

Improved Visible-Light Photocatalytic Activity of g-C₃N₄/CuWO₄ Nanocomposite for Degradation of Methylene Blue [†]

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Abstract: In recent years, heterogeneous semiconductor photocatalysts have attracted great attention in the arena of environmental remediation and solar energy conversion; because, sunlight energy is a renewable, cheap, and accessible source of energy and also converting solar energy to chemical energy can be declined the energy crisis and global warming. Development of visible light heterogeneous photocatalysts with high efficiency and chemical stability is important for catalysis researchers. Among different types of semiconductor material, polymeric graphitic carbon nitride (g-C₃N₄) with a medium band gap of about 2.7 eV has been widely applied in photodegradation of organic pollutants, water splitting, CO₂ reduction, solar cells, energy storage, and organic synthesis. Unfortunately, due to the high rate recombination of photoinduced carriers, the photocatalytic performance of the bare g-C₃N₄ is still poor. Hence, many strategies including metal doping, noble metal deposition, and coupling with semiconductor composites have been employed to modify g-C₃N₄. Herein, we report the synthesis of g-C₃N₄/CuWO₄ nanocomposite via a hydrothermal process. The prepared visible-light-driven nanocomposite exhibited an enhanced photocatalytic activity compared with bare g-C₃N₄ for the degradation of methylene blue (MB) under LED light irradiation.

Keywords: visible-light-driven photocatalyst; g-C₃N₄/CuWO₄; photodegradation; pollutants

1. Introduction

Over the recent past, the global energy crisis and environmental concerns have attracted increasing attention of scientists. Hence, considerable research efforts have focused on visible-light-active photocatalysts for the degradation of organic pollutants and H₂ production due to the increasing demand for environmental care and clean energy harvesting [1]. Development visible light-driven photocatalysts with high effectiveness and good stability has been a hot spot in the field of photocatalysis. Various semiconductors, such as metal oxides, sulfides, carbon-based materials have been used to improve the solar energy utilization capability in the photocatalytic systems [2,3]. Among various types of semiconductors, polymeric graphitic carbon nitride (g-C₃N₄) as the most stable allotrope of carbon nitride has been regarded as a suitable candidate for visible-light-driven photocatalyst because of its unique optical properties, well-suited band gap (2.7 eV), physicochemical stability, and simple preparation [4]. Recently, g-C₃N₄ has useful applications in hydrogen evolution from water splitting, degradation of organic pollutants, CO₂ reduction, energy storage, antibacterial activity [5–9]. However, the pristine g-C₃N₄ has shown low photocatalytic efficiency because of the insufficient visible-light absorbance, and fast recombination of photo-generated charge carriers [10].

To improve the photocatalytic performance of the pristine $g\text{-C}_3\text{N}_4$, many efforts have been undertaken, which mainly include doping of heteroatoms and metals, construction of the mesoporous structure, copolymerization with organic molecules, and coupling with other semiconductors [11–14]. Among these strategies, the construction of heterojunctions with other semiconductors displays a great potential to improve the photocatalytic efficiency of $g\text{-C}_3\text{N}_4$. CuWO_4 is the ideal choice of semiconductor which only employs holes for oxidation reaction. The band edges of the graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) lies in more negative region where generation of superoxide radicals is prevalent, conversely the band edges of CuWO_4 lies in more positive region where generation of hydroxyl radicals is in excess. This feature of these semiconductors is appropriate for the Z-scheme photocatalytic system [15]. Therefore, a great deal of interest has been focused on the development of environmentally, and recyclable benign photocatalytic methods for the degradation of organic dyes [16,17]. In the current research, we present the synthesis of the $g\text{-C}_3\text{N}_4/\text{CuWO}_4$ photocatalyst and investigate its photocatalytic performance for the degradation of methylene blue as an organic pollutant under visible light.

2. Experimental

2.1. General

Reagents and chemicals were all purchased from Aldrich, Merck and Fluka. Spectra of FT-IR were recorded by the method of KBr pellet on a Shimadzu IR-470 spectrometer. Energy dispersive X-ray spectroscopy (EDS) was used to investigate the composition and structure of the samples and was recorded on Numerix DXP-X10P. UV-visible spectra of the samples were recorded on a UV-visible spectrophotometer (UV-1700 Shimadzu, Japan) at a wave length range of 200–800 nm.

2.2. Preparation of Bulk $g\text{-C}_3\text{N}_4$

Bulk $g\text{-C}_3\text{N}_4$ powder was prepared according to the reported method [18]. The melamine was heated at 550 °C in a furnace for 4 h in static air at a ramp of 2.5 °C min^{−1} and the obtained yellow solid was grinded into powder in a mortar.

2.3. Preparation of $g\text{-C}_3\text{N}_4/\text{CuWO}_4$

$g\text{-C}_3\text{N}_4/\text{CuWO}_4$ was prepared by a hydrothermal method. First, 0.811 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3 mmol) and 0.990 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (3 mmol) were dissolved in 30 mL of deionized water. The solution was stirred for 2 h. Then, the synthesized bulk $g\text{-C}_3\text{N}_4$ suspension was added into the above solution, and the mixture was put into an ultrasonic vibration generator for 1 h. The above mixture was then poured into a 50 mL Teflon-sealed autoclave and heated to 200 °C for 18 h. After that, the precipitate was washed with distilled water and ethanol and collected by centrifugation. The obtained precipitate was dried at 100 °C for 12 h.

