Chemosphere 172 (2017) 147–154

Contents lists available at ScienceDirect

Chemosphere

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

Anchoring of silver nanoparticles on graphitic carbon nitride sheets for the synergistic catalytic reduction of 4-nitrophenol

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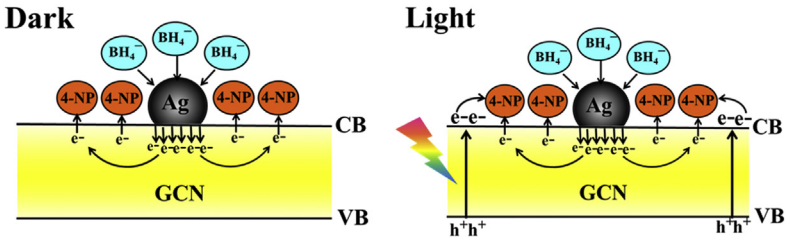
HIGHLIGHTS

- Ag/g-C_3N_4 composite was firstly used for catalytic reduction of 4-nitrophenol.
- Ag/g-C_3N_4 composite exhibited excellent catalytic activity.
- A synergistic effect and interaction of Ag NPs with g-C_3N_4 was studied.
- A catalytic mechanism of composite under different conditions was elucidated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 September 2016
Received in revised form
16 November 2016
Accepted 20 December 2016
Available online 22 December 2016

Handling Editor: Jun Huang

Keywords:
Ag/g-C_3N_4 composite
Electro/photo catalyst
4-nitrophenol
Catalytic activity
Synergistic effect

ABSTRACT

In this paper, a facile process was developed for anchoring of silver nanoparticles on graphitic carbon nitride sheets (Ag/g-C_3N_4) with high catalytic activity for reduction of 4-nitrophenol. The morphology and structure of the as-prepared Ag/g-C_3N_4 composite were investigated by FESEM, TEM, XRD and XPS. The reaction mechanism and the reduction kinetics of 4-nitrophenol under different light irradiation were systematically studied. The results showed that the obtained Ag/g-C_3N_4 composite exhibited a much higher electro/photo catalytic activity and stability for reduction of 4-nitrophenol. Significantly, due to the synergistic effect and interaction between highly dispersed Ag nanoparticles (Ag NPs, ~7.2 nm) and lamellar g-C_3N_4, not only transfer of interfacial charge, but also the separation of photoinduced electrons occurred when the reaction was proceeded under light. In addition, the composite exhibited high stability and reusability during the cycling experiments. The results showed that the Ag/g-C_3N_4 composite is an effective and stable electro/photo catalyst for reduction of 4-nitrophenol.

1. Introduction

Nowadays, as one of the most common contamination, 4-Nitropheonol (4-NP) has gradually increased and widely existed in wastewater produced in the manufacture of industrial and agricultural products (Bae et al., 2016). It has posed a serious threat to human beings and the environment due to its high toxicity, difficulty of natural degradation, and good chemical, biological stability (Zhang et al., 2012). Therefore, effective measures to remove of 4-NP from aqueous systems are of great significance in protecting the ecosystems. Up to now, among many treatment technologies, catalytic reduction of 4-NP to 4-aminophenol (4-AP) via the catalytic activity of noble metal nanostructures using sodium borohydride ($NaBH_4$) as reducing agent has been considered as an effective and eco-friendly route compared with other processes (Peng et al., 2011). Which is also one of the well-studied

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http://dx.doi.org/10.1016/j.chemosphere.2016.12.103
0045-6535/

models for evaluating the catalytic activities of noble metal nanostructures. (Abilash et al., 2011; Shin et al., 2012; Hsu and Chen, 2014; Li et al., 2015b; Teresa et al., 2015). What's more, as a fine organic chemical intermediate, 4-AP, the product of the catalytic reduction has been mainly applied in synthesis of industrial sulfur dyes, production of antipyretic analgesic drugs, such as paracetamol, clofibrate. And it could be used to prepare developer, antioxidant and oil additives (Kong et al., 2013).

Some noble metallic nanoparticles such as Au, Ag and Pt, due to their distinctive properties, have attracted comprehensive attention and been widely applied in electronic, catalyst, biological industry (Huang et al., 2014). Especially, as a common and relatively inexpensive noble metal, Ag nanoparticles (Ag NPs) have been used in electro catalytic reduction of 4-NP to 4-AP (Chiou et al., 2013). Ag NPs with smaller particle size have larger surface area and more active atoms exposed on the surface, exhibiting superior catalytic property (Petronella et al., 2013). However, smaller nanoparticles are easy to agglomerate due to their higher surface energy, thus Ag NPs were usually protected by surface modifiers during the synthesis process. Unfortunately, these organic modifiers would cover around the surface and interact with Ag NPs, which lead to a distinct decrease of their catalytic activities. Hence, loading Ag NPs on inorganic supports to avoid the above problems has been considered as one of the applicable strategies (Singh and Bahadur, 2015). For example, Ag NPs have been decorated onto graphene oxide (Li et al., 2015b), carbon (Chi et al., 2014), carbon nanofibers (Peng et al., 2011), N-doped carbon (Wu et al., 2015), silica (Deng et al., 2007), etc. But among above supports, only the supplementary role has been taken into consideration, while the catalytic property of the supports was usually neglected.

