



Comparison of the photocatalytic effect of magnetic nanocomposites: $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ and $\text{CoFe}_2\text{O}_4/\text{CdS}$ in the degradation of azo dyes

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Abstract

In this study, visible-light-driven cobalt ferrite/cadmium sulphide and cobalt ferrite/graphitic carbon nitride photocatalyst was successfully synthesized via precipitation technique. Cobalt ferrite were decorated on the surface of as-prepared $\text{g-C}_3\text{N}_4$ and cadmium sulphide via the precipitation technique. The structure, morphology, optical, and magnetic properties of the samples were studied by various techniques. The photocatalytic capability was assessed against methylene blue (MB) dye as a model pollutant under visible light irradiation. Compared to pure CoFe_2O_4 and $\text{g-C}_3\text{N}_4$ and CdS nanostructures, the $\text{CoFe}_2\text{O}_4/\text{CdS}$ and $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite showed higher photodegradation of MB. An external magnetic field was able to be used to separate the nanocomposite from the treated solution due to the magnetic properties of the CoFe_2O_4 component. The present study offers a facile method for designing $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite as a photocatalyst with high efficiency and good separability for environmental remediation applications.

Keywords: “Photocatalyst”, “ $\text{g-C}_3\text{N}_4$ ”, “degradation”, “ CoFe_2O_4 ”, “ CdS ”.

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Introduction

Developing effective technologies to eliminate toxic soluble organic pollutants, which pose significant threats to the environment and human health, is essential to purifying water. Nowadays, high population growth and rapid industrialization cause huge water demand in both industry and urban sectors, which enhances pressure on freshwater resources. Meanwhile, various industrial activities have released cistent pollutants and toxic compounds into the surface and underground water resources, which are dangerous to the organisms and the environment. Wastewater containing these organic pollutants can be treated using a variety of methods [1]. Because of their high photosensitivity, environmentally friendly features, and low cost, semiconductor-based photocatalysis is considered a promising technique alongside conventional methods of treating organic contaminants in wastewater [2-4]. In photocatalysis, semiconductors can be excited under UV/Vis irradiation to generate electron-hole pairs. Eventually, hydroxyl radicals, as a potent oxidizing agent for decomposing environmental pollutants, can be caused by photo-produced holes [5-6]. However, designing photocatalyst materials with high activity and operational feasibility remains a substantial challenge. cadmium sulfide (CdS), belonging to the II-VI group, is one of the first semiconductors discovered. It has been of growing interest due to its suitable band gap (approximately 2.4 eV), strong photoresponse in the visible region, and prominent applications, such as solar cells, light emitting diodes, environmental and biological sensors, water purification systems, improved performance in UV-shielding, flame retardant, scratch resistance, chemical resistance, nano-medicine, UV detectors and ultrasonic sensors. The graphitic carbon nitride (g-C₃N₄) has attracted considerable attention as a nonmetallic, environmentally friendly photocatalyst that responds to visible light in the remediation field [7,8]. One of the most critical aspects of photocatalytic applications is the possibility of reusing the catalyst. Some traditional separation rotes, like filtration and coagulation, lead to high energy consumption and severe catalyst loss. Incorporating magnetic nanomaterials into photocatalyst structures is an efficient method of photocatalyst separation from treatment media. Recently, magnetically recyclable hybrid photocatalysts have attracted significant attention as potential candidates for reusability issues. Cobalt ferrite nanoparticles have conceived considerable attention because of its predominance in high coercivity, moderate saturation magnetization, magnetic anisotropy, adequate mechanical hardness as well as suitable chemical stability. Magnetic materials are subject to intense research because of their potential use in catalysis, biomedicine and environmental remediation. It is well known that CoFe₂O₄ is a p-type semiconductor with a band gap of 0.8 eV, and endowed with strong adsorption in the UV and visible light region [9-12]. Due to their small size, the nanoparticles exhibit novel material properties which largely differ from the bulk solid state. A better understanding of magnetism is crucial not only for basic physics but also because of the great technological importance of ferro-magnets in information storage, colour imaging, bio-processing, and ferro-fluids [12-14]. Magnetic properties of a material usually are very sensitive to its shape due to the dominating role of anisotropy in magnetism. The magnetic studies show that the blocking temperature, saturation, and remanent magnetization of nanocrystals are determined by the size. However, the shape of the nanocrystals is a dominating factor for the coercivity of nanocrystals. Herein, a low-cost and straightforward rote was employed to synthesize CoFe₂O₄/CdS and CoFe₂O₄/g-C₃N₄ magnetic nanocomposite for the degradation of methylene blue dye under visible-light irradiation. The structure, microstructural and optical properties of the prepared photocatalysts were studied by various characterization methods. Results suggested that photocatalysts prepared via an efficient and simple method can be effectively used to remove organic dye pollutants.