2.4. Photocatalytic Degradations

In photodegradation process, 50 mg of the $g\text{-C}_3\text{N}_4/\text{CuWO}_4$ photocatalyst was used for degradation of 50 mL aqueous solution of methylene blue MB with 10 ppm concentration under 250 W high pressure mercury lamp irradiation. Before irradiation of light, the suspension was stirred in the dark condition for 30 min to achieve the adsorption-desorption equilibrium between the MB and the photocatalyst. All the photocatalytic experiments were carried out under the same conditions at 25 °C. In the defined intervals (30 min), the sample of suspension (ca. 3 mL) was taken, centrifuged and then the absorption spectrum changes of MB were measured to monitor the MB photodegradation.

3. Results and Discussion

The FT-TR spectra of the $g\text{-C}_3\text{N}_4/\text{CuWO}_4$ is illustrated in Figure 1, which shows that the main chemical structure of the $g\text{-C}_3\text{N}_4$ was remained after coupling with CuWO_4 .

The Energy-dispersive X-ray spectroscopy (EDS) of the g-C₃N₄/CuWO₄ heterostructure in Figure 2 confirmed the presence of Cu, C, N, O and W.

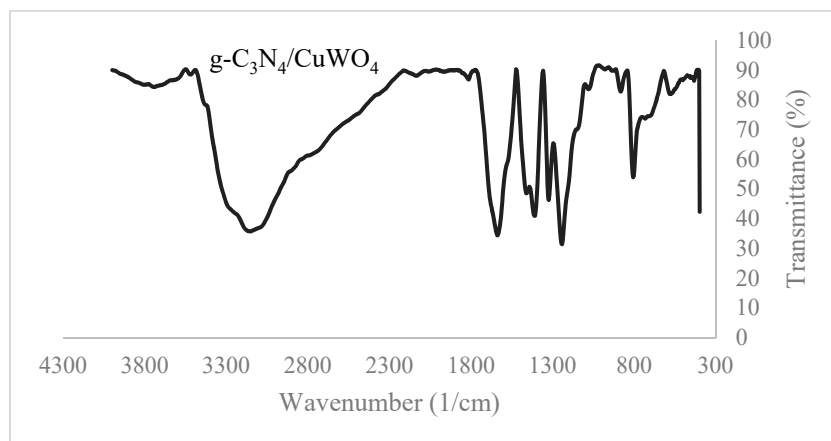


Figure 1. FT-IR spectra of the g-C₃N₄/CuWO₄.

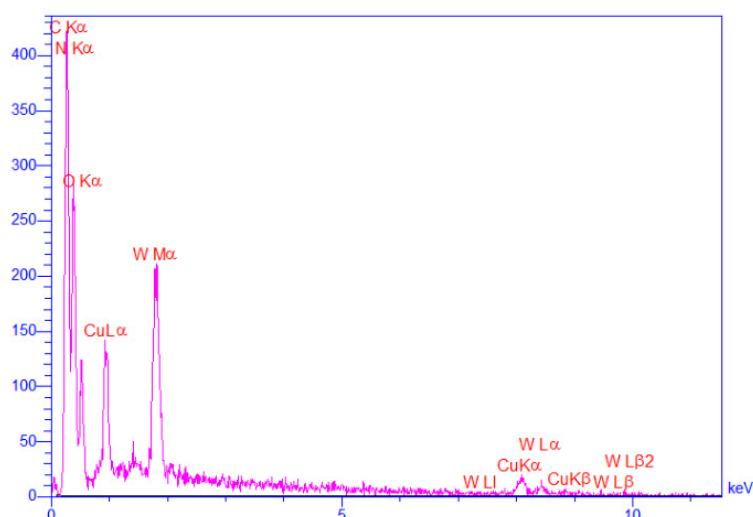


Figure 2. EDS spectra of the g-C₃N₄/CuWO₄.

UV-visible diffuse reflectance spectra were also recorded to investigate the light harvesting ability of the heterostructures and respective band gap calculations (Figure 3). The band gaps of the photocatalysts can be calculated by the equation [19]:

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

where α , A , $h\nu$, and E_g are the optical absorption coefficient, a proportionality constant, a photon energy and the band gap energy respectively. The value of n depends upon the type of optical transition of the semiconductors: for direct transition, value of n is 1 where as for the indirect transition the value of n is 4. Thus, the band gap of the bulk g-C₃N₄ and g-C₃N₄/CuWO₄ calculated from Tauc plot was estimated to be about 2.83 eV and 2.78 eV respectively (Figure 3a,b).

