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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-C₃N₄) nanosheets via a facile oil-bath method. The photocatalytic activity of the Au/monolayer g-C₃N₄ composites under visible light was evaluated by photocatalytic hydrogen evolution and environmental treatment. All of the Au/monolayer g-C₃N₄ composites showed better photocatalytic performance than that of monolayer g-C₃N₄ and the 1% Au/monolayer g-C₃N₄ 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-C₃N₄. Thus, the Au/monolayer g-C₃N₄ composites possessed higher migration and separation efficiencies and lower recombination probability of photogenerated electron-hole pairs than those of monolayer g-C₃N₄. A photocatalytic mechanism for the composites was also proposed.

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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 (H₂) is a source of renewable green energy that is an attractive substitute for fossil fuels. To realize the effective use of H₂ energy, it is necessary to develop H₂ production technologies

that are clean, cheap, efficient, and large-scale [4,5]. Photocatalytic H₂ 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 H₂ production technology [6–8]. However, photocatalytic H₂ evolution technology is currently limited by the low efficiency of photocatalytic H₂ evolution, poor stability of the photocatalyst, and high

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cost of H₂ evolution [9,10]. Therefore, developing affordable, easily prepared photocatalysts for photocatalytic H₂ 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-C₃N₄), 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-C₃N₄ can make use of visible light because of its suitable band gap [14]. Thus, g-C₃N₄ has been widely applied in photocatalytic degradation, air purification, photocatalytic water splitting, and photocatalytic carbon dioxide reduction [15,16]. However, bulk g-C₃N₄ 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-C₃N₄, 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-C₃N₄ is to exfoliate bulk g-C₃N₄ into monolayer g-C₃N₄ nanosheets [23]. At present, there are two main exfoliation methods of g-C₃N₄: liquid exfoliation and thermal exfoliation [24]. Two-dimensional (2D) g-C₃N₄ 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-C₃N₄ [25].

Although 2D g-C₃N₄ nanosheets display greatly improved photocatalytic performance over that of bulk g-C₃N₄, their performance still does not meet the expectations of researchers. Therefore, massive effort has been devoted to optimizing the photocatalytic ability of 2D g-C₃N₄ nanosheets [26]. Doping 2D g-C₃N₄ 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-C₃N₄ nanosheets, which verified the role of the SPR effect in increasing photocatalytic activity [40]. However, the photocatalytic performance of the Ag/2D g-C₃N₄ composites was still less than ideal.

The purpose of this work is to greatly enhance the photocatalytic performance of monolayer g-C₃N₄ and steer the flow of charge carriers by dispersing Au plasmonic nanoparticles on the surface of monolayer g-C₃N₄ nanosheets. The H₂ evolution rate of the resulting Au/monolayer g-C₃N₄ composites is evalu-

ated. The photocatalytic mechanism of the composites is investigated by photocurrent tests.

2. Experimental

2.1. Synthesis of monolayer g-C₃N₄

The monolayer g-C₃N₄ was prepared according to our previous report [23]. 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-C₃N₄.

2.2. Fabrication of Au/monolayer g-C₃N₄ composites

Monolayer g-C₃N₄ (0.1 g) was dissolved in water (10 mL) under sonication. NH₃·H₂O (2 mL), Na₂SO₃ (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 HAuCl₄·4H₂O (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-C₃N₄ composites were obtained by freeze-drying. The samples produced using different masses of HAuCl₄·4H₂O of 0.0011, 0.0021, and 0.0042 g are denoted as 0.5%, 1%, and 2% Au/monolayer g-C₃N₄, respectively.

2.3. Characterization

The samples were analyzed by X-ray diffraction (XRD) by Bruker D8 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of $2\theta = 10^\circ\text{--}80^\circ$. 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. BaSO₄ 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

kHz; power, 0.998 mW.

2.4. Photoelectrochemical measurements

The photocurrent generated by the samples was tested with an electrochemical analyzer (CHI660B, Chen Hua Instruments, Shanghai, China) using a standard three-electrode configuration including a Pt wire counter electrode, Ag/AgCl reference electrode, and Na₂SO₄ (0.1 mol/L) aqueous solution as the electrolyte. The light source was a 500-W Xe arc lamp. Each sample (5 mg) was dispersed in ethanol (0.5 mL) and ethylene glycol (0.5 mL). Then, 20 μ L of each dispersion was drop-cast onto an indium tin oxide (ITO) substrate over a fixed area of 0.5 cm². Each sample-modified ITO electrode was dried under an infrared lamp. A potential of -0.2 V (vs. Ag/AgCl) was used in the photocurrent measurements.