Experimental

• Synthesis of $\text{CoFe}_2\text{O}_4/\text{CdS}$ nanocomposite

0.1 g of CoFe_2O_4 was dispersed in 50 ml of deionized water by ultrasonic waves (150 W, 60min). Then 0.2 g of $\text{Cd}(\text{NO}_3)_2$ and 50 ml of deionized water was added to the mixture containing CoFe_2O_4 . After 20 minutes the mixture of 0.05 g of thiourea and 100 ml of deionized water was transferred into the mixture. NaOH solution was slowly added to the aqueous solution and was stirred for 15 minutes.

• Synthesis of $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite

The $\text{g-C}_3\text{N}_4$ nanosheets were synthesized using melamine as a precursor and heated to 540 °C in a cube furnace with a heating rate of 3 °C min⁻¹ for 4h. After that, the obtained powder was placed in a furnace at 520 °C at a rate of 10 °C/min for 4 h. $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ was synthesized by an in-situ chemical precipitation procedure. The preparation steps are shown in Fig. 1. $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ was synthesized via a chemical precipitation route. Briefly, 0.4 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.2 g $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 100 ml of deionized water. Then, the prepared $\text{g-C}_3\text{N}_4$ (0.8 g) was mixed with the above solution and irradiated by ultrasound for 120 minutes. Following that, NaOH solution (1 M) was added slowly until the solution pH was adjusted to 10. The prepared precipitate was centrifuged, washed, and dried at 90 °C for 24 h.

Results Discussion

The structure and composition of the CoFe_2O_4 nanoparticles was investigated. Figure. 1a shows XRD pattern of sample including cobalt ferrite nanoparticles. The XRD pattern of CoFe_2O_4 reveals the typical diffraction pattern of pure cubic phase (JCPDS No.: 22-1086) with Fd-3m space group which is consistent with pure cobalt ferrite. The composition of the $\text{CoFe}_2\text{O}_4\text{-CdS}$ nanocomposite was also investigated. Presence of both cubic phase (JCPDS No.: 22-1086) and pure hexagonal phase (JCPDS No.: 75-1545) was confirmed and are illustrated in Figure. 1b. The crystalline structures of $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites were analyzed using the XRD method, and the results are shown in Figure 1c. In addition, the diffraction peaks at $2\theta = 3.1^\circ$ and $2\theta = 27.3^\circ$ correspond to the (100) in-plane structural packing of tri-s-triazine units and (002) interplanar stacking peak of conjugated aromatic systems of $\text{g-C}_3\text{N}_4$, (JCPDS card No. 87-1526) respectively.

