



Research paper

Silver/Silver(II) oxide (Ag/AgO) loaded graphitic carbon nitride microspheres: An effective visible light active photocatalyst for degradation of acidic dyes and bacterial inactivation



Devthade Vidyasagar^a, Sachin G. Ghugal^a, Aditi Kulkarni^b, Pragya Mishra^a, Ashok G. Shende^a, Jagannath^c, Suresh S. Umare^{a,*}, Rajamma Sasikala^{d,*}

^a Materials and Catalysis Laboratory, Department of Chemistry, Visvesvaraya National Institute of Technology (VNIT), Nagpur, India

^b CSIR-National Environmental Engineering Research Institute, Nagpur, India

^c Technical Physics Division, Bhabha Atomic Research Centre Trombay, Mumbai, India

^d Chemistry Division, Bhabha Atomic Research Centre Trombay, Mumbai, India

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ABSTRACT

Solar light induced photocatalytic oxidative degradation of organic pollutants and bacterial inactivation is an attractive strategy for water purification. Current work is on the use of silver/silver (II) oxide (Ag/AgO) grown *insitu* on the surface of graphitic carbon nitride (g-C₃N₄) as photocatalyst for the effective utilization of solar radiation, as this system can have extended visible light absorption due to the surface plasmon resonance (SPR) phenomenon of metallic silver. Ag/AgO loaded g-C₃N₄ microspheres (Ag/AgO/g-CNMS) were prepared by a facile thermal heating method. The structural and morphological analysis confirmed the existence of metallic Ag and AgO in mixed phase on the surface of carbon nitride. This composite exhibits significant visible light absorption and a reduction in the bandgap compared to g-C₃N₄ due to the SPR exhibited by the metallic silver and lower bandgap of AgO. Photoelectrochemical studies suggest lower charge transfer resistance and better capacitive behaviour for the composite compared to g-C₃N₄. The composite catalyst shows improved photocatalytic performance for the degradation of acid violet-7 dye (AV-7). Besides, it is found to possess significant bactericidal property for the destruction of *Escherichia coli* (*E. coli*) bacteria. This is the first report on the enhanced photocatalytic activity of a silver-g-C₃N₄ system comprising of silver (II) oxide. The present system containing silver (II) oxide shows significantly improved photocatalytic activity and stability compared to the Ag/Ag₂O/g-C₃N₄ with silver (I) oxide reported earlier. The improved performance of the composite is attributed to the increased optical absorption properties and better separation of photogenerated charge carriers. The reactive oxidative species responsible for the degradation reaction is identified and a plausible degradation pathway for the AV-7 dye is presented. Furthermore, this catalyst is found to be stable and does not show any decrease in the photocatalytic activity even after several repeated cycles.

1. Introduction

The emerging environmental contaminants and energy crisis are global issues of concern [1]. Increased urbanization and high living standards burden the environmental health. Immediate addressing of these challenges requires efficient and low-cost techniques. Photocatalytic degradation of organic pollutants by a clean sustainable solar energy based systems is a very promising and attractive strategy. Semiconductor mediated photocatalysis is widely studied for energy and environmental applications. Recently, there is a growing interest for low cost two dimensional g-C₃N₄ based materials. Due to its unique

structure, excellent properties as semiconductor and nitrogen richness, make it suitable to act as a metal-free catalyst for a broad variety of photocatalytic applications [2]. However, the photocatalytic performance of bulk g-C₃N₄ is still limited due to its fast recombination of photogenerated electron-hole pairs and moderate visible light absorption capacity ($\lambda < 460$ nm).

To improve the photocatalytic performance of g-C₃N₄, visible light absorption is to be enhanced and efficient separation of charge carriers should occur. Modification of bandgap of g-C₃N₄ through elemental doping or copolymerization has proved to be a successful technique to exploit the structural modifications of g-C₃N₄ [3–5]. Another effective

* Corresponding authors.

