Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Plasmonic Ag nanoparticles decorated NiAl-layered double hydroxide/graphitic carbon nitride nanocomposites for efficient visible-light-driven photocatalytic removal of aqueous organic pollutants

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ARTICLE INFO

Keywords:
g-C_3N_4
Layered double hydroxide
Surface plasmon resonance
Nanocomposite
Photocatalytic degradation

ABSTRACT

Ag nanoparticles decorated NiAl-layered double hydroxide/graphitic carbon nitride (Ag/LDH/g-C_3N_4) nanocomposites were synthesized for the first time by an *in situ* hydrothermal method, followed by photoreduction. The visible-light-driven Ag/LDH/g-C_3N_4 nanocomposites exhibited enhanced performance for the photocatalytic degradation of aqueous Rhodamine B and 4-chlorophenol. Notably, the Ag/LDH/g-C_3N_4 nanocomposite with LDH and Ag contents of 15 wt% and 1 wt%, respectively, showed the highest photocatalytic performance, which was far superior to that observed for pure g-C_3N_4, LDH, and the binary Ag/g-C_3N_4 and LDH/g-C_3N_4 composites. The enhanced photocatalytic efficiency was mainly attributed to rapid charge transfer at the Ag/LDH/g-C_3N_4 interfaces and the surface plasmon resonance of the Ag nanoparticles, which promotes the separation efficiency of photogenerated charge carriers and improves optical absorption. Additionally, the Ag/LDH/g-C_3N_4 nanocomposites exhibited excellent photostability during successive experimental runs, with no significant change in degradation performance. These findings are expected to provide new mechanistic insights into the design and construction of efficient visible-light-driven photocatalysts for application in solar energy conversion and environmental remediation.

1. Introduction

Photocatalysis using semiconductor materials has attracted considerable attention for its potential to address clean energy and environmental problems utilizing the abundant and renewable solar energy [1–3]. One of the foremost challenges that must be overcome to realize such photocatalysis for practical use is the development of efficient photocatalysts that function well under solar radiation. For practical use, an ideal semiconductor photocatalyst should be eco-friendly, inexpensive, stable, and have band edges that are suitable for the targeted reaction and correctly positioned to absorb visible light, thus utilizing the main component of the solar spectrum [4,5]. A large number of photocatalytic materials have been investigated for the said purpose, including TiO_2 [6], ZnO [7], CdS [8], WO_3 [9], $SrTiO_3$ [10] etc. However, most of them suffer from intrinsic drawbacks such as UV-only absorption, poor photostability, complicated preparation procedures, and rapid recombination of photogenerated charge carriers. Therefore, it is essential for researchers to design and develop novel visible-light-driven, high-efficiency photocatalytic materials.

Recently, as an analogue of graphite, polymeric graphitic carbon nitride (g-C_3N_4; CN) has emerged as a promising material for photocatalytic applications owing to its unique features, including its chemical and thermal stability, non-toxicity, and narrow band gap (*i.e.*, 2.7 eV) [11,12]. Furthermore, it can be easily and economically prepared on a large scale. In addition, CN, particularly in its two-dimensional (2D) nanosheet form, has a large specific surface area and tunable electronic structure [13].

Since the first report by Wang et al. [11] on the photocatalytic activity of CN for hydrogen generation by water-splitting, there has been significant progress in the development of CN-based catalysts for diverse applications, including the purification of contaminated water, CO_2 photoreduction, gas sensors, and artificial photosynthesis [12,14,15]. Nevertheless, the photocatalytic efficiency of bare CN remains too low for practical applications because of the fast recombination of its photoinduced charge carriers. Consequently, researchers have employed diverse strategies to improve the photocatalytic activity of CN, including doping with foreign elements [16,17], inducing textural porosity [18,19], noble-metal deposition [20–22], and constructing heterojunction composites with other semiconductor materials [23–27].

