Synthesis, characterization of Ag-doped CdS-WO$_2$ nanocomposite and effects of photocatalytic degradation in RhB under visible light irradiation

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Research Article

Keywords: Ag/CdS-WO$_2$, Rh B, Photocatalyst, Visible light irradiation, Degradation

Posted Date: January 5th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1228443/v1

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Abstract

In this paper, the highly stable Ag/CdS-WO$_2$ nanocomposite was fabricated by a facile and capping agent-free hydrothermal technique. The fabricated Ag doped CdS-WO$_2$ nanocomposite were characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and UV-vis diffuse reflectance (DRS) spectroscopy. The photocatalytic performance of synthesized photocatalysts was evaluated for the photodegradation of rhodamine B (Rh B) under visible light irradiation (VLI). The parameters used for the optimization of the photocatalyst were pH, catalyst dose, oxidant dose, and irradiation time. Based on this, a possible reaction mechanism for the enhancement of photocatalytic activity of Ag/CdS-WO$_2$ has been proposed. Hence, we have a tendency to believe it might be a promising material that may be used for the photodegradation of organic pollutants present in wastewater.

1. Introduction

Water is extremely crucial in our environment for the regular weather and the co-evolution of life on Earth. Almost all of the water on the planet is saline, making it unfit for drinking and irrigation. Only 0.77% occurs as liquid fresh water and its distribution are very in homogeneous [1]. Drinking water should be free of pathogenic germs and contamination by toxic compounds like pesticides and industrial chemicals. Clean and fresh drinking water is essential to human and other life [2]. Water pollution is the contamination of water bodies, usually as a result of industrial wastes. For example, releasing inadequately treated wastewater into natural water bodies can lead to degradation of aquatic ecosystems. The waste bearing water, or effluent, and discharged into streams, lakes, or oceans, which in turn dispersed in the pollutants. Textile dyes and other industrial dyes are very easily mixed with fresh water from several industries [3]. Besides, these dyes can be considered as major water pollutants owing to their contained highly toxic organic compounds. In the current year it is estimated that some 30,000 million liters of pollutants are entering our river systems every day, 10,000 million liters from industrial units alone [4]. Synthetic azo dyes are among common environmental pollutants which are used in various 73 industries including textiles, papers, plastics, pharmaceuticals and cosmetic [5].

Advanced oxidation processes in a broad sense, are a set of chemical treatment procedures designed to remove organic and sometimes inorganic materials in water and waste water by oxidation through reactions with hydroxyl radicals (·OH) [6]. In real-world applications of wastewater treatment, however, this term usually refers more specifically to a subset of such chemical processes that employ ozone (O$_3$), hydrogen peroxide (H$_2$O$_2$) and/or UV light. Photocatalysis is the term can be generally used to describe a process in which light is used to activate a substance [7]. Photocatalysis promises a solution to challenges associated with the intermittent nature of sunlight which is considered as renewable and ultimate energy source to power activities on Earth [8]. Homogeneous photocatalysis refers to catalytic reactions in which both the reactants and the catalyst comprises only one phase and the photochemical process takes place in a homogeneous solution. There are 3 types of homogeneous photocatalysis are
UV/H$_2$O$_2$, UV/O$_3$ and UV/O$_3$/H$_2$O$_2$ system. In Heterogeneous photocatalysis, UV/ Semiconductor has most common are transition metal oxides and semiconductors, which have unique characteristics. Semiconductor photocatalysis has been gained great attention as a green approach for complete removal of organic pollutants using freely obtainable solar energy source without discharge any secondary pollution [9].

