$ is confirmed from the appearance of its distinct lattice spacing of 0.476 nm. In addition, the successful construction of heterojunctions between the examined ingredients could be confirmed from their close connection in the illustrated image. The concluded remarks of TEM and HRTEM analyses agree with those of XRD investigation.

Surface and textural characteristics of the heterojunction containing 3 wt% CuCr$_2$O$_4$ as well as those of neat ingredients could be provided from the description of adsorption–desorption isotherms illustrated in Figure 5. In addition, Table 1 shows the surface area of the prepared specimens as considered from the BET formula. A complex mesoporous matrix of neat g-C$_3$N$_4$ is confirmed from the progression of a type IV isotherm along with an H3 hysteresis loop. Interestingly, Table 1 shows that neat g-C$_3$N$_4$ possesses a surface area of 180 m$^2$/g, which is much larger than that possessed by the conventional one. On the other hand, mesoporous texture of neat CuCr$_2$O$_4$ NPs that possess a large surface area (205 m$^2$/g), owing to the utilization of a Pluronic L-64 template during their synthesis, could be affirmed from...
the data of Figure 5 and those of Table 1. The occurrence of pores with a cylindrical shape within CuCr2O4 NPs is illustrated from the presence of a well-identified H3 hysteresis loop in their isotherm. The isotherm acquired by the synthesized heterojunction is of a similar feature as that of neat g-C3N4 with suppressed hysteresis. Such observation illustrates the mesoporous texture with wedge-shaped pores of the heterojunction that might have progressed during exfoliation. The upgrading of the specific surface area acquired by the heterojunction containing a larger quantity of CuCr2O4 NPs is clear from the magnitudes of Table 1. Such conclusions agree with those attained by previous analyses, and all of them support the successful exfoliation of g-C3N4 layers in addition to the successful interaction of CuCr2O4 NPs with g-C3N4.

UV−vis DR spectra of the synthesized specimens could provide information about the optical absorption response of these specimens (Figure 6). An intensified absorption band in the visible range with an absorption edge at 460 nm is obvious within the spectral curve of g-C3N4. Figure 6 affirms that absorption possessed by the synthesized heterojunctions is not only advanced toward a longer wavelength (visible light) but also occurred with greater intensity owing to the connection between CuCr2O4 NPs and g-C3N4. This advancement is magnified with the increase in the CuCr2O4 portion and optimized at the ratio of wt % CuCr2O4.

Tauc’s method was applied to formulate the band gap energy of the diverse specimens to provide knowledge about the heterojunctions established between g-C3N4 and CuCr2O4 within the constructed CuCr2O4@g-C3N4 heterojunctions (Table 2). This observation confirms the successful establishment of heterojunctions of lower band gap energy and so enhanced photocatalytic performance in the visible region.

3.2. Capability of the Photocatalytic H₂ Gas Generation. In this section, the capability of the synthesized photocatalysts toward hydrogen gas generation when exposed to visible light is shown in Figure 7. The decreased capability of neat g-C3N4 and neat CuCr2O4 toward hydrogen gas generation is obvious from the data of Figure 7, which could be credited to the great ability of the induced charges to be

Table 1. BET Surface Area of the Prepared Specimens

| samples                  | \( S_{\text{BET}} \) (m²/g) |
|--------------------------|------------------------------|
| g-C3N4                   | 180.00                       |
| 1.0 wt % CuCr2O4@g-C3N4  | 184.00                       |
| 2.0 wt % CuCr2O4@g-C3N4  | 185.00                       |
| 3.0 wt % CuCr2O4@g-C3N4  | 187.00                       |
| 4.0 wt % CuCr2O4@g-C3N4  | 190.00                       |
| CuCr2O4                  | 205.00                       |

Figure 7. \( \text{H}_2 \) generation capability adopting the diverse prepared specimens.
recombined in these specimens. On the contrary, the capability of hydrogen gas generation is boosted over the CuCr₂O₄-g-C₃N₄ heterojunctions in comparison to those of g-C₃N₄. Furthermore, the heterojunctions of large CuCr₂O₄ portions (3 wt %, 10,776 μmol/g) display the greatest photocatalytic capability of hydrogen gas generation in comparison to other specimens. Subsequent inclusion of CuCr₂O₄ (greater than 3 wt %) displays no further improvement in the capability of hydrogen gas generation. Actually, the heterojunction containing 3 wt % CuCr₂O₄ is capable of photocatalyzing hydrogen gas generation (10,776 μmol/g) thirty times of that possessed by pure g-C₃N₄ (360 μmol/g).