2.5. Photocatalytic activity measurements

Photocatalytic H₂ production by the samples was tested using an online photocatalytic H₂ production system (LbSolar-3AG, PerfectLight, Beijing). Each sample (0.05 g) was dispersed in an aqueous solution consisting of water (90 mL) and hole sacrificial agent (10 mL). The mixtures were degassed before conducting measurements, which were performed using a 300-W Xe lamp (PLS-SXE 300C (BF), PerfectLight, Beijing)

with an optical filter ($\lambda > 400$ nm) as the light source. An online gas chromatograph (GC D7900P, thermal conductivity detector, nitrogen carrier gas, 5 Å molecular sieve column, Shanghai Feichomp) was used to determine the photocatalytic H₂ evolution rate.

The photocatalytic activities of the samples were investigated by their photodegradation of ciprofloxacin (CIP) and methyl orange (MO) under visible-light irradiation. The light source was a 300-W Xe lamp with a 400-nm cutoff filter. Each sample (0.0150 g) was dispersed in CIP or MO aqueous solution (10 mg/L, 50 mL). The reaction used a pump to provide oxygen. To ensure that absorption-desorption equilibrium was reached on the photocatalyst surface, the suspension was stirred for about 30 min in the dark before light exposure. The experiments were conducted under continuous stirring at 30 °C. Every 30 min, a 3.5 mL aliquot of the suspension was extracted and centrifuged. The supernatant was analyzed using a UV-vis spectrophotometer (UV-2450, Shimadzu, Japan). The contents of pollutants were determined using the maximum absorption wavelengths of CIP of 276 nm and of MO of 463 nm.

3. Results and discussion

3.1. Enhancement of photocatalytic activity

Fig. 1(a) shows the photocatalytic performance of the

Fig. 1. (a) Photocatalytic H₂ evolution by the photocatalysts (0.05 g) in 10 vol% triethanolamine aqueous solution under visible-light irradiation. (b) Stability test of 1% Au/monolayer g-C₃N₄ for H₂ evolution under visible-light irradiation. Photocatalytic activity of monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites for the degradation of CIP (c) and MO (d) under visible-light irradiation.

Au/monolayer g-C₃N₄ composites in H₂ evolution from water. The pure monolayer g-C₃N₄ showed low photocatalytic H₂ evolution activity under visible-light irradiation with an H₂ evolution rate of 153 $\mu\text{mol g}^{-1} \text{h}^{-1}$. All of the Au/monolayer g-C₃N₄ composites exhibited enhanced photocatalytic activity compared with that of the pure monolayer g-C₃N₄. In particular, the 1% Au/monolayer g-C₃N₄ composite exhibited the highest H₂ evolution rate of 565 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is in line with that of previously reported Au/g-C₃N₄ photocatalysts (Table S1). These results indicated that the introduction of Au plasmonic nanoparticles raised the photocatalytic performance of monolayer g-C₃N₄. The optimal Au content to maximize the H₂ evolution rate was 1%. This result indicates that a moderate amount of Au plasmonic nanoparticles dispersed on the surface of the monolayer g-C₃N₄ nanosheets facilitated charge transport. Although the SPR effect of the 2% Au/monolayer g-C₃N₄ should be enhanced compared with that of the composite with 1% Au, the number of active sites of monolayer g-C₃N₄ will decrease because Au covers more of the surface of monolayer g-C₃N₄. The excess Au nanoparticles do not enhance the migration and separation efficiency of photogenerated electron-hole pairs, and may serve as recombination centers of photogenerated electron-hole pairs, thus lowering the H₂ evolution rate [41–43].