Titanium dioxide (TiO$_2$) has been widely used as a photocatalyst in many environmental and energy applications due to its efficient photoactivity, high stability, low cost, and safety to the environment and humans [10]. When used in water treatment applications, TiO$_2$ has a poor affinity toward organic pollutants, especially hydrophobic organic pollutants. Cadmium sulfide, a visible-light responsive photocatalyst with a band gap of 2.4 eV, is one of the most prominent semiconductor photocatalysts [11]. In this study, the influences of Ag/CdS-WO$_2$ Nano composite on the photodegradation of organic pollutant in aqueous solution were investigated. Hence, the objectives of this work are, (i) To synthesis Ag doped CdS-WO$_2$ ternary nanocomposite via hydrothermal method. And prepare the photocatalyst with suitable semiconductor material. (ii) To characterized the synthesized material by using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR), UV-vis diffuse reflectance spectra (DRS). (iii) To study the photocatalytic performance of the pure CdS, pure WO$_2$, CdS-WO$_2$ and Ag/CdS-WO$_2$ photocatalyst by their ability in the photocatalytic degradation of Rhodamine-B (RhB) as a target textile pollutant under visible-light irradiation. (iv) To study the optimization of different process parameters and effects like pH, catalyst concentration, concentration of oxidants (persulphate), and irradiation time. (v) Finally, To propose a possible reaction mechanism related to the enhanced photocatalytic degradation of Ag/CdS-WO$_2$ photocatalyst.

2. Materials And Methods

2.1. Chemicals

Cetyl trimethyl ammonium bromide (CTAB), sodium sulfide (Na$_2$S), ethanol (EtOH) and sodium hydroxide (NaOH), cadmium nitrate [Cd (NO$_3$)$_3$], were purchased from SDFCL, India. Silver nitrate (AgNO$_3$, 99%) was obtained from Sigma-Aldrich. Tungstic acid (H$_2$WO$_4$, 99%) and Hydrogen peroxide (30% w/v of H$_2$O$_2$) was obtained from Nice chemicals, India. Rhodamine B (98%) was purchased from UNI-CHEM. Double distilled-water (ddH$_2$O) water was used throughout the experiments, prepared by typical laboratory distillation unit. All chemicals were of analytical grade and were used without any further purification.

2.2. Synthesis of CdS

In a typical procedure, 50 mL of 1 M cadmium nitrate, 25 mL of distilled water, 25 mL of ethanol and 0.34 g CTAB were mixed in a beaker. To this solution, 50 mL of 1M Na$_2$S, 25 mL ethanol and 25 mL distilled water were added with vigorous stirring. Following this 20 mL of 2M NaOH was added with vigorous stirring which gives a light yellow precipitate. This mixture was transferred to a 250 mL Teflon-lined stainless steel autoclave, followed by heating at 100°C for 2 h [12]. Following this, it was cooled to room
temperature and the residue obtained was separated by centrifugation, washed several times with distilled water, ethanol and then dried in oven at 40°C, to get the resulting is the yellow coloured cadmium sulphide.

### 2.3. Synthesis of WO₂

2 g of tungstic acid and 0.895 g of CTAB were dissolved in 50 mL of distilled water. Then, the solution was transferred into a Teflon-lined autoclave. The hydrothermal reaction was carried out in hot air oven at 120 °C for 12 h and then it allowed cooling at room temperature. The obtained yellow color precipitate was collected, washed with deionized water and ethanol several times to remove impurities, and dried in hot air oven at 60 °C for 6 h [13].

### 2.4. Synthesis of CdS-WO₂

For preparing CdS-WO₂ composite, 0.2 g of the above prepared WO₂ was dissolved in 80 ml ethanol to make a non-homogenous mixture and sonicated for half an hour. 1 g of CdS nanoparticles which was synthesized by the simple hydrothermal method was mixed in 100 ml of water and sonicated for half an hour. The above prepared WO₂ suspension was added into the CdS mixture and sonicated for 30 more minutes. The resulting mixture was filled into a Teflon-lined stainless-steel autoclave at 200°C for 12 h. The obtained precipitates were filtered and rinsed many times with distilled water and ethanol. Finally, the formed product was dried at 60°C for 12 h [14].

