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Facile synthesis, characterization and photocatalytic performance of Au-Ag alloy nanoparticles dispersed on graphitic carbon nitride under visible light irradiations

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ABSTRACT

The well-dispersed nanoparticles of Au-Ag alloys on graphitic carbon nitride (g-C_3N_4), with varying ratios of Au, were synthesized by a facile route. The diffuse reflectance spectroscopy (DRS) verified the upsurge in the intensity of characteristic surface plasmonic resonance (SPR) absorption bands with the increasing Au contents. The photoluminescence (PL) spectroscopy estimated the role of surface dispersed Au-Ag alloy NPs on the luminescence properties of g-C_3N_4 and the suppression the probable recombination of photo-generated excitons. The structural characterization by XRD and morphological assessment by SEM revealed the uniform dispersion of Au-Ag alloy nanoparticles on the surface of g-C_3N_4 whereas XPS analysis endorsed the presence of Au and Ag in metallic form. The HRTEM analysis confirmed the homogeneous distribution of Au and Ag contents in the alloys. The photocatalytic activity of the Au-Ag/g-C_3N_4 was evaluated in the exposure of natural sunlight and artificial visible light for the degradation of dye substrate and compared with that of g-C_3N_4, Ag/g-C_3N_4 and Au/g-C_3N_4. The Au-Ag alloy modified g-C_3N_4 photocatalysts exhibited significantly higher activity for the decolorization of Rhodamine B in the visible light as compared to pure, Ag and Au loaded g-C_3N_4 that signified the contributing role of SPR in the degradation process. The individual role of SPR in the photocatalytic process was also verified by using monochromatic (532 nm) visible laser light. The mineralization ability of the synthesized alloy catalysts was estimated by TOC removal efficiency. The kinetics of the degradation/mineralization processes under various experimental conditions was also evaluated.

1. Introduction

Environmentally friendly remediation of contaminated water, hazardous solid wastes, and toxic air is the uphill challenge, facing the contemporary world in general and scientific and environmental researchers in particular. Numerous research works based on biochemical, analytical, and physiochemical methods for the environmental remediation and water purification have been carried out. The ingenious and pioneering work on photocatlytic water splitting using TiO_2 sparked off widespread research on photocatalysis for various energy and environmental applications [1]. TiO_2 is a popular semiconductor photocatalyst due to its unique electronic and optical features, low cost, chemical stability and non-toxicity [2]. Initially, TiO_2 and various doped and composite variants of it have been used for the removal of organic and inorganic pollutants, disinfection of microganisms, inactivation of cancer cells, splitting of water to produce hydrogen gas, cleaning up of industrial waste and oil spills. However, the large band gap energy (3.2 eV)

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of TiO_2 prevents it from being catalytically effective in the visible spectral region, which accounts for 42% of the abundant solar radiations [3,4]. The advent of nanotechnology, coupled with the rapid advancements in material science has brought about the new generations of pure, modified, doped, composite and engineered variants of innumerable semiconducting photocatalytic materials.

Graphitic carbon nitride (g-C_3N_4) was one such material, first reported in 2009 as a metal free visible-light driven organic photocatalyst by Wang et-al. and it was applied for water splitting under visible radiation with triethanolamine as a sacrificial electron donor [5]. However, g-C_3N_4 has an inherent constraint of having a high rate of photogenerated electron-hole recombination. In order to reduce the charge recombination, many g-C_3N_4 based composites have been synthesized and used as a photocatalysts [6,7]. In addition to the g-C_3N_4 based composites, other modification on g-C_3N_4 like doping with nonmetal and noble metal has been reported and this modification to certain extent improved the textural porosity and charge recombination [8–10]. It was also reported that g-C_3N_4 loaded with nanoparticles of noble metals can efficiently absorb visible light and enhance photocatalytic activity due to surface plasmon resonance effect and this effect can be favorably harnessed by modifying the particle size, shape and environment [11]. Other recent works on the modified g-C_3N_4 aiming at make it workable in the broader visible light spectrum and to reduce the photogenerated electron-hole recombination of carriers are gold nanoparticles supported Au/C_3N_4 nanocomposite [12], Ag-modified mesoporous g-C_3N_4 [13], heterostructured g-C_3N_4/Ag/TiO_2 [14], Ag/C_3N_4 core–shell plasmonic composite [15] and g-C_3N_4/Ag_2O nanocomposite [16].

In the current study, we synthesized (i) g-C_3N_4 loaded with well-dispersed Au-Ag alloy nanoparticles with three different measures of Au contents in the Au-Ag alloy, (ii) pure g-C_3N_4 and (iii) g-C_3N_4 loaded with Au nanoparticles and (iv) g-C_3N_4 loaded with Ag nanoparticles. The optical characterizations (absorption spectra, diffuse reflectance spectra, and photoluminescence spectra) and the morphological characterizations (XRD, XPS, FESEM, and HRTEM) were carried out for pure, noble metal and alloy loaded variants of g-C_3N_4. These studies indicated that the three Au-Ag alloy loaded variants of g-C_3N_4, particularly show the positive attributes for a good photocatalysts, like increased absorption in the wide spectral range, reduced electron-hole recombination, and increased surface plasmon resonance compared to pure and single metal loaded counterparts. All the synthesized materials were used as a photocatalyst in the process of photocatalytic degradation (decolorization and mineralization) of Rhodamine B dye under artificial visible light and sunlight. It was found that particularly, the photocatalyst with 3% Au in Au-Ag/g-C_3N_4 under sunlight showed a remarkable result in the photocatalytic processes of decolorization and the removal of total organic carbon in Rhodamine B dye. Being prone to SPR assisted charge generation and transfer process, the performance of the as synthesized catalysts was evaluated under the exposure of low energy laser generated monochromatic light (532 nm, green). The mineralization efficiency of the catalysts was monitored by TOC measurements. The degradation as well as mineralization data were subjected to Langmuir-Hinshelwood kinetic model for the evaluation of the kinetics.