The performance of Au/monolayer g-C₃N₄ and that of previously reported Ag/monolayer g-C₃N₄ are compared in Fig. S1 [40]. The 1% Au/monolayer g-C₃N₄ composite showed a higher H₂ evolution rate (565 $\mu\text{mol g}^{-1} \text{h}^{-1}$) than that of 1% Ag/monolayer g-C₃N₄ (173 $\mu\text{mol g}^{-1} \text{h}^{-1}$), suggesting that Au/monolayer g-C₃N₄ possessed higher photocatalytic activity than Ag/monolayer g-C₃N₄ at the same doping amount. In addition, the H₂ evolution rate of 1% Au/monolayer g-C₃N₄ was also higher than that of 2% Ag/monolayer g-C₃N₄ (342 $\mu\text{mol g}^{-1} \text{h}^{-1}$), which was the optimal doping amount in our previously reported system. Therefore, compared with our previously reported Ag/monolayer g-C₃N₄ composites, Au/monolayer g-C₃N₄ displayed dramatically improved photocatalytic activity at a much lower doping amount.

The photocatalytic performance of Au/monolayer g-C₃N₄ composites was also evaluated by photodegradation of CIP and MO under visible-light irradiation (Fig. 1(c) and (d)). To rule out the photosensitization process of the Au/monolayer g-C₃N₄ composites, CIP was chosen as a model colorless organic pollutant. CIP is a widely used antibiotic. However, CIP in aquatic environments seriously threatens human health and the safety of ecosystems, so the degradation of CIP has become an important issue. As shown in Fig. 1(c), compared with that of the pure monolayer g-C₃N₄, all of the Au/monolayer g-C₃N₄ composites exhibited enhanced photocatalytic activity for CIP degradation under visible-light irradiation. This clearly indicates that the introduction of Au to monolayer g-C₃N₄ enhances its photocatalytic activity. The 1% Au/monolayer g-C₃N₄ exhibited the highest photocatalytic activity of the composites; its photocatalytic degradation efficiency of CIP was about 61% after irradiation for 3.5 h, which was almost 3.4 times higher than that of pure monolayer g-C₃N₄ (18%). The photocatalytic degradation efficiencies of 0.5% and 2% Au/monolayer g-C₃N₄

were about 41% and 36% after irradiation for 3.5 h, respectively.

Moreover, the photocatalytic degradation of MO was investigated to further evaluate the photocatalytic activity of the Au/monolayer g-C₃N₄ composites; the results are presented in Fig. 1(d). After irradiation for 3.5 h, only about 21% MO was degraded by the pure monolayer g-C₃N₄. The photocatalytic activity increased remarkably when Au nanoparticles were introduced onto the monolayer g-C₃N₄. Again, 1% Au/monolayer g-C₃N₄ possessed the highest photocatalytic activity of the composites; its photocatalytic degradation efficiency of MO was about 98% after irradiation for 3.5 h. In contrast, the photocatalytic degradation efficiencies of 0.5% and 2% Au/monolayer g-C₃N₄ were about 82% and 71% after irradiation for 3.5 h, respectively. The photocatalytic degradation kinetics of the organic pollutants CIP and MO were also determined (Fig. S2).

The results of activity tests presented above indicated that the Au content of the composites had a considerable effect on their photocatalytic performance. The optimal Au content of the Au/monolayer g-C₃N₄ composites was approximately 1%. An appropriate Au content dispersed well on the surface of the monolayer g-C₃N₄ to promote the separation and transfer of photoinduced charge carriers. The photocatalytic H₂ evolution rate decreased when the Au content exceeded 1% because the excess Au nanoparticles might function as a recombination center or cover the active sites of monolayer g-C₃N₄, lowering its adsorption capacity, thereby decreasing the efficiency of charge separation and transfer [42,43]. Therefore, it was important to optimize the ratio of Au nanoparticles to monolayer g-C₃N₄.

The stability and reusability of a photocatalyst are also relevant to its practical application. Therefore, recycling reactions were conducted for photocatalytic H₂ evolution and the photodegradation of CIP and MO over 1% Au/monolayer g-C₃N₄ under visible-light irradiation; the results are presented in Fig. 1(b) and S3, respectively. After several continuous cycles, no obvious decay of the photocatalytic activity of 1% Au/monolayer g-C₃N₄ was observed, which meant that the composite had high photocatalytic stability. Furthermore, the XRD patterns of 1% Au/monolayer g-C₃N₄ before and after the photocatalytic reactions (Fig. S3(c)) revealed that there was no apparent change in the crystal structure of the sample after several photocatalysis cycles. This indicates that the Au/monolayer g-C₃N₄ composites are very stable during the photodegradation process.