E-mail addresses: ssumare@chm.vnit.ac.in (S.S. Umare), sasikala@barc.gov.in (R. Sasikala).

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way to enhance the photocatalytic performance of g-C₃N₄ is by the construction of semiconductor-semiconductor heterojunctions to promote the charge separation of photo induced electrons and holes. 2D polymeric g-C₃N₄ with its flexible nature, favors the formation of heterojunctions with various other semiconductors like metal oxides [6–8], mixed oxides [9,10], metal chalcogenides [11,12] and organic semiconductors [13]. Combining g-C₃N₄ with metal atoms such as silver (Ag) facilitate the migration and separation of charge carriers with easy mass diffusion [14]. Reports of g-C₃N₄/silver based heterojunctions are available, where g-C₃N₄ is combined with Ag₂O [15], Ag₂CO₃ [16], Ag₃PO₄ [17,18], Ag₃VO₄ [19], Ag₂S [20], AgCl [21], AgBr [22], and AgI [23], all of which enhance the photocatalytic performance of bulk g-C₃N₄.

In our current work, we report the use of Ag/AgO/g-C₃N₄ microspheres (Ag/AgO/g-CNMS), for the photocatalytic degradation of AV-7 dye and effective antimicrobial activity under visible light irradiation. It is known that the optical properties and bandgap of silver oxide varies with the synthesis methods from 1.12–1.71 eV [24–26]. Hence, silver oxide was synthesized by an *in situ* growth of Ag/AgO on g-C₃N₄ in which 2D g-C₃N₄ sheets were moulded to 3D spheres using SiO₂ hard template. In this system, a co-existence of bivalent silver (II) oxide with metallic Ag⁰ is observed on g-C₃N₄ to form a novel combination of photocatalyst. Although, several studies on Ag/Ag₂O/g-C₃N₄ are already reported, where Ag exists in +1 oxidation state, to the best of our knowledge, a combination of g-C₃N₄ and Ag/AgO has never been addressed. It is expected that Ag/AgO with g-C₃N₄ can improve the visible light absorption and enhance the separation of photogenerated charge carriers, which can increase its photocatalytic efficiency.

2. Experimental section

2.1. Materials

All the chemicals, melamine (Finar Chem. Ltd, 99%), silver nitrate (AgNO₃) GR grade (Merck, India), tetraethyl orthosilicate (TEOS) (Aldrich, 98%), Acid Violet-7 (Aldrich, dye content ca. 85%), were of analytical grade and used without any further purification. Millipore water (conductivity < 0.15 mS cm⁻¹) was used throughout the experiments.

2.2. Synthesis of Ag/AgO/g-CNMS

10 g of melamine was dissolved in 100 mL of millipore water and 5 mL of 4 M HCl. To this 6 mL of TEOS was added instantly and stirred for 5 min. This was followed by the addition of calculated amount of AgNO₃ and liq-NH₄OH (5 mL). The obtained product was washed with acetone and dried at 80 °C for 2 h. The white powder obtained was annealed at 550 °C for 2 h in a muffle furnace to obtain a pale grey colored compound. This powder was treated with NH₄HF₂ and kept it overnight to remove SiO₂ and to obtain Ag/AgO/g-CNMS grey powder. Concentration of AgNO₃ was varied to synthesize different Ag/AgO(x)/g-CNMS composites where x = 1, 2, 5, 10, 15 and 20% by weight.

2.3. Characterization

XRD analysis of the samples was performed for the structural characterization in the 2θ range between 10° and 80° using an X-ray diffractometer (Rigaku: Miniflex-II-DD34863) using Cu Kα radiation (λ = 0.15418 nm) operated at 30 kV and 15 mA at a scan rate of 5° min⁻¹. X-ray photoelectron spectroscopy (XPS) studies were carried out on a VG Microtech electron spectrometer using Mg Kα X-rays (hν = 1253.6 eV) as the primary source of radiation. The chamber pressure was maintained at 1 × 10⁻⁹ Torr. Appropriate correction for charging effect was made with the help of the C 1 s signal appearing at 284.5 eV. XPS Peak 4.1 software was used to fit the XPS peaks. The decomposition of the spectra curves into individual components was

performed using a combination of Gaussian and Lorentzian functions after background subtraction by the Shirley method. The TEM images were taken using a FEI Tecnai T-20 electron microscope operating at 300 kV. Energy dispersive X-ray spectroscopy analysis was carried out using Zeiss FESEM. UV–vis diffuse reflectance spectra (UV–vis DRS) of all samples were recorded using a Jasco (model V-670) spectrophotometer equipped with an integrating sphere accessory. Barium sulfate was used as reference for the reflectance spectra. Electrochemical studies were carried out by a PARSTAT 4000 (Princeton Applied Research, Ametek, USA) Potentiostat/Galvanostat using a conventional three-electrode system. Thermogravimetric analysis of prepared catalyst was carried by using a thermal analyzer TGA-DTA 7200 (Hitachi). The identification of degradation products was performed by using a Waters Micromass Q-TOF mass spectrometer, Waters Alliance 2795 electrospray ionization mass spectrometry (ESI-MS). Inductively Coupled Plasma–Mass Spectrometer (Perkin Elmer, NexION 300x) used for tracing of Ag metal leaching.

2.4. Photocatalytic experiments

The photocatalytic activity of the prepared Ag/AgO/g-CNMS was evaluated for the degradation of 20 mgL⁻¹ aqueous solution of Acid Violet-7 (AV-7) dye. Degradation experiments were performed in a lab made photo-irradiator fitted with compact fluorescent lamps (12 lamps of 100 W each, Oreva) vertically and equidistantly on the base of the rectangular galvanized iron chamber containing air circulation to minimize the heating effect. The radiation of these lamps mainly contains visible light along with very low amount of UV light (~3%). For each photocatalytic experiment, 100 mL of aqueous AV-7 (20 mgL⁻¹) solution was taken in a beaker containing 0.1 g of catalyst under ambient conditions. Prior to irradiation, reaction mixture was magnetically stirred in the dark for 30 min to ensure uniform dispersion and adsorption-desorption equilibrium between the dye molecules and the catalyst surface. The photocatalytic activity was measured by taking a small volume of clear supernatant liquid from reaction mixture at regular intervals of time, centrifuged it and analyzed by UV–vis Spectrophotometer (Shimadzu, UV-1800) at λ_{max} = 523 nm. Concentration of solution remained unchanged when it was irradiated without catalyst and in dark control experiment.

2.5. Bacterial culture and antimicrobial test

Autoclave sterilized glassware were used for antibacterial test experiments. Gram-negative *Escherichia coli* (*E. coli*) (ATCC 25933) were used as a target microorganism for antimicrobial tests. For photocatalytic antimicrobial experiments, *E. coli* was transferred to 30 mL of liquid Luria Bertani (LB) culture medium from solid LB agar plate and grown at 28 °C for 12 h. Then the bacteria were diluted with broth to 10⁵ cfu/ml and concentration of bacteria was determined by measuring optical density at 600 nm. Calculated amount of catalyst was suspended in 30 mL of *E. coli* culture medium and illuminated under visible light source. The light source of illumination used was 100 W tungsten lamp located at 22 cm away from the sample. To quantify the antimicrobial test, about 1 mL of the catalyst suspended bacterial mixture was withdrawn after the photo irradiation. To ensure the growing bacterial colonies were legible, 0.1 mL of the treated solution was spread on solid LB medium and continued to incubate at constant temperature of 28 °C for 24 h, and then counted to determine the bactericidal efficiency. For better comparison, control experiments were carried out simultaneously without catalyst and without light illumination. The amount of catalyst used for antimicrobial study was optimized. The percentage of growth inhibition was determined by comparing the survival colony counts with corresponding colony counts of control sample.

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