2. Experimental

2.1. Synthesis of photo-catalysts

Pure g-C_3N_4 was prepared by direct pyrolysis of melamine at 500 °C for 4 h at the heating rate of 10° C/min, whereas the de-amination treatment was performed at 550 °C for 2 h as per procedure detailed in the literature [17]. As detailed below, the modified Turkevich method was adopted for depositing different compositions of Au-Ag alloy nanoparticles at the surface of g-C_3N_4 [18]. In Au-Ag alloy loaded g-C_3N_4 photocatalysts, the proportion of Ag was fixed at 1%, whereas the amount of Au was varied as 0.5%, 1% and 3% with respect to the weight of g-C_3N_4. The required amounts of 0.01 M $HAuCl_4 \cdot 3H_2O$ and 0.01 M $AgNO_3$ precursor solutions were mixed and boiled under vigorous stirring (400–600 rpm). To this mixture, 1 ml of freshly prepared sodium citrate was added and re-boiled for 30 min that resulted in Au-Ag colloidal nanoparticles solution. The appropriate amount of g-C_3N_4 was dispersed in colloidal Au-Ag nanoparticles solution and ultrasonically stirred. The dispersion of Au-Ag nanoparticles and g-C_3N_4 was further subjected to UV light irradiation for photo-impregnation process under vigorous stirring for 30 min. A 450 W Xenon arc lamp equipped with UV band pass filter, Oriel, USA was used as the UV source. The slurry was filtered, washed and dried overnight at 110 °C under vacuum. The same method was adopted for the synthesis of 1% Ag and 1% Au loaded g-C_3N_4. In the further discussions, the Au-Ag alloy loaded g-C_3N_4 variants with 0.5% Au, 1% Au and 3% Au in Au-Ag/g-C_3N_4 are designated as 0.5% Au-Ag/g-C_3N_4, 1% Au-Ag/g-C_3N_4 and 3% Au-Ag/g-C_3N_4 respectively.

2.2. Characterization of synthesized catalysts

The crystal structure of synthesized catalysts was analyzed with wide angle X-ray diffractometer (Philips X'Pert PRO 3040/60) equipped with Cu-Kα radiation source in $2\theta = 10^\circ - 2\theta = 90^\circ$ range. The microstructure and morphology of prepared samples were examined with field emission scanning electron microscopy (SEM, Tescan Lyra-3). The fine structure analysis of as synthesized powders was carried out by transmission electron microscopy (TEM), JEM2100F, JEOL at 200KV. A JASCO, V-670, UV-vis-NIR spectrophotometer was used for recording the solid-state absorption and diffused reflectance spectra (DRS) of the synthesized catalysts using $BaSO_4$ pellet as a reference. The photoluminescence emission spectra were acquired by spectro-flourometer (Horiba Jobin Yvon), using the Xenon lamp as excitation source. For photoluminescence studies, all the samples were excited with the wavelength of 365 nm, and the emission spectra were recorded in the 400–700 nm wavelength range. The XPS profile of 3% Au-Ag/g-C_3N_4 sample was acquired by a wide survey scan using X-ray Photoelectron Spectrometer (PHI 5000 Versa Probe II, ULVAC-PHI Inc.). The binding energy was varied between 0 eV to 1100 eV. The oxidation states of the metallic components were evaluated by comparing the obtained binding energy values with that of standard values. Gaussian model was applied for curve fitting and the identification of the number and precise binging energy of each state.

2.3. Methodology of photo degradation study

The photocatalytic performance of the synthesized photocatalysts (g-C_3N_4, Ag/g-C_3N_4, Au/g-C_3N_4, 0.5% Au-Ag/g-C_3N_4, 1% Au-Ag/g-C_3N_4, and 3% Au-Ag/g-C_3N_4) was evaluated for the degradation (decolorization/mineralization) of Rhodamine B (10 ppm) in 200 ml cylindrical glass reactor made up of Pyrex® glass. A 450-W Xe arc lamp (Oriel, USA) equipped with UV cut off filter was used as an excitation source as shown in Supplementary Information File (see Fig. S1). The experiments were performed in batches. Prior to photocatalytic studies, the dark experiments were performed to establish the adsorption-desorption equilibrium between the dye and catalysts. In a typical photocatalytic experiment in visible light irradiation, 100 ml of dye/catalyst suspension containing, 100 mg of the respective catalyst, was exposed to visible light (420–800 nm) for 240 min under stirring. The samples (5 ml each) were drawn from the reactor after every 15 min in the initial 60 min, after every 30 min in the next hour and after 60 min in the final 120 min. After