3.2. Catalyst characterization

XRD was used to study the crystallinity and purity of the samples. Typical diffraction patterns of monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites are shown in Fig. 2(a). Monolayer g-C₃N₄ exhibited a strong (002) peak at around 27.4°, which was attributed to the stacking of the conjugated aromatic system and confirmed that monolayer g-C₃N₄ was indeed g-C₃N₄ [44]. The Au/monolayer g-C₃N₄ hybrid composites also displayed the (002) peak at the same position, suggesting that

Fig. 2. XRD patterns (a) and FT-IR spectra (b) of the monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites.

the introducing of Au had no effect on the crystal structure of monolayer g-C₃N₄. Furthermore, the diffraction peaks observed at 38.2°, 44.3°, 64.6°, and 77.6° in the XRD patterns of the Au/monolayer g-C₃N₄ composites could be assigned to the (111), (200), (220), and (311) planes of metallic Au nanoparticles, respectively [45]. With increasing Au content, the intensity of the diffraction peaks from Au nanoparticles increased gradually. No diffraction peaks from Au were detected for 0.5% Au/monolayer g-C₃N₄, which was attributed to its low content of Au.

Fig. 2(b) depicts the Fourier transform infrared (FT-IR) spectra of the monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites. The FT-IR spectra were similar for the pure mono-

layer g-C₃N₄ and Au/monolayer g-C₃N₄ composites, which indicates that all the Au/monolayer g-C₃N₄ composites retained the same chemical structure as that of pure monolayer g-C₃N₄. The band at about 808 cm⁻¹ corresponded to the characteristic breathing mode of the s-triazine units [46]. The absorption bands observed at about 1242, 1325, 1415, 1565 and 1640 cm⁻¹ were assigned to the typical stretching vibration modes of CN heterocycles [47]. N-H stretching vibrations were observed between 3600 and 3000 cm⁻¹ [48].

The chemical composition and chemical states of monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites were further determined by X-ray photoelectron spectroscopy (XPS). Fig 3(a) shows the survey scan of pure monolayer g-C₃N₄ and

Fig. 3. XPS analysis of the pure monolayer g-C₃N₄ and 1% Au/monolayer g-C₃N₄. (a) Survey; (b) C 1s; (c) N 1s; (d) Au 4f.

Au/monolayer g-C₃N₄ composites; C, N, and O were found in the as-prepared samples. In addition, 1% Au/monolayer g-C₃N₄ contained Au. These results indicated that there were no other impurities in the Au/monolayer g-C₃N₄ composites and Au was successfully doped on monolayer g-C₃N₄. The high-resolution C 1s spectrum in Fig. 3(b) could be fitted with two peaks at about 284.8 and 288.5 eV. The peak at 284.8 eV corresponded to carbon contamination, and that at 288.5 eV was assigned to the typical aromatic C–N=C motif [49]. The high-resolution N 1s spectrum in Fig. 3(c) could be deconvoluted into three peaks at about 398.9, 400.4, and 401.5 eV, which were attributed to nitrogen atoms in the C=N–C, C–N(–C)–C, and C–N–H functional groups, respectively [50]. Based on these XPS analysis, the molecular structure of monolayer g-C₃N₄ remained unchanged after the introduction of a small amount of Au. In addition, the high-resolution Au 4f spectrum in Fig. 3(d) could be deconvoluted into two peaks at about 83.8 and 87.4 eV, which were assigned to Au 4f_{7/2} and Au 4f_{5/2}, respectively. These values were consistent with reported literature [51], further confirming the presence of metallic Au in the Au/monolayer g-C₃N₄ composites.

The morphologies of the monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Fig. 4. Fig 4(a) reveals that monolayer g-C₃N₄ was electron transparent and its surface was wrinkled, indicating that monolayer g-C₃N₄ consisted of ultrathin nanosheets with a structure like that of graphene. Fig 4(b) reveals that 1% Au/monolayer g-C₃N₄ was also wrinkled, illustrating that the introduction of Au plasmonic nanoparticles did

not damage the ultrathin nanosheet structure of g-C₃N₄. Au plasmonic nanoparticles with a diameter of about 10 nm were dispersed on the surface of the monolayer g-C₃N₄ nanosheets. The SEM image in Fig. 4(c) of 1% Au/monolayer g-C₃N₄ further confirmed that the composite maintained its ultrathin nanosheet structure. Chemical element mapping analysis was used to confirm the existence of Au in the composites. As illustrated in Fig. 3(d–f), C, N, and Au were distributed in similar areas, which indicated the existence and uniform distribution of these elements. Importantly, Fig. 3(f) showed that Au was homogeneously distributed, further confirming the presence of Au plasmonic nanoparticles in the Au/monolayer g-C₃N₄ composites.

