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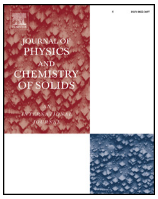

Dramatic visible photocatalytic performance of g-C_3N_4-based nanocomposite due to the synergistic effect of AgBr and ZnO semiconductors

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ABSTRACT

In this study, we synthesized a novel visible-light-driven photocatalyst with excellent photocatalytic activity, g-C_3N_4/AgBr/ZnO, as a ternary nanocomposite for pollutant degradation via a facile method. This coupling was favorable due to charge transfer between the semiconductors to yield a Z-scheme photocatalysis system, and thus the separation of photo-excited electron–holes was improved. The structure, morphology, and optical properties of the photocatalyst were determined by using characterization techniques, including X-ray diffraction, transmission electron microscopy, scanning electron microscopy with energy dispersive X-ray spectroscopy and its elemental mapping, N_2 adsorption-desorption analysis, ultraviolet-visible diffuse reflectance spectroscopy, photoluminescence, fourier transform infrared spectra, and zeta potential measurements. The photocatalytic activity of the g-C_3N_4/AgBr/ZnO heterostructure was evaluated with different weight ratios during the degradation of the cationic pollutant methylene blue (MB) under exposure to visible light. The optimal photocatalyst with a g-C_3N_4 content of 30% exhibited superior activity during the degradation of MB and the rate constant of 0.041 min^{-1} was about 4.6 times higher than the rate constant of the pure g-C_3N_4. In addition, we assessed the photosensitization of MB and its effect on the photodegradation process. We propose a possible mechanism to explain the photocatalytic activity of the prepared ternary nanocomposite based on experiments with reactive species scavengers. Finally, the reusability and stability of the photocatalyst was investigated after four cycles.

1. Introduction

Increasing concerns about environmental issues have motivated researchers to identify suitable semiconductor photocatalysts for degrading pollutants [1–7]. The most widely investigated semiconductor is TiO_2 because it has many advantages as an excellent photocatalyst when exposed to ultraviolet (UV) light due to its wide band gap. Sunlight is the best energy source for solving environmental issues but only 4% of the sunlight is in the UV region and most of the solar spectrum lies in the visible region, so an ideal material should have a band gap that absorbs light in the visible range. In addition, it should be non-toxic, abundant, thermally and chemically stable, and inexpensive. Polymeric graphite-like carbon nitride (g-C_3N_4) has an appropriate optical band gap of 2.7 eV, and thus it has attracted much attention in recent years [8–14]. Despite these excellent features, g-C_3N_4 has a rapid recombination rate for photogenerated electrons and holes, which hinder its applications as a photocatalyst. Many attempts have been made to address this problem in order to enhance the photocatalytic activity of g-C_3N_4, including nanoporous structure design [15], morphology control [16–18], doping with metal or non-metal ions such as Cu [19], V [20], Ag [21], B [22], P [23], and F [24], and coupling with other semiconductor materials with well-aligned band gaps such as TiO_2 [25], BiOX [26], AgX [27], $BiVO_4$ [28], Ag_2S [9], and some clusters [29]. These attempts to modify g-C_3N_4 with dopants created mid-gap states to increase the absorption of visible light, but these states could also act as recombination centers for photogenerated electron–hole pairs and decrease the photocatalytic efficiency. However, constructing a heterostructure by coupling g-C_3N_4 with other semiconductors may improve the separation of the photogenerated carriers and obtain higher photocatalytic performance.

In our previous studies, we prepared a new and improved photocatalyst with enhanced photocatalytic activity for degrading pollutants [30–34], where we employed silver bromide and zinc oxide to modify g-C_3N_4. Zinc oxide is of particular interest because its appropriate direct band gap of 3.03 eV, high electron mobility, and high redox potential make it a good photocatalyst [35]. However, ZnO cannot be applied under illumination with visible light. Silver bromide is a fascinating semiconductor with a band gap of about 2.5 eV and it can degrade

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pollutants under irradiation with visible light [36], but it is hindered by the rapid rate of recombination between electron and hole pairs. The locations of the conduction band (CB) and valence band (VB) in ZnO and AgBr make them highly suitable for combining with g-C_3N_4 to form a good heterojunction. To the best of our knowledge, no previous study has reported the use of a ternary g-C_3N_4/AgBr/ZnO nanocomposite as a photocatalyst. In order to assess the photocatalytic activity of this photocatalyst, we tested the photodegradation of methylene blue (MB) as an organic pollutant under irradiation with visible light. We explored the issue of catalyst photosensitization by MB by determining the changes in the UV-visible (UV-Vis) absorption spectra for MB during the photodegradation process [37]. Furthermore, we investigated whether the degradation of the dye was due to the photocatalytic activity of the photocatalyst or MB photosensitization.

2. Experimental section

2.1. Materials and methods

Potassium bromide and hydrogen chloride were purchased from Sigma-Aldrich and used without further purification. Silver nitrate, zinc nitrate hexahydrate, dicyandiamide, and sodium hydroxide were purchased from Merck and used without further purification. X-ray powder diffraction (XRD) was performed with a Bruker D8 Advance X-ray diffractometer (Philips, PW 1730, Netherland) with Cu Kα radiation in the range of 2θ = 10–80°. Transmission electron microscopy (TEM) was conducted using a CM30 system with an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) micrographs was prepared with a MIRA3, TESCAN instrument equipped with energy dispersive X-ray (EDX) and elemental mapping. UV-Vis diffuse reflectance spectroscopy (DRS) was performed with an AvaSpec-2048 TEC spectrometer. Photoluminescence (PL) spectra were recorded for the samples at room temperature using an Agilent-G980A instrument. Fourier transform infrared spectroscopy (FTIR) spectra were obtained for the samples using a RAYLEIGH WQF-510 A system in the wave number range of 4000–600 cm^{-1}. Zeta potentials were recorded with a Zetasizer (Nano ZS, Malvern, UK) at room temperature. The specific surface areas were estimated using the BET (Brunauer–Emmett–Teller) method, and the adsorption branch of isotherm based on the BJH (Barrett-Joyner-Halenda) model was used to calculate the pore size distributions. An ultrasonic bath was used to protonate g-C_3N_4.

