



Silver oxide decorated graphitic carbon nitride for the realization of photocatalytic degradation over the full solar spectrum: From UV to NIR region



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ABSTRACT

To achieve fully utilization of solar energy, development of an efficient full solar spectrum light responsive photocatalyst is strongly needed. Besides, the smaller particle sizes, better dispersion and more heterojunction interfaces can enhance the photocatalytic performance of photocatalysts. Assembling graphite-like carbon nitride (g-C₃N₄) with a narrow bandgap semiconductor to form a heterostructure which can increase the charge-separation efficiency and harvest the light from UV to near-infrared (NIR) region would be ideal for photocatalysis. Here, we report a facile synthesis of Ag₂O/g-C₃N₄ heterostructures by *in-situ* growth Ag₂O nanoparticles (NPs) onto surface of g-C₃N₄ nanosheets (NSs) to display superior UV–visible–NIR full spectrum photocatalytic activities and favorable stability. TEM results show that the obtained Ag₂O NPs with the size of 8 nm are uniformly dispersed on the surface of g-C₃N₄ NSs, which reveals that g-C₃N₄ is probably a promising support template for *in-situ* growth of nano-sized materials. The mechanism for improving the photocatalytic performance of the Ag₂O/g-C₃N₄ heterostructures is proposed. It is demonstrated that the Ag₂O/g-C₃N₄ heterostructures not only enhance the production of photogenerated electron-hole pairs by extending the visible and NIR light absorption region due to the visible and NIR harvesting of highly dispersed smaller Ag₂O NPs on the surface of g-C₃N₄ NSs, but also facilitate electron-hole separation by the heterojunction formed by intimate contact between Ag₂O and g-C₃N₄. Moreover, the formation of a certain amount of metal Ag⁰ on the surface of Ag₂O under illumination contribute to the high stability and charge transfer of Ag₂O/g-C₃N₄ heterostructures.

1. Introduction

In the past decades, focus has been on how to make full use of solar energy to be efficiently applied in clean and renewable resource [1]. Solar energy is distributed in UV, visible and near-infrared (NIR) light with a proportion of about 5%:45%:50% [2]. Due to the economical, efficient, clean and environment-friendly properties, photocatalytic technologies have attracted extensive attention to maximal utilization in hazardous organic pollutions removal or stable hydrogen fuel production via solar energy conservation [3]. However, the photocatalytic activities are still far from satisfactory owing to the traditional UV or visible responsive photocatalysts, the fast recombination of photo-induced carriers, and/or low photocatalytic efficiencies [4]. Therefore, the development of novel NIR-light or even full solar spectrum (UV, visible and NIR) responsive photocatalysts with high photocatalytic efficiencies have become important.

Recently, some narrow bandgap semiconductors, such as Ag₂O, has recently attracted significant attention [5]. Moreover, with the increasing concerns over NIR photocatalytic nanomaterials, the importance of such Ag₂O is receiving considerable attention because of their negligible toxicity, narrow bandgap, and large absorption coefficient [6]. The low energy bandgap (0.9–1.2 eV) of Ag₂O nanoparticles (NPs) means that it can absorb NIR light without the necessity of further doping processes [7]. These works revealed that Ag₂O could perform as a potential excellent NIR photocatalyst.

Among the numerous types of photocatalysts, graphitic carbon nitride (g-C₃N₄) has shown great potential since the pioneering work reported in 2009 for water splitting under visible light irradiation by Wang et al. [8]. As a kind of metal-free polymeric material, g-C₃N₄, especially the two dimensional (2D) g-C₃N₄ nanosheets (NSs), has recently been regarded as a promising visible-light responsive candidate for water splitting and organic degradation due to their large

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surface area, medium band gap (2.4–2.8 eV), environmentally benign and exceptional chemical stability [9]. However, most of the as-prepared g-C₃N₄ material has a high recombination rate of photogenerated carriers with inefficient light absorption above 460 nm; thus greatly restricting its practical applications [10]. To challenge these limitations, many strategies have been developed to improve the photocatalytic activity of g-C₃N₄, including metal or metal-free doping [11], nano/mesoporous structural modification [12], and dye-/nanocrystal-sensitization [13]. Besides, constructing a heterostructure has attracted much attention [14], because the typical 2D sheets of g-C₃N₄ could provide a suitable scaffold for contacting with other nano-sized photocatalysts and achieving nanocomposites with promising interface, which is beneficial to improving the rate of charge transfer [15]. Zhang et al. [16] constructed efficient ZnIn₂S₄/g-C₃N₄ composite with enhanced visible photocatalytic activity, and they considered that this enhanced photoactivity is mainly attributed to the efficient interfacial transfer of photoinduced carriers from g-C₃N₄ to ZnIn₂S₄. Li et al. [17] synthesized the AgIO₃/g-C₃N₄ heterojunction nanocomposites by *in situ* precipitation and growth strategy at room temperature. The as-prepared composites exhibited remarkable visible photocatalytic degradation activity owing to the synergetic effect between AgIO₃ and g-C₃N₄, including matching potentials, the large contact region, and effective charge separation. Therefore, it is believed that coupling g-C₃N₄ NSs with other narrow bandgap photocatalysts, such as Ag₂O, to form a heterostructure is expected to promote photogenerated charge separation and extend light absorption range to even NIR region to obtain the full solar spectrum photocatalytic activity. However, studies adopting this designed strategy to achieve full solar spectrum photocatalysis have never been reported by now.

Herein, we constructed Ag₂O NPs supported on g-C₃N₄ NSs with intimate interfacial contact, which demonstrated high efficiency for photocatalytic degradation organic contaminant under UV, visible, and NIR light for the first time. In this process, the ultrathin g-C₃N₄ NSs not only perform as the support to form heterostructures, but also are employed as dispersants to confine the aggregation of Ag₂O NPs, leading to ultrafine Ag₂O NPs uniformly packed throughout the surface of g-C₃N₄ NSs. Furthermore, this kind of Ag₂O/g-C₃N₄ heterostructure has greatly overcome the drawbacks compared with the single component and realized high charge separation efficiency, strong redox ability, and long-term stability. The photocatalytic process including light absorption, charge separation and transfer of the synthesized Ag₂O/g-C₃N₄ heterostructure was investigated, which indicate improved charge separation efficiency and longer lifetime. The proposed mechanism of the photocatalytic activity for Ag₂O/g-C₃N₄ heterostructures is also discussed.

2. Experimental section

2.1. Preparation of photocatalysts

g-C₃N₄ nanosheets were prepared according to the previously reported method [18]. Ag₂O/g-C₃N₄ heterostructures were prepared by a simple chemical precipitation method and the mass ratio was fixed to 1:1 to 3:1. In a typical process, 0.1 g g-C₃N₄ nanosheets were dispersed in 50 mL of distilled water, and then 0.59–4.77 g of AgNO₃ was added to the suspension. After the mixture was stirred magnetically for 30 min, 50 mL of 0.2 M NaOH was dropped to the above mixture of AgNO₃ and g-C₃N₄. The amount of NaOH was more than sufficient to produce Ag₂O precipitating from the added AgNO₃, and the final pH is 14. Finally, The as-prepared Ag₂O/g-C₃N₄ heterostructures were washed with deionized water and dried in the oven at 50 °C overnight. For comparison, pure Ag₂O particles was also obtained in the absence of g-C₃N₄ nanosheets during the preparation process of Ag₂O/g-C₃N₄ heterostructures.

2.2. Characterization

Powder X-ray diffraction (XRD) pattern of samples were collected on a Bruker D8 Advance powder X-ray diffractometer with Cu K α ($\lambda = 0.15418$ nm). Field-emission (FEI) scanning electron microscope (FESEM, Nova 450, USA) and high resolution transmission electron microscope (HRTEM, JEOL-2100, Japan) were performed to characterize the morphologies of the samples. X-ray photoelectron spectroscopy (XPS) technique was carried out on a Thermo ESCALAB 250XI instrument. UV–vis–NIR diffuse reflectance spectrophotometry (DRS) were tested using a UV–vis–NIR spectrophotometer (Hitachi UV-3101). The electron spin resonance (ESR) signals were performed on a Bruker model ER200-SRC spectrometer. Simulated sunlight was used to irradiate the sample, respectively. Steady and transient photoluminescence (PL) curves of the as-fabricated products were obtained on a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) under the excitation of a hydrogen flash lamp with the wavelength at 800 nm (nF900, Edinburgh Instruments).

2.3. Photocatalytic and photoelectrochemical activity test

The photocatalytic experiments were carried out by adding 20 mg photocatalysts into 20 mL of 20 mg/L methyl orange (MO) solution in the vessel and were conducted in an XPA photochemical reactor. A 300 W mercury lamp with a maximum emission at 356 nm, a 350 W xenon lamp with a UV cutoff filter ($\lambda > 420$ nm), and a 300 W infrared lamp with filter glasses to filter UV and visible light were used as UV, visible, and NIR light sources, respectively. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium between the dye and the surface of the catalyst under normal atmospheric conditions. Transient photocurrent responses (PEC) and electrochemical impedance spectroscopy (EIS) curves were measured under NIR light irradiation (740 nm, 100 mW/cm²) with light on-off switches of 50 s in a three-electrode electrochemical cell in the 0.1 M Na₂SO₄ electrolyte, in which Pt foil and Hg/Hg₂Cl₂/KCl (saturated) electrode were used as the counter and reference electrodes, respectively.

3. Results and discussion

3.1. Structure and composition of Ag₂O/g-C₃N₄ heterostructures

The Ag₂O/g-C₃N₄ heterostructures were developed through the growth of improved NIR absorption of a layer Ag₂O NPs on the surface of g-C₃N₄ NSs to achieve the full solar spectrum (UV, visible, and NIR) photocatalytic property (Scheme 1). Compared with the yellow color of g-C₃N₄ NSs, a black powder was obtained for the Ag₂O/g-C₃N₄ heterostructures. First, to certify the successful fabrication of the Ag₂O NPs on g-C₃N₄ NSs, the as-prepared heterostructure was examined by powder XRD characterization (Fig. 1). In the g-C₃N₄ sample (black curve), the XRD diffraction peak located at 27.4° is (002) plane for interlayer stacking of the conjugated aromatic system planes of graphitic C₃N₄ layered structure with an interlayer distance of 0.326 nm, while the other one at 13.0° ($d = 0.675$ nm) can be attributed to (100) plane for the in-plane structural repeating units of tri-s-triazine (JCPDS 87-1526) [19]. This two diffraction peaks are in accordance with those of hexagonal g-C₃N₄ in the literature [20]. As shown in red curve, six diffraction peaks at 26.7°, 32.8°, 38.0°, 54.9°, 65.4° and 68.7° can be indexed to the (110), (111), (200), (220), (311), and (222) planes of pure and well-crystallized cubic phase Ag₂O (JCPDS 43-0997) [21]. Both hexagonal phase g-C₃N₄ and cubic phase Ag₂O could be observed in the Ag₂O/g-C₃N₄ heterostructures (blue curve), and no other impurity peaks could be found in XRD pattern, indicating the successful fabrication of Ag₂O NPs on the surface of the g-C₃N₄ with a layered structure. Moreover, Ag₂O/g-C₃N₄ heterostructures with other mass ratios at 1:1, 1.5:1 and 3:1 are also obtained (Fig. S1), With

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