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Fabrication of cost effective g-C_3N_4 + Ag activated ZnO photocatalyst in thin film form for enhanced visible light responsive dye degradation

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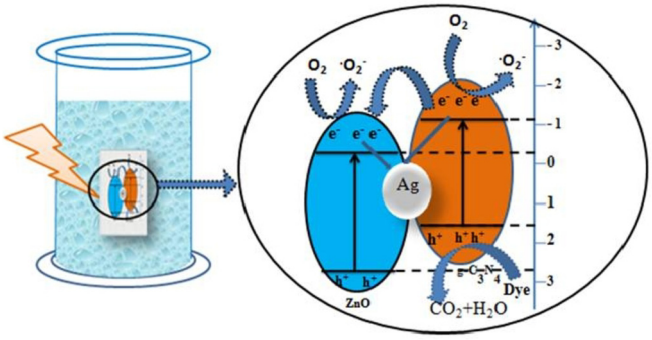
HIGHLIGHTS

- Cost effective ZnO film is activated for visible light responsive photocatalysis through g-C_3N_4 + Ag incorporation.
- The photocatalytic mechanism involved in this study is addressed with appropriate supporting evidences.
- Low cost preparation method is adopted for g-C_3N_4.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study is to analyze the photocatalytic dye degradation efficacy of ZnO/g-C_3N_4/Ag composite thin films prepared using a simple jet nebulizer spray pyrolysis technique. The XRD results confirm the presence of phases related to silver and graphitic carbon nitride in addition to the host ZnO wurzite structure. The photocatalytic studies show that the addition of Ag and g- C_3N_4 remarkably improves the photocatalytic efficiency of ZnO. The ZnO/g-C_3N_4/Ag thin film causes 96 and 99% decomposition of Methylene Blue (MB) and Malachite Green (MG) dye molecules, respectively. The mineralization of the dyes is confirmed by COD measurements. To find the optimum operating pH of the dye, the point of zero charge and the pH corresponding to the maximum surface negative charge of ZnO/g-C_3N_4/Ag film are found out experimentally. The possible mechanism and reasons for the enhanced photocatalytic activity of the ZnO/g-C_3N_4/Ag thin films are discussed with appropriate evidences and related literature.

1. Introduction

In the recent past, due to the fast growth of industrialization, water resources are severely polluted by effluents discharged from the textile, paper, leather and cosmetic industries which generally contain a large amount of organic dyes [1–3]. These dyes are highly toxic and cause various health issues upon inhalation [4,5].

Of the various methods available to remove the dye molecules present in the effluents [6,7], photocatalysis is a promising technology as it is inexpensive and requires simple and easy operating conditions

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[8,9]. Specifically, visible light photocatalysis attracts more attention, as 46% of the solar energy is in the visible region [10].

Among the semiconductor photocatalysts, TiO_2 is widely used because of its strong oxidizing power, and high photosensitivity [2,11,12]. Zinc oxide (ZnO) is considered as the desirable alternative to TiO_2 due to its comparable band gap (3.37 eV), low-cost, good thermal and high chemical stability [9,13]. Most importantly, compared to TiO_2, ZnO can absorb a large fraction of the solar spectrum [14–16]. However, the fast recombination of charge carriers and low efficiency in the visible region due to the wide band gap are the major limitations of ZnO. To address these drawbacks and thereby to improve the photocatalytic efficacy of zinc oxide under visible region, various ZnO based composites are developed by coupling with certain metals and semiconductors [3,17,18]. Among the various transition metals, Ag is reported to be the best partner to enhance the photocatalytic activity of ZnO [19–21]. Similarly, graphitic carbon nitride (g-C_3N_4) - a polymeric metal free semiconductor having graphite like 2D layered structure and high environment stability [22] – is a desirable cost-effective partner to ZnO which shows photocatalytic activity under visible region owing to its narrow band gap (2.70 eV). Besides, ZnO - g-C_3N_4 combination has effective separation of charge carriers due to the conjugated π structure of g- C_3N_4 [23].

Considering the above mentioned points, ZnO/g-C_3N_4/Ag composite thin films have been prepared using a homemade automated jet nebulizer spray technique and the photocatalytic degradation activity of the prepared thin film samples have been studied against two different dyes *viz.* methylene blue (MB) and malachite green (MG).