2.2. Synthesis of g-C_3N_4 and protonation treatment

Bulk g-C_3N_4 was prepared by heating dicyandiamide as described previously [38]. First, 2 g of dicyandiamide was placed in a ceramic crucible and heated to 350 °C at a rate of 2.9 K min^{-1}, and kept at this temperature for 2 h in a flowing nitrogen atmosphere. Next, the product was heated at a rate of 3.3 K min^{-1} to a temperature of 550 °C and held at this temperature for another 2 h in a flowing nitrogen atmosphere. The carbon nitride obtained was crushed into powder. An ultrasound bath was used to protonate the prepared graphitic carbon nitride, where 1.0 g of g-C_3N_4 was ultrasonicated in HCl (0.5 M, 200 mL) for 1 h, before magnetic stirring at room temperature for 4 h [39]. The protonated g-C_3N_4 was then washed with deionized water until neutral conditions and dried at 70 °C in air for 12 h. The protonated g-C_3N_4 was denoted as PCN.

2.3. Development of pg-C_3N_4/AgBr/ZnO (CN/AB/ZO) and pg-C_3N_4/AgBr (CN/AB)

The CN/AB/ZO samples were prepared via a sonication-assisted deposition-precipitation technique. Typically, 0.15 g of the PCN was added to 20 mL of ethanol and sonicated for 1 h. Next, a solution of KBr (0.374 g in 50 mL double distilled water) was added to the suspension in excess to ensure that the amount of halide ions from KBr was more than sufficient to precipitate Ag^+ on the g-C_3N_4 surface. The mixture was stirred magnetically for 1 h. An aqueous solution of $AgNO_3$ (0.32 g, 20 mL) was then added dropwise to the suspension. The dropwise addition of $AgNO_3$ was necessary to avoid the rapid nucleation process by Ag^+ and Br^- on PCN in the solution. After stirring for 1 h at room temperature, we added 0.32 g of zinc nitrate hexahydrate dissolved in 20 mL double distilled water. The resulting mixture was stirred vigorously at room temperature for 3 h. An aqueous solution of NaOH (5 M) was then added dropwise to the solution under strong stirring at room temperature until the pH of the suspension reached 10. Subsequently, the suspension was refluxed for 3 h. The product obtained was filtered and the precipitate was washed with double distilled water and ethanol two times to remove the unreacted reagents, before drying in an oven at 60 °C for 24 h. Different weight ratios of g-C_3N_4 were obtained and designated as CN/AB/ZO x, where x is the approximate weight ratio of g-C_3N_4 relative to AgBr and ZnO in equal amounts. Thus, CN/AB/ZO 60, CN/AB/ZO 50, CN/AB/ZO 40, CN/AB/ZO 30, and CN/AB/ZO 20 nanocomposites were prepared in this manner. Table 1 shows the composition measured for each sample. For comparison, pg-C_3N_4/AgBr was prepared using the same procedure but without the addition of $Zn(NO_3)_2.6H_2O$ and NaOH, where addition of $AgNO_3$ was followed by stirring for 3 h at room temperature, filtering the product, and washing with double distilled water and ethanol several times. The prepared sample was dried in an oven at 60C for 24 h. The product was designated as CN/AB.

Table 1
Percentage compositions of the different weight ratios for the photocatalysts.

	g-C_3N_4	AgBr	ZnO
CN	100	0	0
CN/AB	75.2	24.8	0
CN/AB/ZO 60	70.9	23.4	5.7
CN/AB/ZO 50	59.3	32.8	7.9
CN/AB/ZO 40	42.2	46.6	11.2
CN/AB/ZO 30	25.1	60.0	14.9
CN/AB/ZO 20	17.1	66.8	16.6

2.4. Photocatalytic activity test

The prepared nanocomposites were tested by investigating the degradation of the organic dye MB at room temperature under irradiation with visible light provided by a 300 W halogen lamp (Osram), where a glass lid filtered wavelengths lower than 420 nm. First, the amount of photocatalyst was optimized for the degradation process. As shown in Fig. 1, 40 mg of the photocatalyst obtained the highest MB removal efficiency. In a typical photocatalytic experiment, the photocatalyst (0.04 g) was dispersed in MB solution (100 mL, 5.0 mg L^{-1}). Before illumination, the suspension was stirred magnetically in darkness for 30 min to ensure that the adsorption–desorption equilibrium was reached. At irradiation time intervals of 20 min, 4 mL of the suspension was collected and centrifuged for 10 min. The catalyst-free MB solution was then analyzed with a UV-Vis spectrophotometer (Raleigh UV-1600) at a wavelength of 665 nm with distilled water as a reference sample.

3. Results and discussion

3.1. Synthesis of CN/AB/ZO 30

The synthesis of the photocatalyst is shown schematically in Fig. 2. First, g-C_3N_4 was prepared from melamine. Next, it was protonated to increase its activity and then highly dispersed in water to react with other composites. KBr and $AgNO_3$ were used to form AgBr nanocomposites coupled with g-C_3N_4. $Zn(NO_3)_2.6H_2O$ was added to form Zn^{2+} in the structure and the addition of NaOH made the solution alkaline, so ZnO nanocomposites formed in the structure of g-C_3N_4.