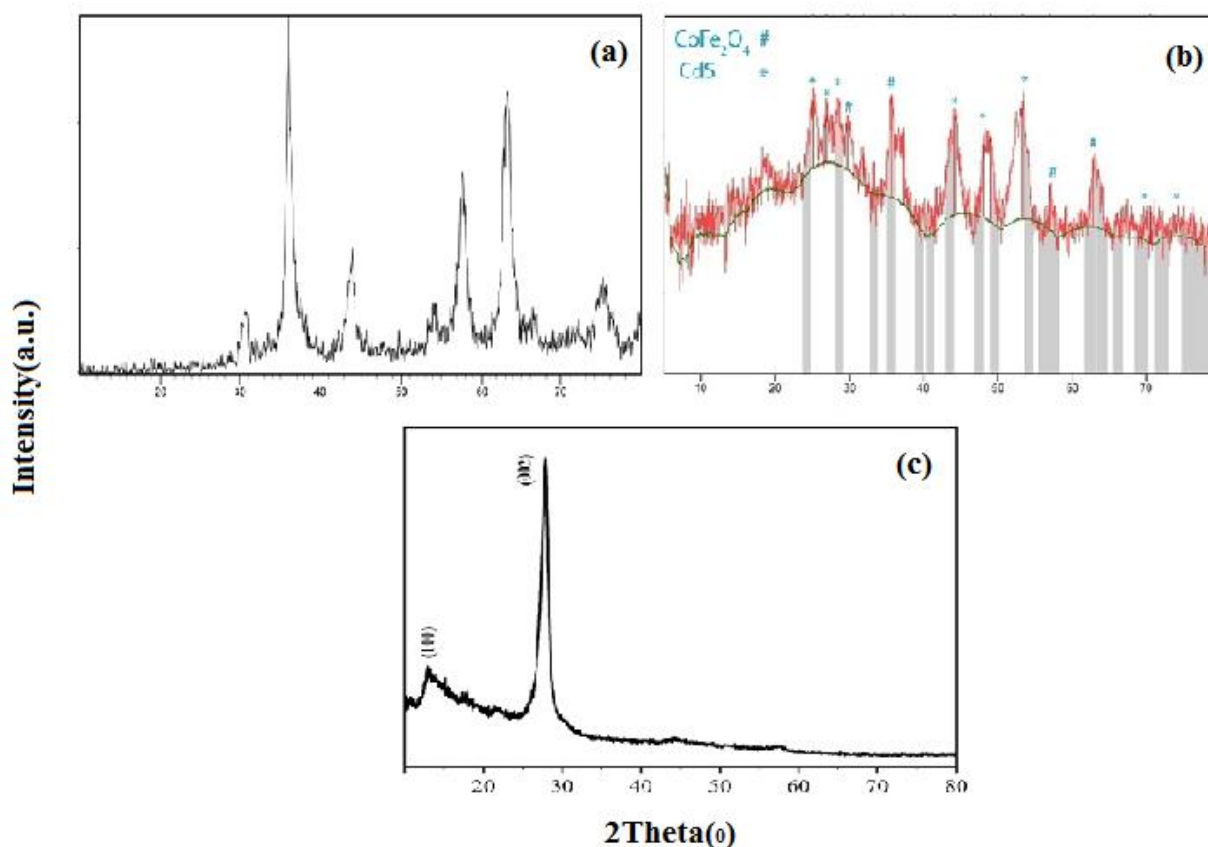


Figure (1) XRD pattern of CoFe_2O_4 (a) $\text{CoFe}_2\text{O}_4\text{-CdS}$ (b) $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ (c) nanocomposite

Figure. 2a illustrate SEM images of the as-synthesized surfactant-free CoFe_2O_4 nanoparticles obtained at 80°C in 100 ml of solvent. These conditions were chosen as a basic reaction in this work. The results confirmed that synthesized nanostructures were formed from nanoparticles with average diameter size less than 90 nm. Figure. 2b illustrate SEM images of the as-synthesized $\text{CoFe}_2\text{O}_4\text{-CdS}$ obtained at 80°C in 200ml of solvent. That result confirms nanocomposites with average size around 50 nm were obtained. The SEM image of CF-gCN nanocomposite in Figure. 3c shows the graphite-like layers with small agglomerate and irregular blocks.