The optical properties of a material greatly affect its photocatalytic activity, so the optical properties of the pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites were investigated by UV-vis diffuse reflectance spectroscopy. As shown in Fig. 5, compared with the light absorption of pure monolayer g-C₃N₄, all of the Au/monolayer g-C₃N₄ composites exhibited enhanced light absorption with a slight red shift. The UV-vis absorption spectra of the Au/monolayer g-C₃N₄ composites displayed a broad absorption peak in the range of about 500–650 nm, which was ascribed to the SPR of Au nanoparticles [51]. The absorption intensity and SPR effect obviously increased with Au content, which was related to the color of the as-prepared samples (sample color changed from white to light grey with increasing Au content). The SPR absorption improved the visible-light absorption intensity and range of the composites, thus enhancing their utilization efficiency of solar energy, which might contribute to enhanced their photocatalytic activity.

3.3. Possible photocatalytic mechanism

The separation, transfer, and recombination of photogenerated electron-hole pairs greatly influence the photocatalytic properties of a material. To elucidate the possible photocatalytic mechanism of the samples, photoluminescence (PL), photocurrent, and electrochemical impedance spectroscopy (EIS)

Fig. 4. (a) SEM image of monolayer g-C₃N₄. (b) TEM image of 1% Au/monolayer g-C₃N₄. (c) SEM image of 1% Au/monolayer g-C₃N₄. Chemical element mapping images of 1% Au/monolayer g-C₃N₄ C 1s (d) N 1s (e), and Au 4f (f).

Fig. 5. Optical absorption spectra of the pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites.

Fig. 6. (a) PL spectra of the pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites. (b) Photocurrent responses of the pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites under visible-light irradiation ([Na₂SO₄] = 0.1 mol/L). (c) Nyquist plots of the pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites in the dark ([Na₂SO₄] = 0.1 mol/L).

measurements were performed. Fig. 6(a) displays the PL spectra of pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites. The emission peaks for all samples were at the same position centered around 450 nm, suggesting that introducing Au plasmonic nanoparticles did not affect the position of the emission peak of g-C₃N₄. The PL intensity of the Au/monolayer g-C₃N₄ composites was weaker than that of monolayer g-C₃N₄, indicating that the introduction of Au greatly lowered the recombination probability of photogenerated electron-hole pairs [52]. The PL results showed that introducing Au was conducive to charge separation in the Au/monolayer g-C₃N₄ composites, which then bring about higher photoactivity.

Next, the photocurrents of pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites were measured to further analyze their separation and transfer of photogenerated electron-hole pairs; the results are displayed in Fig. 6(b). The photocurrents remained stable after five intermittent on-off irradiation cycles and all the composites exhibited a higher photocurrent response than that of monolayer g-C₃N₄. As the Au content increased from 0.5% to 1%, the photocurrent responses gradually rose, which means that the photogenerated electron-hole pairs in the Au/monolayer g-C₃N₄ composites were separated more effectively. The photocurrent response of the composites then gradually decreased as Au content increased to 2%, indicating that the excess Au nanoparticles might be-

come new recombination centers, resulting in the decline of photocatalytic activity. These results are consistent with the photocatalytic activity of the composites, explaining why 1% Au/monolayer g-C₃N₄ possessed the best photocatalytic performance of the composites.

To better understand the role of Au nanoparticles in the photocatalytic activity of the composites, EIS analysis was performed. The Nyquist plots of pure monolayer g-C₃N₄ and Au/monolayer g-C₃N₄ composites are shown in Fig. 6(c). A smaller arc radius for a photocatalyst indicates more efficient charge separation and transfer [53]. All the Au/monolayer g-C₃N₄ composites exhibited a smaller arc radius than that of pure monolayer g-C₃N₄, in good agreement with the photocatalytic activities of these materials. These results illustrate that introducing Au to g-C₃N₄ facilitated charge separation and transfer. The arc radius of the Nyquist plot of 1% Au/monolayer g-C₃N₄ was the smallest of the samples, indicating that 1% Au/monolayer g-C₃N₄ had the fastest charge transfer rate, which was reflected by it exhibiting the highest photocatalytic activity of the materials.