### 2.5. Synthesis of Ag/CdS-WO₂ Nano composite

Ag/CdS-WO₂ (5 wt %) Nano composite was made by adding 0.5 g of CdS-WO₂ into 40 ml ethylene glycol solution with constant stirring for 20 min. afterward, the mixture was heated for 2 h at 180°C; then 0.025 g (2.7%) AgNO₃ was added with constant stirring for 30 min. The resulting mixture was cooled at room temperature, washed by ethanol three times, and finally dried at 60°C for 3 h [15].

Figure 1 shows the Schematic methodology of synthesis of Ag/CdSWO₂ nanocomposite.

### 2.6. Characterization of photocatalysts

X-ray diffraction (XRD) patterns of the synthesized photocatalysts were recorded using a X-ray diffractometer (Mini Flex II, Japan) with Cu Kα radiation (λ ¼ 0.154 nm) at a scan speed of 3°/min. The phase purity was ascertained using X-ray diffraction. The Fourier transform infrared (FT-IR) spectra were recorded to study the interaction among CdS and WO₂ with a wavenumber ranging from 4000–400 cm⁻¹ using a JASCO 460 plus FT-IR instrument. UV-vis diffuse reflectance spectra (DRS) were recorded using a Shimadzu 2100 spectrophotometer in the range of 200–800 nm.

### 2.7. Photocatalytic degradation studies

The photocatalytic activity of the as-synthesized photocatalyst was evaluated by the photo degradation of RhB under visible-light irradiation using a photocatalysis chamber. A 250W tungsten halogen lamp
was employed as a source of visible-irradiation. A 75 mL of the RhB dye solution to achieve a catalyst concentration of 1.0 g/L. Prior to light irradiation, the suspension was magnetically stirred in the dark for 60 min to reach an adsorption-desorption equilibrium at room temperature [16]. During irradiation, 4 mL of aliquots was collected at regular time interval and then the photocatalyst was removed by centrifugation. The characteristic absorption wavelength of 554 nm for RhB was followed by using a UV-visible spectrometer (Jasco-630) Japan.

3. Results And Discussions

3.1. XRD studies

The crystalline phase and the purity of the as-synthesized bare CdS, bare WO$_2$, CdS-WO$_2$, and Ag/CdS-WO$_2$ nanocomposites were examined by XRD results are depicted in Fig. 2. The phase and structure of CdS semiconductor were investigated by XRD technique. The powder XRD pattern of CdS nanoparticles was well matched with the hexagonal phase structure (JCPDS File no. 10–0454). The diffraction peaks appeared at 20.93°, 35.04°, 43.52°, 48.8°, 52.02°, 55.97°, and 61.09° corresponding to the (101), (102), (110), (103), (201), (004), and (104) planes, respectively. No impurity peak was observed. Furthermore, peak broadening was observed implying either the amorphous nature of the compound or the nano crystalline behavior of the sample [12]. The XRD pattern of pure WO$_2$ displayed monoclinic crystal structure corresponding to the (002), (200), (120), (112), and (222), diffraction at 2θ = 21.02°, 24.47°, 26.85°, 27.94°, and, 42.03°, (JCPDS no. 43-1035). The XRD patterns of Ag/CdS-WO$_2$ Nano composites contain only monoclinic WO$_2$ peaks with no other peaks of CdS. Due to less available content of CdS nanoparticles may be the reason for absence of CdS peaks. However, the peak intensity of WO$_2$ increased with an ascending amount of CdS in the Ag/CdS-WO$_2$ Nano composites [17].