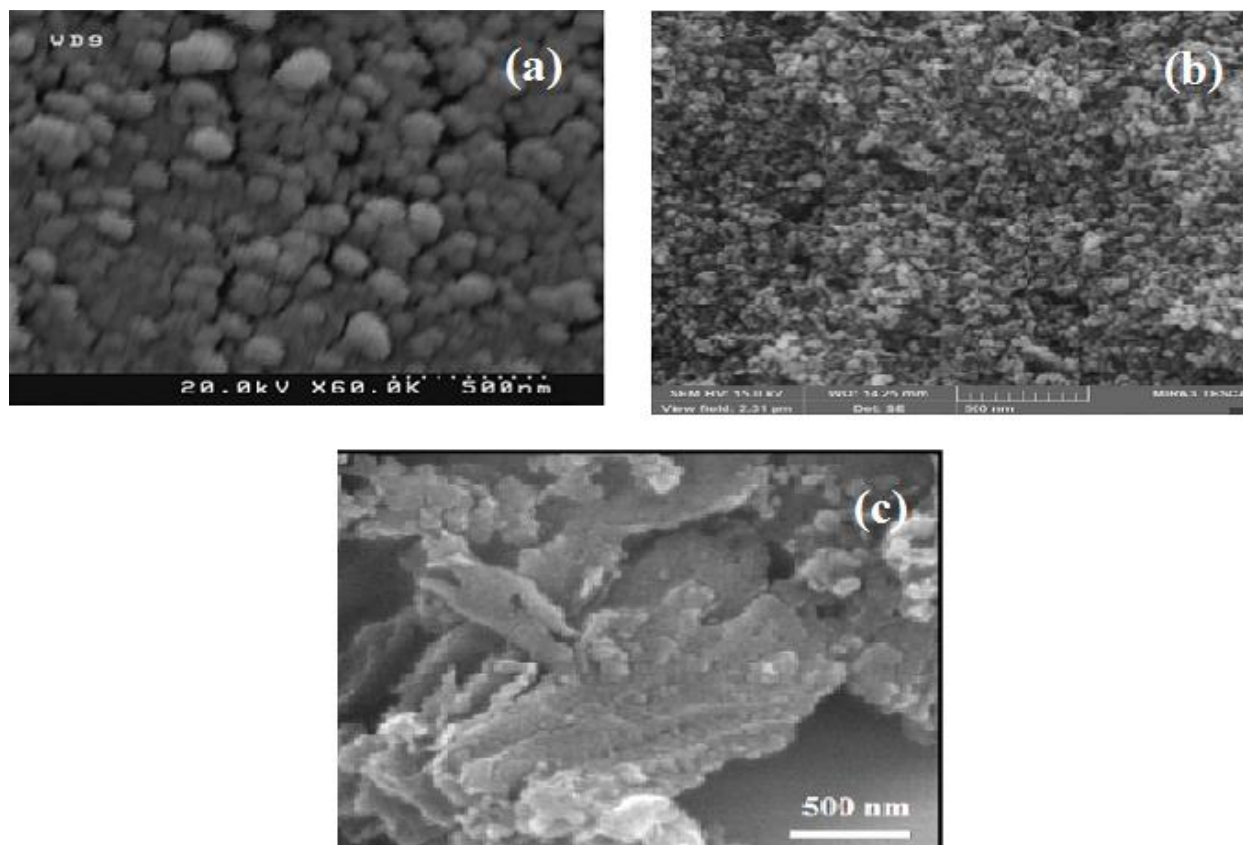


Figure (2) XRD SEM of CoFe_2O_4 (a) $\text{CoFe}_2\text{O}_4\text{-CdS}$ (b) $\text{CoFe}_2\text{O}_4\text{-g-C}_3\text{N}_4$ (c) nanocomposite

The photocatalytic activity of the prepared nanocomposites was studied by measuring the degradation of the aqueous solution of MB. Fig. 3a and Fig. 3b in order illustrates the absorption spectrum of MB in the presence of $\text{CoFe}_2\text{O}_4\text{-CdS}$ and $\text{CoFe}_2\text{O}_4\text{-g-C}_3\text{N}_4$ nanocomposite at a different time of light illumination. It can be seen that with increasing irradiation time, the intense absorption peak at 665 nm decreases gradually due to the photocatalytic reaction.

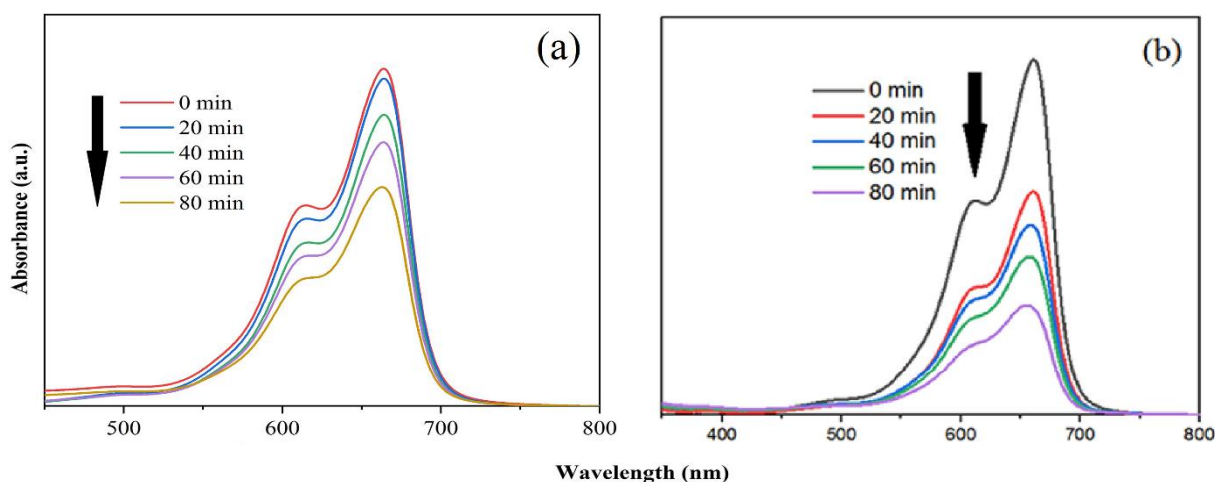


Figure (3) UV-VIS absorption spectra of MB in the presence of CoFe_2O_4 (a) $\text{CoFe}_2\text{O}_4\text{-CdS}$ (b) $\text{CoFe}_2\text{O}_4\text{-g-C}_3\text{N}_4$ (c) nanocomposite

Conclusions

In this work, the photocatalytic activity of $\text{CoFe}_2\text{O}_4/\text{CdS}$ and $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite was investigated and the possible mechanism of $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ to degradation of MB has been discussed. The results revealed that the $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite has better photocatalytic activity than the $\text{CoFe}_2\text{O}_4/\text{CdS}$ nanocomposite. On the other hand, it was easily separated using an external magnetic field from the treated solution.

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