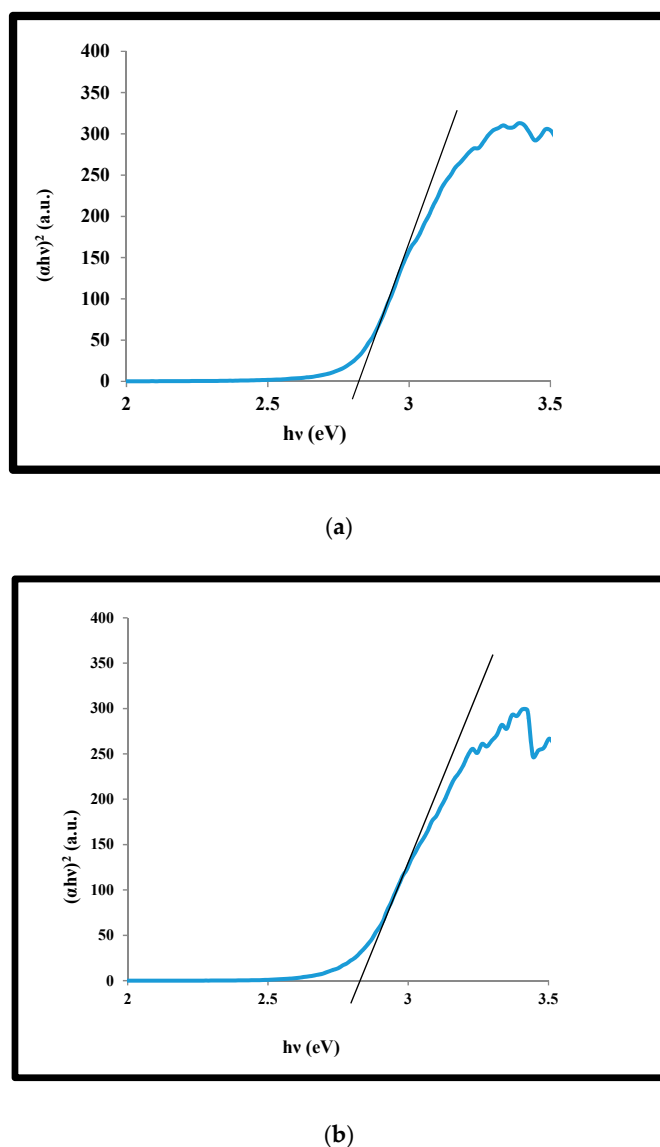


Figure 3. Tauc plot for the determination of band gap for the bulk $g\text{-C}_3\text{N}_4$ (a), and $g\text{-C}_3\text{N}_4/\text{CuWO}_4$ (b).

The photocatalytic activity of the $g\text{-C}_3\text{N}_4/\text{CuWO}_4$ were evaluated through methylene blue (MB) degradation under visible light irradiation, and the results are shown in Figure 4. From Figure 4, before light irradiation, 48.0% of MB was removed on $g\text{-C}_3\text{N}_4/\text{CuWO}_4$ after 60 min. After visible light illumination for 180 min, about 97.0% of MB was removed in the presence of $g\text{-C}_3\text{N}_4/\text{CuWO}_4$.

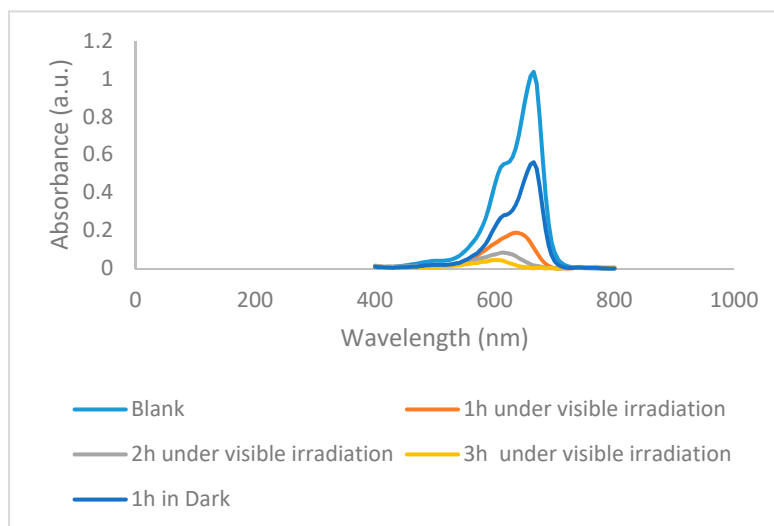


Figure 4. Photocatalytic activity of the g-C₃N₄/CuWO₄.

4. Conclusions

In this study, we have demonstrated the synthesis of a superior visible-light-driven photocatalyst

g-C₃N₄/CuWO₄ by a hydrothermal method. Under visible light irradiation, the photocatalyst g-C₃N₄/CuWO₄ showed an enhanced photocatalytic performance than g-C₃N₄ which can be attributed to the contribution of CuWO₄ for the efficient separation and easy transfer of photogenerated electron-hole pairs. More than high efficiency, excellent stability in the photocatalysis process and easy separation of nanophotocatalyst are from main advantageous of (g-C₃N₄/CuWO₄) in the photodegradation reaction.

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