3.2. FT-IR spectroscopy studies

The purity and functional group composition of the synthesized CdS, WO$_2$, CdS–WO$_2$ and Ag/CdS-WO$_2$ were investigated by using a Fourier transform infrared (FT-IR) spectroscopy in the region of 400–4000 cm$^{-1}$ [18]. The FT-IR spectrum of CdS, WO$_2$, CdS–WO$_2$ and Ag/CdS-WO$_2$ Nano composites is shown in Fig. 3. In the FT-IR spectrum of pure CdS, the absorption peaks at 541 cm$^{-1}$ and 1032 cm$^{-1}$ are assigned to Cd–S stretching modes and bending modes of H–O–H of absorbed water molecules in sulphide products [19]. In the spectrum of WO$_2$, the sharp peak at 542 cm$^{-1}$ corresponds to the stretching vibration modes of O–W–O bonds. The absorption peaks at 1434 and 1654 cm$^{-1}$ corresponds to the asymmetric and bending vibration of water on the surface of the WO$_2$ in the sample [20]. The characteristic broad peak at 3453 cm$^{-1}$ may be due to the stretching frequency of the O-H stretching [21]. The sharp absorption peaks at 541 and 1038 cm$^{-1}$ due to the Cd–S stretching modes and broad peak at 3527 cm$^{-1}$ is for O-H stretching. The new distinct peak observed at 1026 cm$^{-1}$ for the Ag doped CdS-WO$_2$
photocatalysts corresponds to asymmetric valence S=O vibration [22]. Thus, the FT-IR results clearly indicate the existence of Ag in the CdS-WO₂ photocatalyst.

### 3.3. Optical absorption studies

The light absorption properties of CdS, WO₂, CdS-WO₂ and Ag/CdS-WO₂ photocatalysts were investigated by UV-vis diffuse reflectance spectroscopy and the spectral characteristics are displayed in Fig. 4. The absorption photo peaks for the synthesized CdS, WO₂, CdS-WO₂ and Ag/CdS-WO₂ are found to be at 423, 510, 525 and 485 nm, respectively and the corresponding calculated band energy gap values are 2.93, 2.43, 2.36 and 2.55 eV, respectively. It should be noted that the visible light absorption capacity is increased for the CdS with the introduction of WO₂. As seen from the Figure 4 the variation of CdS photocatalyst exhibited a limited photocatalytic performance towards degradation of RhB with an efficiency of 82.5, 93.2, 95.0 and 96.5% after 90 min irradiation, respectively [23–25]. The degradation of RhB dye is due to the synergistic effect of both adsorption and photo catalysis. It should be noted that a significant improvement of RhB degradation can be found in the presence of both catalyst and light.

### 3.4. Photocatalytic degradation studies

#### 3.4.1. Effect of pH

The photocatalytic activities of prepared catalysts were investigated at different pH values (3–9). At increased pH (i.e., > 8) the degradation of rhodamine B decreased because of the formation of aromatic hydroxylated species that appears in the form of anions and competes with the adsorption of dye molecules which results in a decrease in degradation efficiency. Therefore the condition of optimum pH is mandatory for avoiding the wastage of excess quantity of catalyst; furthermore, it helps in maximum assimilation of visible light for enhanced photodegradation [26]. In Fig. 5 graph (a) shows the variation of pH trend of catalysts. CdS shows maximum degradation of 65% at neutral pH = 7. WO₂ shows better degradation because of the availability of the enhanced active sites on 75% at neutral pH (i.e., 7). Similarly, the CdS-WO₂ catalyst showed maximum degradation of 76% at neutral pH = 7. The ultimate degradation of 90% by Ag/CdS-WO₂ was even more than the other two catalysts. As a result of the loading of Ag on CdS-WO₂ surface, the possibilities of dye molecules adsorption on the surface of the catalyst enhance due to the increased availability of active sites.

#### 3.4.2. Effect of catalyst concentration

For the optimization of catalyst dose in degrading rhodamine B dye, the amount of CdS, WO₂, CdS-WO₂, and Ag/CdS-WO₂ was varied from 10 to 90 mg/100 ml. Figure 6 shows that by increasing catalyst dose the degradation intensifies due to the availability of enhanced active sites. The trend remained up to a certain limit (i.e., Ag/CdS-WO₂ = 75, 150, 225, 300 mg/100 ml) above which the results showed reduced
degradation of rhodamine B due to the formation of agglomerates [27]. Hence the maximum degradation is obtained at the above-mentioned catalyst loading of specific catalysts.