Construction of heterojunction composites by combining two different semiconductors, particularly into 2D layered architectures with

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https://doi.org/10.1016/j.cattod.2017.12.019
Received 24 August 2017; Received in revised form 6 December 2017; Accepted 18 December 2017

Please cite this article as: Tonda, S., Catalysis Today (2017), https://doi.org/10.1016/j.cattod.2017.12.019

suitable band edge potentials, is considered one of the most promising approaches to prevent the recombination of photogenerated charge carriers [28]. For instance, Li et al. [29] developed CN/Bi_2WO_6 layered composite photocatalysts that exhibited improved activity for CO_2 reduction as compared to that of bare CN and Bi_2WO_6. Furthermore, Xiang et al. [30] synthesized a graphene-CN composite with a unique stacking structure, which significantly enhanced the separation of photogenerated charge carriers and thus promoted photocatalytic H_2 generation performance.

Thus, the merits of layered composite photocatalysts motivated us to design similar layered composites by coupling CN with other layered semiconductor materials, such as layered double hydroxides (LDHs) [31,32]. In addition to the similarity of their layered structures to those of CN, the tunable chemical composition, surface hydroxyl group basicity, and visible-light responsiveness of LDHs make them an excellent choice for coupling with CN [33–35]. We reasoned that combining CN and LDHs with similar layered configurations would integrate their respective merits, thereby imbuing the resulting composites with enhanced photocatalytic properties.

Another strategy used to enhance photocatalytic efficiency is to prepare a noble-metal-loaded three-component heterojunction system. This has been demonstrated to improve the visible-light-absorption efficiency of catalysts owing to the surface plasmon resonance (SPR) phenomenon of noble metals [22,36,37].

Therefore, in the present work, highly efficient NiAl-LDH/CN nanocomposites decorated with Ag nanoparticles (NPs) were synthesized by an *in situ* hydrothermal method, followed by photoreduction. We believe that this is the first report on the synthesis and application of Ag-loaded LDH/g-C_3N_4 nanocomposites for the photodegradation of aqueous organic contaminants. The photocatalytic performance of the synthesized Ag/LDH/CN nanocomposites was assessed by the photodegradation of colored (Rhodamine B) and colorless (4-chlorophenol) aqueous organic contaminants under visible-light illumination. Furthermore, the effect of LDH content and the role of the Ag NPs on the degradation performance of the present system were systematically investigated, and a possible mechanism for the excellent photocatalytic performance of the Ag/LDH/CN nanocomposites was proposed based on the results of trapping, photoluminescence, and photocurrent experiments. The photostability of the synthesized nanocomposites was also examined by performing successive experimental runs.

2. Experimental section

2.1. Fabrication of photocatalysts

Melamine, nickel nitrate hexahydrate, aluminum nitrate nonahydrate, ammonium fluoride, urea, and silver nitrate were purchased from Sigma-Aldrich. All chemicals in this work were used as received without additional treatment.

Bulk CN was prepared by low-temperature thermal condensation using melamine as a precursor. Approximately 5 g of melamine was placed in an alumina boat and heat treated at 550 °C for 2 h under static air conditions in a muffle furnace. After heat treatment, the obtained yellow-colored product was ground into a fine powder and collected for further use.

To synthesize pure CN nanosheets, 2 g of the as-synthesized bulk CN was added to 50 mL HCl (~36%) and stirred for 30 min. The obtained pale yellow dispersion was then washed with water several times until the pH became neutral, followed by drying at 80 °C in air overnight. Approximately 200 mg of the acid-treated CN powder was re-dispersed in 250 mL of water and subjected to ultrasonic treatment for 1 h. The resulting suspension was collected and centrifuged at low rpm to remove unexfoliated bulk CN. Then, the white-colored supernatant was dried in an oven to obtain CN nanosheet powder.

