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Enhanced photocatalytic activity of $Ag/g\text{-}C_3N_4$ composite

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ABSTRACT

Silver-graphite carbon nitride ($Ag/g\text{-}C_3N_4$) was designed and synthesized through a simple green chemical route. The photocatalyst was comprehensively characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), High-resolution transmission electron microscopy (HR-TEM), and X -ray photoelectron spectroscopy (XPS). The HR-TEM results indicate that the synthesized Ag spherical–like nanoparticles were randomly loaded on the surface of graphitic carbon nitride ($g\text{-}C_3N_4$). In addition, the $Ag/g\text{-}C_3N_4$ nanocomposites exhibited 2.5 times higher photocatalytic activity than pristine $g\text{-}C_3N_4$ for the degradation of malachite green (MG) dye under UV irradiation.

1. Introduction

Graphitic carbon nitride ($g\text{-}C_3N_4$) is a well-known semiconductor material with a graphite-like layered structure. It has been used extensively in electrochemical water splitting [1] and as a photocatalyst for hydrogen generation and pollutant degradation [2] due to its band gap energy (~2.7 eV), visible light absorption, high thermal and chemical stability, non-toxicity, easy preparation, abundance, and environmental benignity [3]. However, the use of $g\text{-}C_3N_4$ is limited in many practical applications because of disadvantages such as (i) a high recombination rate of its photogenerated electron-hole pairs, (ii) low visible-light utilization efficiency, (iii) low specific surface area, (iv) low electrical conductivity, and (v) low photocatalytic activity due to the narrow absorption band and poor quantum yield according to density functional theory (DFT) calculations [4,5].

Many approaches have been developed to improve the photocatalytic properties of $g\text{-}C_3N_4$. One promising method is decorating $g\text{-}C_3N_4$ with metal nanoparticles or carbon nanomaterials, which can effectively capture photogenerated electrons in $g\text{-}C_3N_4$ and improve the catalytic efficiency [6,7]. Ag hybrids are significantly inexpensive, thermodynamically and electrochemically stable at high pH [8], and excellent properties in photocatalysis [9]. However, carbon-supported Ag has attracted extensive interest because carbon material can act as excellent support material due to their large surface area, unique electrical properties, and low cost [10].

Recently, carbon-supported metal nanoparticles and semiconductor materials have been reported as effective photocatalysts for degrading chemical complexes under ambient temperature with ultraviolet or visible light illumination. Recently Bao and Chen [11] were synthesized $AgCl/Ag/g\text{-}C_3N_4$ composites using a modified deposition-precipitation method. The composites were evaluated for the photocatalytic degradation of rhodamine B and methyl orange in aqueous solution under visible light irradiation. The $AgCl/Ag/g\text{-}C_3N_4$ composite showed higher photocatalytic activity than Ag/AgCl and $g\text{-}C_3N_4$ individually. Lü et al. [4] synthesized Ag nanoparticles that were successfully loaded on $g\text{-}C_3N_4$ sheet using a simple wet-chemical pathway. The photocatalyic activity of the synthesized $Ag/g\text{-}C_3N_4$ composites was evaluated for the decolorization of methyl orange, and the composite showed higher photocatalytic activity under visible light irradiation. Lin et al. [12] prepared in -situ growth of Ag and $g\text{-}C_3N_4$ quantum dots (CNQDs) onto the surface of $B_{i2}MoO_6$. CNQDs/Ag/Bi_2MoO_6 composite showed higher photocatalytic performance (100%) towards degradation of rhodamine B under visible-light irradiation compared with pure Bi_2MoO_6, Ag/Bi_2MoO_6, and CNQDs/Bi_2MoO_6. Recently, Ma et al. [13] $g\text{-}C_3N_4/C@Bi_2MoO_6$ composite was successfully synthesized using a hydrothermal method. β-Naphthol is efficiently degraded over $g\text{-}C_3N_4/C@Bi_2MoO_6$ composite under visible

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light irradiation. Nanocomposites have generally been synthesized by various chemical and physical methods, but these methods involve toxic chemicals. Alternatively, the synthesis of nanocomposites through green route is simple, rapid, inexpensive, and eco-friendly.

Cassia obtusifoluia Linn belongs to the Caesalpinnaceae family and is commonly known as Takla or Chakunda in India. This plant used as vegetable and cultivated in India, Sri Lanka, Bangladesh, and many tropical countries. It grows in well-drained, fertile soil [14]. Recently, Katrina and Wu [15] (2014) effectively used *Cassia obtusifolia* seed gum to remove total suspended solids and chemical oxygen demand from the effluent of palm oil mills.

Malachite green (MG; $C_{23}H_{25}N_2Cl$) is a cationic triphenyl methane dye and widely used in the cotton, wool, silk, paper, and jute industries [16]. MG is well known as an antibacterial, antiseptic, and antiprotozoan agent, but its oral consumption is hazardous, carcinogenic, mutagenic, genotoxic, and respiratoxic due to presence of the nitrogen [17,18]. In humans, MG can cause vomiting, jaundice, Heinz body formation, cyanosis, quadriplegia, increased heart rate, and tissue necrosis [19]. This discharge of MG into streams not only affects the hydrosphere but also interferes with the transmission of sunlight into the streams and thus reduces the photosynthesis rate [20]. Therefore, the removal of MG from industrial effluent is necessary before discharge into the environment.