### 3.4.3. Effect of oxidant concentration

In order to examine the role of $S_2O_8^{2-}$, experiments of the photocatalytic degradation of RhB employing different initial concentrations of the oxidant in the range of 3 to 13 mM. The influence of oxidant dose for dye degradation was observed for three different catalysts CdS, WO$_2$, CdS-WO$_2$, and Ag/CdS-WO$_2$. And the results are depicted in Figure 7. It is evident that the degradation increased with increase in concentration of $S_2O_8^{2-}$ under the experimental conditions studied. The percentage of decolourization is increased with the increase in of the initial per sulfate concentration 43.41, 72.40, 74.40% and 79.32%. The enhancement can be attributed to the ability of persulfate to act as an electron acceptor [28].

Due to its high potential (2.6 eV) sulphate radicals which is a powerful oxidant that can able to participate in RhB degradation. This is the reason for decrease of rate [29].

\[
S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{2-} + SO_4^{2-}
\]

\[
SO_4^{2-} + H_2O \rightarrow SO_4^{2-} + HO^- + H^+
\]

\[
SO_4^{2-} + h^+ \rightarrow SO_4^{2-}
\]

\[
SO_4^{2-} + HO^- \rightarrow SO_4^{2-} + HO^-\]

### 3.4.4. Effect of irradiation time

Optimization of time can be attained by keeping the above three parameters pH, oxidant dose, and amount of catalyst constant and time was altered (10–90 min). The degradation was monitored for four different catalysts such as CdS, WO$_2$, CdS-WO$_2$, and Ag/CdS-WO$_2$. After complete time intervals, the catalysts were taken from the reaction mixture and their absorbances were checked using a spectrophotometer. Fig. 8 shows the UV–visible spectra of RhB irradiated with visible light at different time intervals in the presence of the Ag/CdS-WO$_2$ photocatalyst. The obtained results are presented in terms of percentage degradation in Fig. 9. It is clear from the results that, percentage degradation increases successively over time. After 70 min the highest efficiencies were recorded with the catalysts, therefore 70 min was selected as the optimum time from the best efficiency of respective catalysts under corresponding optimized conditions.

### 3.5. Reaction Kinetics

For the quantitative study of RhB degradation, the pseudo first-order kinetic model was employed to analyze the experimental data. For photocatalytic experiments, the equation is specifically designed when we take the concentration of the pollutant in the mill molar range.
\[ \ln \frac{C_0}{C} = -kt \]

Where \( C_0 \) is the initial concentration, \( C \) is the final concentration of RhB at time \( t \). The plot of \( \ln (C_0/C) \) versus time gives a linear response, and the value of \( k \) can be analyzed from the slope of pseudo first-order reaction and displayed in figure 10. The results clearly state that the \( k \) (rate constant) value of different dye concentrations like 75, 150 and 225 g/L of Ag/CdS-WO\(_2\) for the degradation of RhB. Results shows the 75 g/L of Ag/CdS-WO\(_2\) was higher than 150 and 225 g/L of Ag/CdS-WO\(_2\) which reveals the fact that the combination of both of the catalysts further enhances the degradation ability as compared to the individual catalyst. Finally, Ag/CdS-WO\(_2\) was the novel nanocomposite with unique characteristics among other composites.