2. Experimental procedures

2.1. g-C_3N_4 powder preparation

The g-C_3N_4 powder was prepared using simple pyrolysis method reported by Jinghai Liu et al. [24]. Appropriate amount of urea was put in a covered crucible and placed in muffle furnace. The g-C_3N_4 as yellow powder was obtained by heating at 550 °C for 3 h.

2.2. Preparation of precursor solution for thin film deposition

The starting solution was prepared by dissolving zinc acetate dihydrate with optimum volume proportions of methanol, acetic acid and doubly deionised water (7:2:1). This precursor solution was stirred using a magnetic stirrer for 30 min to obtain a clear spray solution. For ZnO/g-C_3N_4/Ag films, required amount of silver nitrate (source material for Ag) and g-C_3N_4 were added to the precursor solution.

2.3. Deposition process

Pristine ZnO and ZnO/g-C_3N_4/Ag films were deposited using a nebulizer spray pyrolysis unit (NSP), the construction details of which are reported in our previous work [25]. Nebulizer spray pyrolysis technique offers several advantages which include the following: It is a simple and cost effective technique operated with simple solution flow control. It can be used to deposit multi-component composite films. It does not require vacuum for deposition and involves soft carrier gas flow when compared to ordinary spray pyrolysis. By appropriately changing the process parameters such as substrate temperature (Ts), nozzle to substrate distance (NSD), spray rate, deposition time, solution concentration etc., we can get films with a wide range of characteristics suitable for different applications [26,27]. Prior to the deposition process, the glass substrates were immersed into hydrochloric acid for 24 h and ultrasonicated with deionised water for 1 h. Finally, the substrates were cleaned with acetone to remove any contamination present on the surface. Cleaned glass substrates were placed on the hot plate and the temperature was maintained at 350 ± 5 °C using a chromel–alumel thermocouple. Deposition parameters employed in this work are presented in Table 1.

Table 1
Deposition parameters employed in this study.

Deposition parameters	
Host Material	Zinc acetate dihydrate
Dopant Materials	g-C_3N_4 and Ag
Solvent	Doubly deionised water, methanol and acetic acid
Spray time	14s
Spray interval	7s
Nozzle to substrate distance	10 cm
Nozzle diameter	10 mm

2.4. Photocatalytic test

The coated film sample was mounted using a sample holder inside the test tube filled with 100 mL of a MB/MG aqueous solution (1×10^{-5} mol/L) and subjected to visible light illumination (500 W Tungsten lamp with 420 nm cut-off filter). The coated face of the sample was set such that it was exposed to the light radiation from the lamp. The distance between the lamp and the sample was kept as 9 cm. During the photocatalysis process, the concentration of the dye solution was monitored every 15 min by observing the intensity of the characteristic peak of the tested dye. Before starting the photocatalysis experiment, the test dye in solution form was kept under dark for 1 h to attain the adsorption-desorption equilibrium. Degradation efficiency (η) was estimated from the characteristic absorption peaks of MB and MG dyes (664 and 616 nm) using the following formula [28].

$$\text{Degradation efficiency}(\eta) = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 is the initial concentration of dye solution and C_t is the concentration at the time of irradiation.

2.5. Chemical oxygen demand (COD) measurements

The MB and MG dye samples were refluxed with $HgSO_4$, $K_2Cr_2O_7$, $AgSO_4$ and H_2SO_4 for 2 h and titrated with ferrous ammonium sulfate (FAS) using ferroin indicator. The COD was calculated using the equation [29]:

$$COD = \frac{(\text{Blank titer value} - \text{dye sample titer value}) \times \text{normality of FAS} \times 8 \times 1000}{volume\ of\ sample}$$

2.6. Point of zero charge (PZC) of ZnO/g-C_3N_4/Ag samples

For finding the PZC of the samples, NaCl solution (40 ml) was prepared with different pH values. To keep this solution at different pH levels (2–11 in this study in steps of 1) required amount of HNO_3/NaOH was added for each case. A digital pH meter was used to measure the pH of the prepared solutions. A ZnO/g-C_3N_4/Ag thin film sample was put into each of the solution taken in conical flasks so that the sample was completely immersed into the solution. These conical flasks were placed in a shaker-incubator for continuous shaking for 24 h at 20 °C. Final pH of each solution was noted and the difference between initial and final pH was calculated as ΔpH for each case. From the plot drawn for ΔpH vs initial pH, the PZC was noted which is the pH value at which ΔpH is zero.

3. Results and discussion

3.1. Structural study

X-ray diffractometer was used to analyze the structural properties,