The consequence of the photocatalyst dose (0.4−2.4 g/L) for the optimized heterojunction (3% CuCr₂O₄-g-C₃N₄) on the ability of hydrogen gas generation is assessed (Figure 8A).

![Figure 8](image)

**Figure 8.** (A) Consequence of the 3 wt % CuCr₂O₄-g-C₃N₄ load. (B) Stability of the 3 wt % CuCr₂O₄-g-C₃N₄ heterojunction.

The capability of the optimized heterojunction to produce hydrogen gas is improved continuously, reaching its maximum magnitude (12,600 μmol/g), with the increase in the photocatalyst dose up to 1.6 g/L. This optimized dose (1.6 g/L) represents the greatest number of exposed active sites without pronounced hindrance of visible-light absorption that might take place owing to the possible particle aggregation when a higher dose is applied.44

The capability of the regenerated 3 wt % CuCr₂O₄-g-C₃N₄ photocatalyst to photocatalyze the hydrogen generation reaction many times (5 runs) was assessed (Figure 8B). The data illustrates that excellent efficiency is attained by the recycled photocatalyst even after application for five times, affirming the greater stability and applicability of such a nanocomposite.

3.3. Photocatalytic Performance and the Proposed Mechanism of CuCr₂O₄-g-C₃N₄ Heterojunctions. Obviously, the improved photocatalytic performance of the examined heterojunctions toward hydrogen generation when exposed to visible light is connected with their boosted visible-light absorption (Figure 6), which is supported by their declined band gap values (Table 2). These factors operate in the same direction, which is the enhancement of the photocatalytic performance of the progressed heterojunctions owing to the improvement of the generation of the photoinduced charges (especially for the specimens of higher CuCr₂O₄ contents).

Not only the capability of the photocatalyst to absorb visible light and/or to induce the generation of the charges but also their performance to separate the induced charges govern the photocatalytic efficiency. So, PL emission spectra of the examined photocatalysts were assessed (Figure 9). The improved ability of the CuCr₂O₄-g-C₃N₄ heterojunctions to separate the induced charges and to hinder their recombination in comparison to those of the pure components is obvious from the suppressed PL emission spectra attained by these heterojunctions (Figure 9).45,46 The CuCr₂O₄ content within the formulated heterojunction plays an important role in the PL emission suppression, which becomes more pronounced for the heterojunction of 3 wt % CuCr₂O₄. So, the developed heterojunctions between the pure components (g-C₃N₄ and CuCr₂O₄ NPs) of the CuCr₂O₄-g-C₃N₄ nanocomposite, optimized at the 3 wt % CuCr₂O₄ content, succeed to hinder the recombination between the induced charges.

The photocurrent response of the prepared specimens was assessed in order to examine the separation between the induced charges (Figure 9B). Enhanced photocurrent density is acquired by the specimens made of CuCr₂O₄-g-C₃N₄ heterojunctions of various contents of CuCr₂O₄ NPs in comparison to those of the pure components.47 Furthermore, the improvement of the photocurrent response is found to be controlled by the CuCr₂O₄ content that becomes maximum at 3 wt % CuCr₂O₄. Subsequent inclusion of CuCr₂O₄ NPs displays no extra improvement in the photocurrent density values, affirming that the nanocomposites that accommodate 3 wt % CuCr₂O₄ NPs are capable of separating between the induced charges with the maximum efficiency in comparison to other specimens.

Previous investigations affirm that the surface area of the examined photocatalysts, separation between the induced charges, dispersion of the CuCr₂O₄ NPs, recombination between the induced charges, and the capability of the photocatalysts to absorb visible light are the most essential parameters that govern the photocatalytic performance.