### 3.6. Photocatalytic degradation mechanism

The electron in the valence band (VB) is excited to the conduction band by visible light absorption and the generation of hole (\( h^+ \)) in the valence band [30]. The electrons and holes transfer to the surface of the CdS and react with the molecular oxygen (\( O_2 \)) and \( H_2O \) to generate the superoxide radical anion (\( \cdot O_2^- \)) and hydroxyl radical (\( \cdot OH \)), which act as the active center and strong oxidizing agent for the photocatalytic activity [23, 24, 28, 29]. The degradation of RhB under the irradiation of the stimulated visible light depends on two reactions like de-ethylation and decomposition of chromophore structure of the RhB. These processes can be characterized by the shift of the maximum absorption band (\( \lambda_{\text{max}} \)) and change in the absorption maximum \( C_{\text{max}}/C_{\text{o, max}} \) respectively [31]. Thus the process of producing photoexcited \( e^- \) can be used to generate more \( \cdot O_2^- \) from \( O_2 \), subsequently accelerating reaction with organic dyes. At the same time, holes in the valence band (\( h^+ \)) also have certain degrading ability to RhB. Combined with two active species \( \cdot O_2^- \) and \( h^+ \), photo catalyst can degrade organic dyes in a short time [32].

Thus, the promising reaction mechanism involving RhB dye photodegradation can be given as follows:

\[
\text{Ag/CdS-WO}_2 + \text{hv} \rightarrow e^- + h^+ \\
e^- + O_2 \rightarrow \cdot O_2^- \\
\cdot O_2^- + 2H_2O + e^- \rightarrow 2\cdot OH + 2HO^- \\
\cdot O_2^- + \text{RhB dye} \rightarrow \text{products} \\
h^+ + \text{RhB dye} \rightarrow \text{products}
\]

Based on the above calculations, the probable photocatalytic degradation mechanism in the presence of nanocomposite photocatalyst is shown schematically in the Fig. 11,
4. Conclusions

The highly stable Ag/CdS-WO$_2$ nanocomposite was fabricated by a facile and capping agent-free hydrothermal technique. The effect of photocatalyst amounts; initial dye concentration and K$_2$S$_2$O$_8$ become studied. The degradation of RhB follows pseudo-first order kinetics in all cases. The results of this study clearly showed that the presence of oxidants could have an important impact on the photocatalytic degradation efficiency of the parent compound as well as on the transformation rate of the organic intermediates. The degradation efficiency was found to be strongly influenced by the concentration levels of the S$_2$O$_8^{2-}$. The initial concentration of S$_2$O$_8^{2-}$ showed an obviously positive effect on the degradation process appreciably enhancing photodegradation efficiency of RhB. S$_2$O$_8^{2-}$ showed the most pronounced effect on the decomposition of RhB. The addition of a minute amount of oxidant is an inexpensive way to greatly improve the degradation rate of a photocatalyst. The novel composite Ag/CdS-WO$_2$ has valuable applications in pollutant degradation.

Declarations

Competing interests: The authors declare no competing interests.

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**Figures**
Figure 1

Schematic methodology of synthesis of Ag/CdS-WO$_2$ nanocomposite
Figure 2

XRD spectrum of (a) CdS, (b) WO₂, (c) CdS-WO₂ and (d) Ag/CdS-WO₂

Figure 3

FT-IR spectrum of CdS, WO₂, CdS–WO₂ and Ag/CdS-WO₂ Nanocomposites
Figure 4

UV-DRS of CdS, WO₂, CdS–WO₂ and Ag/CdS-WO₂ Nanocomposites
Figure 5

Optimization of reaction parameter of pH using CdS, WO$_2$, CdS–WO$_2$ and Ag/CdS-WO$_2$
Figure 6
Optimization of reaction parameter of catalyst dose using Cds, WO$_2$, CdS–WO$_2$ and Ag/CdS-WO$_2$

Figure 7
Optimization of reaction parameter of oxidant dose using Cds, WO$_2$, CdS–WO$_2$ and Ag/CdS-WO$_2$

Figure 8
UV–visible spectra of RhB at different time intervals of Ag/CdS-WO$_2$
Figure 9
Optimization of reaction parameter of irradiation time using CdS, WO$_2$, CdS–WO$_2$ and Ag/CdS-WO$_2$

Figure 10
Pseudo-first-order kinetic fitted curves of Rh B over Ag/CdS-WO$_2$ composite

Figure 11
The schematic representation of Ag/CdS-WO$_2$ nanocomposite photocatalyst towards the degradation of RhB under VLI.