The Ag/LDH/CN nanocomposites were synthesized by an *in situ* hydrothermal method followed by photoreduction. Initially, binary LDH/CN composites were fabricated using an *in situ* hydrothermal process. The typical procedure was as follows: A certain amount of as-synthesized CN nanosheet powder was dispersed in 160 mL of deionized water through ultrasonic treatment, and then nickel nitrate hexahydrate (0.006 M) and aluminum nitrate nonahydrate (0.002 M) were added to the suspension, which was ultrasonicated for another 10 min. Subsequently, NH_4F (0.016 M) and urea (0.04 M) were mixed with the above solution and agitated for 30 min. Thereafter, the obtained suspension was transferred to a 200 mL autoclave and heat treated at 120 °C for 24 h. Then, the resultant material was washed repeatedly with water until the pH became neutral and dried at 80 °C overnight. A series of LDH/CN composites were synthesized with different weight percentages of LDH to CN, *i.e.*, 5, 10, 15, and 20 wt%. Pure LDH was also synthesized by a similar procedure but in the absence of CN [38].

To obtain the Ag/LDH/CN nanocomposites, Ag NPs were deposited on LDH/CN through a photoreduction method using methanol as a hole scavenger. In brief, 100 mg of the LDH/CN composite synthesized above was dispersed in 50 mL of methanol/water (1:4 vol ratio) with ultrasonication, and an amount of silver nitrate calculated to deposit 1 wt% of Ag on the LDH/CN was added to the suspension. Then, the obtained suspension was degassed with argon for 10 min under stirring. Subsequently, the suspension was photoirradiated for 20 min using a 400 W mercury lamp under magnetic stirring. The solid product was then collected by centrifugation, washed with water, and dried at 80 °C overnight to obtain the Ag/LDH/CN nanocomposites. A series of Ag/LDH/CN nanocomposites with 1 wt% Ag and 5, 10, 15, and 20 wt% LDH to CN were synthesized and denoted as ALDHCN-5, ALDHCN-10, ALDHCN-15, and ALDHCN-20, respectively. A binary Ag/CN (1 wt% Ag on CN) composite was also synthesized as a reference material under similar conditions, but in the presence of CN rather than LDH/CN.

2.2. Material characterization

The synthesized materials were thoroughly characterized using a range of methods. X-ray diffraction (XRD) spectra were recorded using a Rigaku (D/Max-2500) diffractometer with Cu K_α radiation. UV–vis diffuse reflectance spectroscopy (DRS) analysis was performed using a SHIMADZU UV-2600 UV–vis spectrophotometer, and $BaSO_4$ was used as a reference. A SHIMADZU RF-6000 spectrofluorophotometer was employed for photoluminescence (PL) measurements using an excitation wavelength of 365 nm. Fourier transform infrared (FT-IR) spectra were obtained using a PerkinElmer (Frontier) FT-IR/NIR spectrometer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results were obtained using a Hitachi (SU8220) FESEM and a Hitachi (HT 7700) TEM, respectively. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. A TA Instruments Q500 thermogravimetric analyzer was used for thermogravimetric analysis (TGA).

2.3. Photocurrent and electrochemical impedance spectroscopy (EIS) measurements

Photocurrent and EIS characteristics were investigated using an IVIUM Technologies electrochemical workstation with indium tin oxide (ITO) deposited with the photocatalyst as the working electrode, a platinum foil as the counter electrode, and Ag/AgCl as a reference electrode. A 300 W Xe lamp was used as the light source to measure the transient photocurrent responses of the synthesized photocatalysts and an aqueous Na_2SO_4 (0.5 M) was used as the supporting electrolyte. EIS measurements were performed at an open circuit potential with a sinusoidal ac perturbation of 10 mV over the frequency range 10 mHz–100 kHz, and these experiments were employed in 10 mM $K_3[Fe(CN)_6]$ containing KCl (0.1 M) solution. The working electrodes were fabricated by adding 15 mg of catalyst powder to 0.5 mL of ethanol and 20 μL of Nafion solution (5 wt%), which was then ground to make a slurry. The resulting slurry was then evenly spread as