To confirm that the reason for the enhanced photocatalytic performance of the composites was hot electron injection rather than formation of a Schottky junction, the photocurrents of monolayer g-C₃N₄ and 1% Au/monolayer g-C₃N₄ were measured under UV irradiation ($\lambda = 365$ nm). As shown in Fig. 7(a),

Fig. 7. (a) Photocurrent responses of the pure monolayer g-C₃N₄ and 1% Au/monolayer g-C₃N₄ under UV irradiation ($\lambda = 365$ nm). (b) Schematic illustration of the proposed mechanism for photocatalytic H₂ evolution over the Au/monolayer g-C₃N₄ composites.

the photocurrent intensity of 1% Au/monolayer g-C₃N₄ was nearly the same as that of monolayer g-C₃N₄ under UV light, which meant that the photogenerated electrons in the CB of monolayer g-C₃N₄ could not be transferred to the surface of Au plasmonic nanoparticles. That is, a Schottky junction did not play a part in the charge flow process. Therefore, it could be speculated that hot electron injection increased the efficiency of the whole photocatalytic process. As presented in Fig. 7(b), when the Au/monolayer g-C₃N₄ was exposed to visible light, a high density of hot electrons was generated in the Au plasmonic nanoparticles through the SPR effect. The hot electrons then flowed into the CB of monolayer g-C₃N₄ to participate in the photocatalytic reaction, resulting in increased photocatalytic activity.

Based on the above analysis results, a possible photocatalytic H₂ evolution mechanism of Au/monolayer g-C₃N₄ system was proposed, as presented in Fig. 7(b). Under visible-light irradiation, Au plasmonic nanoparticles and monolayer g-C₃N₄

were both excited to separate electron-hole pairs. The hot electrons then transferred to the CB of monolayer g-C₃N₄ because of the SPR effect. Finally, the hot electrons could unite with H⁺ to produce H₂, and the holes could react with triethanolamine to produce the oxidation product.

The possible photocatalytic mechanism of photocatalytic degradation by the Au/monolayer g-C₃N₄ composites is now discussed further. To reveal the main active oxygen species in the photocatalytic process, electron spin resonance (ESR) and trapping experiments were performed using 1% Au/monolayer g-C₃N₄. Fig. 8(a) shows the ESR spectra of superoxide radicals (O₂^{•-}). There was no ESR signal in the dark and the obvious characteristic peaks of O₂^{•-} were observed visible-light irradiation. These results illustrate that O₂^{•-} could only be generated when visible light reached the surface of the as-prepared sample. In contrast, no signals from hydroxyl radicals (•OH) were detected (Fig. 8(b)), which signified that •OH was not the main active species; instead, O₂^{•-} played an im-

Fig. 8. ESR spectra of 1% Au/monolayer g-C₃N₄ under visible-light irradiation. (a) Superoxide radical and (b) hydroxyl radical. Trapping experiments of active species during the photodegradation of (c) CIP and (d) MO in the presence of 1% Au/monolayer g-C₃N₄ under visible-light irradiation. (e) Schematic illustration of the proposed mechanism for photodegradation of pollutants.

portant role in this photocatalytic reaction. Moreover, according to the results of trapping experiments in Fig. 8(c) and (d), generated holes also affected the photocatalytic degradation process. In the trapping experiments, *tert*-butanol was used as an $\bullet\text{OH}$ scavenger and triethanolamine was used as a hole scavenger. Fig. 8(c) reveals that the photodegradation efficiency of CIP over 1% Au/monolayer g-C₃N₄ was strongly inhibited upon the addition of triethanolamine. Conversely, the photocatalytic degradation efficiency only slightly changed upon the addition of *tert*-butanol. Therefore, holes were another main active species and $\bullet\text{OH}$ were not. The same results were found for MO photodegradation (Fig. 8(d)), which indicates that the photocatalytic mechanism might be the same for photodegradation of MO and CIP. The ESR and trapping experiments revealed that $\text{O}_2^{\bullet-}$ and holes were the main species affecting the photocatalytic activity of this system. The proposed photocatalytic degradation mechanism based on these results is presented in Fig. 8(e). Under visible-light irradiation, Au plasmonic nanoparticles and monolayer g-C₃N₄ were both excited to separate electron-hole pairs. The hot electrons were transferred to the CB of monolayer g-C₃N₄ because of the SPR effect. The hot electrons could unite with O_2 to produce $\text{O}_2^{\bullet-}$, then $\text{O}_2^{\bullet-}$ reacted with pollutants. Meanwhile, the holes also could react with pollutants.