Dyes have been removed from industrial effluents using various physical methods (reverse osmosis, ultrafiltration, micro filtration and adsorption), chemical methods (coagulation or flocculation, combined with flotation and filtration, electro kinetic coagulation, electroflotation, irradiation, or electro chemical process, and conventional oxidation methods by oxidizing agents), biological methods, and photocatalysis [21–24]. Photocatalysts have been widely studied to degrade organic compounds that contaminate air or water or to convert them into harmless chemicals to decrease the damage caused by organic dye pollution to the environment and humans. In this study, we prepared Ag/g-C_3N_4 photocatalyst by a green chemical method for the first time (Fig. 1). The synthesized composites were 6 nm in size with spherical shapes. They were used effectively for the photo degradation of MG, and the Ag/g-C_3N_4 showed higher photo catalytic activity than g-C_3N_4.

2. Materials and methods

2.1. Chemicals

All the reagents used were of Analytical grade and used as received without further purification. MG, melamine, and silver nitrate were purchased from Sigma-Aldrich, South Korea. *Cassia obtusifoluia* Linn. was purchased from an herbal medicine shop in Gyeongsan, South Korea. Double distilled water (DDW) was used throughout this work.

2.2. Collection, processing and preparation of Cassia obtusifoluia Linn seed extract

Dried seeds of *Cassia obtusifoluia* Linn were collected from a local herb shop and thoroughly washed under tap water to remove any adhered dust particles present on the surface, followed by rinsing with DDW. The cleaned seeds were completely dried at room temperature (RT) using blotting paper. The dried seeds were ground into fine powder using a mortar and pestle and stored in an airtight container at RT for further use. A 10 g amount of the fine

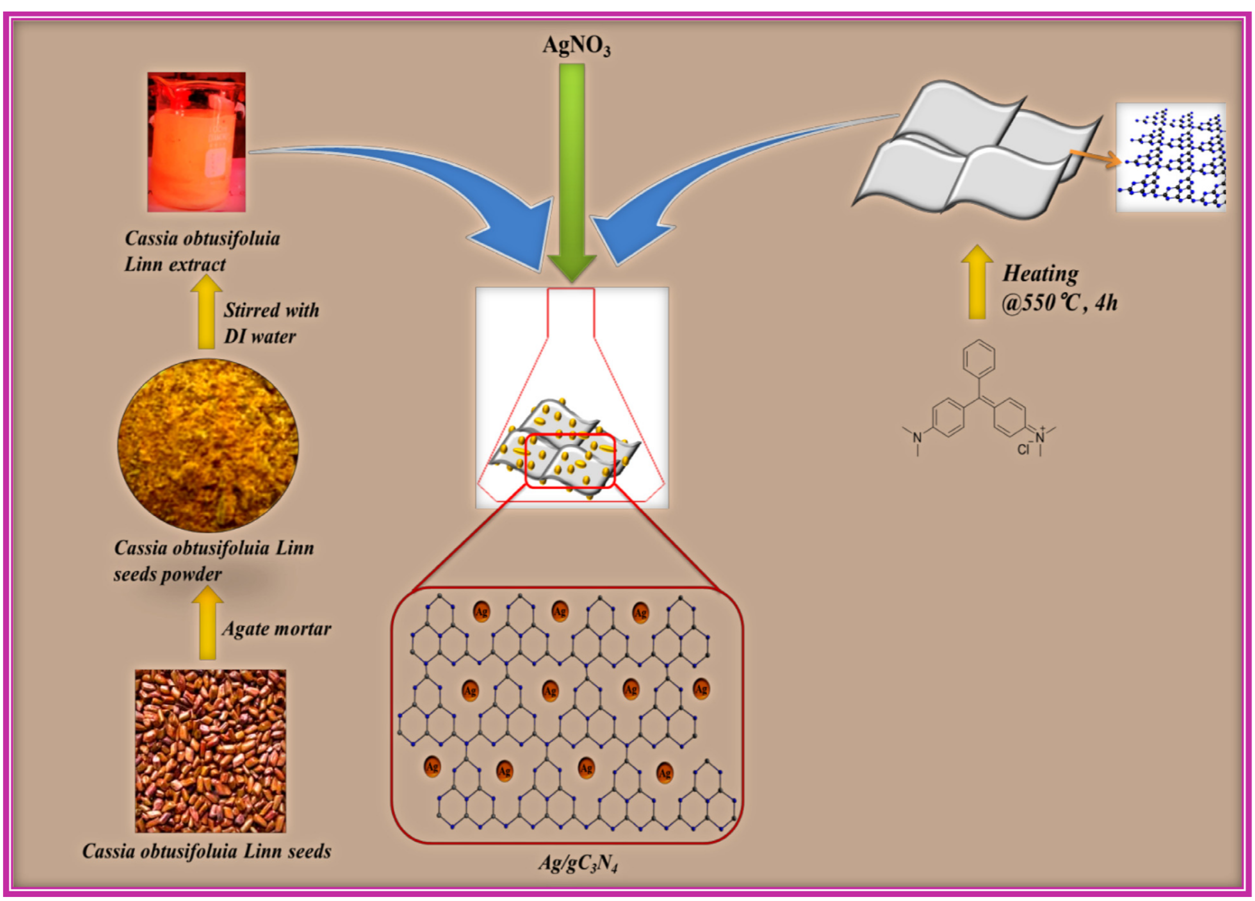

Fig. 1. Schematic diagram of green chemical synthesis procedure for preparation of Ag/g-C_3N_4 photocatalysts.