Recently, graphite-like carbon nitride (g-C_3N_4, GCN) has attracted more and more attention because of its high adsorption capacity, good electron conductivity and large specific surface area. In addition, it has been recognized as the most stable allotrope of carbon nitride under ambient conditions due to its excellent thermal stability and acid-alkali-resistance (Wang et al., 2011; Tu et al., 2013; Li et al., 2015a). In some studies, owing to being a nontoxic metal-free semiconductor which possesses outstanding optical property, GCN has attracted much scientific interest in the photocatalytic field (Carlsson, 2008; Sridharan et al., 2013; Cao and Yu, 2014; Dong et al., 2014; Li et al., 2014; Wei et al., 2015; Zhu et al., 2015; Ong et al., 2016).

More importantly, on the one hand, as one of the π-conjugated materials with many π-π conjugations on the surface, GCN can adsorb molecules. On the other hand, due to the nature of the lamellar structure, GCN is usually well-crystallized which can promote the charge transfer (Pan et al., 2012). What's more, different from other inorganic π-conjugated materials, GCN is a kind of soft polymer which can be easily loaded by other materials (Chen et al., 2014; Lv et al., 2015; Sridharan et al., 2015; Tian et al., 2015). For the aforementioned reasons, GCN is an ideal carrier for the loading of Ag NPs, which can be applied for the catalytic reduction of 4-NP. Yang et al. have prepared silver deposited graphitic carbon nitride, but they used it as a plasmonic photocatalyst with enhanced visible-light photocatalytic activity for degradation of methyl orange (MO) and *p*-nitrophenol (PNP) under aerobic conditions (Yang et al., 2013b).

In this paper we report the synthesis and simultaneous anchoring of silver nanoparticles on GCN by one-step method. And a systematic study was performed to investigate the catalytic reduction of 4-NP using Ag/g-C_3N_4 (Ag/GCN) composites as catalysts under different conditions of light irradiation. All the experiments were done under an anaerobic condition. The catalytic mechanism of Ag/GCN catalyst was proposed, the synergistic effect of highly dispersed Ag NPs with small particle size (~7.2 nm) and photocatalytic GCN promoted the transfer of the interfacial charge and photoinduced electrons, hence Ag/GCN exhibited significantly enhanced catalytic activity for the reduction of 4-NP to 4-AP. Furthermore, the reusability of the catalyst was evaluated by five consecutive catalytic runs. And it is interesting that the reduction of 4-NP can be accelerated significantly, when the reaction was carried out under irradiation of xenon (Xe) lamp.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, 99.9%), sodium borohydride ($NaBH_4$) and 4-nitrophenol (4-$C_6H_5NO_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Thiourea (CN_2H_4S) were purchased from Tianjin Chemical Reagent Co., Ltd. All reagents were of chemical reagent grade and used without further purification.

2.2. Preparation of GCN, Ag/GCN catalysts

GCN was synthesized on the basis of a procedure reported previously (Dong et al., 2014). Typically, 10 g of thiourea was calcined at 550 °C in air atmosphere for 2 h in a muffle furnace at a heating rate of 10 °C/min. Ag/GCN composites with different Ag contents (3, 5, 8, 10, 12, 15 wt%, denoted as, Ag/GCN-3, Ag/GCN-5, Ag/GCN-8, Ag/GCN-10, Ag/GCN-12, Ag/GCN-15, respectively) were synthesized by photochemical reduction. 0.6 g of GCN powder was dispersed in 30 mL of water, a certain quantity of $AgNO_3$ (0.01 mol/L) aqueous solution was added into above suspension under stirring. After that, the mixture was irradiated by a 300 W Xe lamp with continuous stir for 2 h, and then the product was washed and finally dried in a vacuum oven at 50 °C for further use.

2.3. Characterization

Crystal structure of the obtained samples were analyzed by X-ray diffraction (XRD) using a Philips X'Pert PRO diffractometer with Cu K_α radiation (λ = 1.5418 Å) at room temperature. The morphology of the samples were investigated by transmission electron microscope (TEM, Tecnai G2 20, FEI Company, Holland) with an acceleration voltage of 200 kV and field emitting scanning electron microscope (FESEM, Sirion 450, FEI Company, Holland) at 20 KV with an energy dispersive spectroscope (EDS). X-ray photoelectron spectroscopy (XPS) was accomplished using a Kratos/Axis Ultra DLD-600W spectrometer with Mg Kα source. Molecular structures were analyzed by Fourier transform infrared (FT-IR) spectrometer (Bruker VERTEX70). The thermal gravimetric and differential thermal analysis of samples were performed on Diamond TG/DTA (PerkinElmer Instruments) in an argon flow at a heating rate of 10 °C/min to determine the contents of silver in the Ag/GCN composites. The room temperature photoluminescence (PL) spectra were detected on a fluorescence spectrometer (RF-5301PC, Japan) with excitation wavelength of 325 nm. Ultraviolet–visible (UV–vis) diffuse reflection spectra were recorded on a Lambda 35 using $BaSO_4$ as a reference.

2.4. Catalytic reduction of 4-NP

To study the catalytic activity, 3 mL of a freshly prepared aqueous solution of $NaBH_4$ (3×10^{-1} M) was introduced to 150 mL solution of 4-NP (1.03×10^{-4} M), then 15 mg of Ag/GCN composite was added to the above solution. During the catalytic experiment, about 3 mL of mixture was sampled and filtered through a 0.45 μm membrane filter at an interval of 2 min for the measurement of UV–vis absorption spectra (UV-670 spectrophotometer, Mapada).