4. Conclusions

An Au/monolayer g-C₃N₄ plasmonic photocatalyst was successfully synthesized by an oil-bath method. The Au/monolayer g-C₃N₄ composites exhibited enhanced photocatalytic activity compared with that of monolayer g-C₃N₄ and 1% Au/monolayer g-C₃N₄ possessed the highest photocatalytic performance. The enhanced photocatalytic activity was chiefly attributed to the SPR effect of the Au nanoparticles, which promoted ultrafast hot electron transfer from Au plasmonic nanoparticles into the CB of monolayer g-C₃N₄, inducing higher transfer and separation efficiencies of the photogenerated electron-hole pairs.

References

- [1] T. Bhowmik, M. K. Kundu, S. Barman, *ACS Catal.*, **2016**, 6, 1929–1941.
- [2] G. G. Liu, T. Wang, H. B. Zhang, X. G. Meng, D. Hao, K. Chang, P. Li, T. Kako, J. H. Ye, *Angew. Chem. Int. Ed.*, **2015**, 54, 13561–13565.
- [3] R. G. Li, *Chin. J. Catal.*, **2017**, 38, 5–12.
- [4] X. Tan, H. A. Tahini, S. C. Smith, *ACS Catal.*, **2016**, 6, 7071–7077.
- [5] G. G. Liu, G. X. Zhao, W. Zhou, Y. Y. Liu, H. Pang, H. B. Zhang, D. Hao, X. G. Meng, P. Li, T. Kako, J. H. Ye, *Adv. Funct. Mater.*, **2016**, 26, 6822–6829.
- [6] K. L. Corp, C. W. Schlenker, *J. Am. Chem. Soc.*, **2017**, 139, 7904–7912.
- [7] Q. Han, B. Wang, J. Gao, L. T. Qu, *Angew. Chem. Int. Ed.*, **2016**, 55, 10849–10853.
- [8] H. Ahmad, S. K. Kamarudin, L. J. Minggu, M. Kassim, *Renewable*

Graphical Abstract

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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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A gold nanoparticle/monolayer graphitic carbon nitride plasmonic photocatalyst prepared by a facile oil-bath method displayed a high photocatalytic hydrogen evolution rate of 565 $\mu\text{mol g}^{-1} \text{h}^{-1}$ because of the regulated flow of charge carriers.

- Sustainable Energy Rev.*, **2015**, 43, 599–610.
- [9] L. Yuan, C. Han, M. Q. Yang, Y. J. Xu, *Int. Rev. Phys. Chem.*, **2016**, 35, 1–36.
- [10] K. Maeda, K. Domen, *Bull. Chem. Soc. Jpn.*, **2016**, 89, 627–648.
- [11] G. G. Zhang, Z. A. Lan, X. C. Wang, *Chem. Sci.*, **2017**, 7, 3062–3066.
- [12] G. P. Dong, Y. H. Zhang, Q. W. Pan, J. R. Qiu, *J. Photochem. Photobiol. C*, **2014**, 20, 33–50.
- [13] Y. F. Li, R. X. Jin, Y. Xing, J. Q. Li, S. Y. Song, X. C. Liu, M. Li, R. C. Jin, *Adv. Energy Mater.*, **2016**, 6, 1601273.
- [14] Y. H. Li, W. K. Ho, K. L. Lv, B. C. Zhu, S. C. Lee, *Appl. Surf. Sci.*, **2018**, 430, 380–389.
- [15] X. P. Dong, F. X. Cheng, *J. Mater. Chem. A*, **2015**, 3, 23642–23652.
- [16] W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.*, **2016**, 116, 7159–7329.
- [17] C. M. