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Gold/monolayer graphitic carbon nitride plasmonic photocatalyst for ultrafast electron transfer in solar-to-hydrogen energy conversion

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ABSTRACT

Gold (Au) plasmonic nanoparticles were grown evenly on monolayer graphitic carbon nitride (g-C_3N_4) nanosheets via a facile oil-bath method. The photocatalytic activity of the Au/monolayer g-C_3N_4 composites under visible light was evaluated by photocatalytic hydrogen evolution and environmental treatment. All of the Au/monolayer g-C_3N_4 composites showed better photocatalytic performance than that of monolayer g-C_3N_4 and the 1% Au/monolayer g-C_3N_4 composite displayed the highest photocatalytic hydrogen evolution rate of the samples. The remarkable photocatalytic activity was attributed largely to the successful introduction of Au plasmonic nanoparticles, which led to the surface plasmon resonance (SPR) effect. The SPR effect enhanced the efficiency of light harvesting and induced an efficient hot electron transfer process. The hot electrons were injected from the Au plasmonic nanoparticles into the conduction band of monolayer g-C_3N_4. Thus, the Au/monolayer g-C_3N_4 composites possessed higher migration and separation efficiencies and lower recombination probability of photogenerated electron-hole pairs than those of monolayer g-C_3N_4. A photocatalytic mechanism for the composites was also proposed.

1. Introduction

Energy crises and environmental pollution are two major challenges facing the contemporary world that force people to move away from their dependence on fossil fuels [1–3]. Hydrogen (H_2) is a source of renewable green energy that is an attractive substitute for fossil fuels. To realize the effective use of H_2 energy, it is necessary to develop H_2 production technologies that are clean, cheap, efficient, and large-scale [4,5]. Photocatalytic H_2 evolution can translate solar energy into chemical energy and has the advantages of high product purity, carbon-free environmental friendliness, simplicity, and low energy consumption, thereby making it a promising H_2 production technology [6–8]. However, photocatalytic H_2 evolution technology is currently limited by the low efficiency of photocatalytic H_2 evolution, poor stability of the photocatalyst, and high

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cost of H_2 evolution [9,10]. Therefore, developing affordable, easily prepared photocatalysts for photocatalytic H_2 evolution has attracted much attention. Metal-free semiconductor materials are desirable to realize solar energy conversion without using toxic heavy metals [11].

A representative metal-free semiconductor photocatalyst is graphitic carbon nitride (g-C_3N_4), which has excellent physical and chemical properties, such as high chemical and thermal stability, commendable photoelectric properties, and powerful antioxidant behavior [12,13]. Importantly, g-C_3N_4 can make use of visible light because of its suitable band gap [14]. Thus, g-C_3N_4 has been widely applied in photocatalytic degradation, air purification, photocatalytic water splitting, and photocatalytic carbon dioxide reduction [15,16]. However, bulk g-C_3N_4 possesses several disadvantages, such as low specific surface area, a high recombination rate of photogenerated electron-hole pairs, and sluggish reaction kinetics [17–19]. These disadvantages severely limit the photocatalytic activity of bulk g-C_3N_4, so it is necessary to improve its photocatalytic performance by modification strategies such as nanostructure formation, molecular doping, construction of heterojunctions, and elemental doping [20–22]. One approach to improve the photocatalytic efficiency of g-C_3N_4 is to exfoliate bulk g-C_3N_4 into monolayer g-C_3N_4 nanosheets [23]. At present, there are two main exfoliation methods of g-C_3N_4: liquid exfoliation and thermal exfoliation [24]. Two-dimensional (2D) g-C_3N_4 nanosheets possess a larger specific surface area with more active sites, higher separation efficiency of photogenerated electron-hole pairs, and increased electron transport compared with the corresponding properties of bulk g-C_3N_4 [25].

Although 2D g-C_3N_4 nanosheets display greatly improved photocatalytic performance over that of bulk g-C_3N_4, their performance still does not meet the expectations of researchers. Therefore, massive effort has been devoted to optimizing the photocatalytic ability of 2D g-C_3N_4 nanosheets [26]. Doping 2D g-C_3N_4 nanosheets with a plasmonic metal (like Au, Ag, Pd, Pt, Rh, or Ir) could further enhance its ability to absorb visible light through the surface plasmon resonance (SPR) effect, which is one of the most common and effective strategies to enhance photocatalytic activity [27–30]. As many researchers have reported [31–39], when a plasmonic metal is coupled with a semiconductor, hot electrons are generated in the plasmonic metal by overcoming the Schottky barrier under visible-light irradiation. Then, a high density of hot electrons flows into the conduction band (CB) of the semiconductor to trigger the reduction reaction, resulting in increased photocatalytic activity. Previously, our group designed a plasmonic composite consisting of Ag nanoparticles supported on monolayer g-C_3N_4 nanosheets, which verified the role of the SPR effect in increasing photocatalytic activity [40]. However, the photocatalytic performance of the Ag/2D g-C_3N_4 composites was still less than ideal.

The purpose of this work is to greatly enhance the photocatalytic performance of monolayer g-C_3N_4 and steer the flow of charge carriers by dispersing Au plasmonic nanoparticles on the surface of monolayer g-C_3N_4 nanosheets. The H_2 evolution rate of the resulting Au/monolayer g-C_3N_4 composites is evaluated. The photocatalytic mechanism of the composites is investigated by photocurrent tests.

2. Experimental

2.1. Synthesis of monolayer g-C_3N_4

The monolayer g-C_3N_4 was prepared according to our previous report [1]. Melamine (2 g) was placed in a crucible and then annealed at 550 °C for 4 h after heating at a rate of 2 °C/min in a muffle furnace. The obtained sample was ground into a powder and then annealed again at 550 °C under the same conditions, the obtained white sample was monolayer g-C_3N_4.

2.2. Fabrication of Au/monolayer g-C_3N_4 composites

Monolayer g-C_3N_4 (0.1 g) was dissolved in water (10 mL) under sonication. $NH_3{\cdot}H_2O$ (2 mL), Na_2SO_3 (0.01 g), and isooctane (10 mL) were added to the mixture. The stirred mixture was heated in an oil bath (95 °C) for 10 min, and then $HAuCl_4{\cdot}4H_2O$ (0.0011, 0.0021, or 0.0042 g) was added dropwise. The mixture was stirred at 95 °C for 1 h. The sample was collected by centrifugal separation and then washed several times with pure water. The Au/monolayer g-C_3N_4 composites were obtained by freeze-drying. The samples produced using different masses of $HAuCl_4{\cdot}4H_2O$ of 0.0011, 0.0021, and 0.0042 g are denoted as 0.5%, 1%, and 2% Au/monolayer g-C_3N_4, respectively.

2.3. Characterization

The samples were analyzed by X-ray diffraction (XRD) by Bruker D8 diffractometer with Cu K_α radiation (λ = 1.5418 Å) in the range of 2θ = 10°−80°. The structural information for samples was measured by Fourier transform infrared spectroscopy (FTIR, Avatar 470, Thermo Nicolet) using the standard KBr disk method. The morphology and structure of the samples were investigated with scanning electron microscope (SEM) and transmission electron microscopy (TEM). The SEM images were taken on a field-emission microscope by a JEOL JSM-7001F. The transmission electron microscopy (TEM) images were collected with a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. Elemental compositions were detected by X-ray photoelectron spectroscopy (XPS) analysis which was performed on an ESCALab MKII X-ray photo-electron spectrometer using the Mg K_α radiation. Ultraviolet visible (UV-vis) diffuse reflectance spectrums (DRS) of the samples were measured by using a UV-vis spectrophotometer (Shimadzu UV-2450, Japan) in the range of 200 to 800 nm. $BaSO_4$ was used as the reflectance standard material. The photoluminescence (PL) spectra of the samples were obtained by a QuantaMaster & TimeMaster Spectrofluorometer with an excitation wavelength at 325 nm. X-band ESR spectra were recorded at ambient temperature on a JES FA200 spectrometer. The settings for the ESR spectrometer were as follows: center field, 336.496 mT; sweep width, 5 mT; microwave frequency, 9.5 GHz; modulation frequency, 100