The constructed CuCr₂O₄-g-C₃N₄ heterojunction is composed of two semiconductors: an n-type semiconductor (g-C₃N₄) and a p-type semiconductor (CuCr₂O₄), and so, two mechanisms are proposed to describe the separation between the induced charges. The first proposed mechanism is type II p-n. Meanwhile, the second mechanism is known as an S-scheme or Z-scheme mechanism.48,49 Evidently, the potentials possessed by the valence and conduction bands govern immensely the pathway of the induced charges and so affect
the redox reaction mechanism involving hydrogen production from glycerol solution. The band edge position of both valence (\(E_{VB}\)) and conduction (\(E_{CB}\)) bands of the components of the CuCr\(_2\)O\(_4\)-g-C\(_3\)N\(_4\) nanocomposite could be assessed from the following formula

\[
E_{CB} = X - E_e - 0.5E_g
\]

\[
E_{VB} = E_{CB} + E_g
\]

where \(E_g\) is the band gap of the semiconductor, \(X\) is the electronegativity, and \(E_e\) is the energy of the free electron (4.5 eV). The assessed potentials of valence bands of g-C\(_3\)N\(_4\) and CuCr\(_2\)O\(_4\) are in the sequence of +1.56 and +1.92 eV, while those of the conduction bands are in the sequence of −1.12 and +0.52 eV. The potential possessed by the conduction band of CuCr\(_2\)O\(_4\) is lower than that of g-C\(_3\)N\(_4\) and so, the photoinduced electrons are transferred from the conduction band of g-C\(_3\)N\(_4\) to that of CuCr\(_2\)O\(_4\). The proposed mechanism of such transference could be stated as a Z-scheme rather than a type II p-n heterojunction one. This conclusion could be attributed to the fact that the redox potential of hydrogen ion—hydrogen conversion reaction is much larger than that of the transferred electrons on the CuCr\(_2\)O\(_4\) conduction band (Figure 10). We can summarize the proposed mechanism as follows:

when the nanocomposite is exposed to visible light, electrons are induced and moved from the valence bands of the pure ingredients to the conduction bands, and at the same time, holes are preserved in the valence bands. After that, induced electrons are moved from the conduction band of g-C\(_3\)N\(_4\) to that of CuCr\(_2\)O\(_4\) whereas holes are moved from the valence band of CuCr\(_2\)O\(_4\) to that of g-C\(_3\)N\(_4\), bringing about enhanced separation as well as suppressed recombination between the photoinduced charges. So, hydrogen gas could be generated via reduction of hydrogen ions by the accumulated electrons in CuCr\(_2\)O\(_4\) or via oxidation of glycerol via the accumulated holes in g-C\(_3\)N\(_4\). In conclusion, the synthesized heterojunctions displayed upgraded photocatalytic performance toward hydrogen production from glycerol solution.

4. CONCLUSIONS

A simple ultrasonication-assisted routine was adopted to synthesize CuCr\(_2\)O\(_4\)-g-C\(_3\)N\(_4\) heterojunctions of varied proportions of CuCr\(_2\)O\(_4\). The synthesized heterojunctions displayed upgraded physicochemical and photocatalytic features like expanded surface area, adequate dispersion of the CuCr\(_2\)O\(_4\) NPs over the g-C\(_3\)N\(_4\) surface, a large capability to absorb visible light, and suppressed recombination as well as boosted separation between induced charges. The quantity of CuCr\(_2\)O\(_4\) within the heterojunction played an important role in controlling the photocatalytic characteristics of the synthesized heterojunctions reaching its optimum content at 3 wt %. The prepared heterojunctions displayed upgraded performance toward hydrogen generation from glycerol solution when subjected to visible light in comparison to those of the pure ingredients. The 3 wt % CuCr\(_2\)O\(_4\)-g-C\(_3\)N\(_4\) heterojunction was able to photoproduce hydrogen from glycerol solution thirty times of that produced by pure g-C\(_3\)N\(_4\). The transference of the induced charges through the developed heterojunctions could be described by a Z-scheme mechanism.

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ACKNOWLEDGMENTS

This project was funded by the Deanship of Scientific Research (DSR) at the King Abdulaziz University, Jeddah, Saudi Arabia under grant no. G: 37-130-1441. The authors therefore acknowledge DSR for technical and financial support.

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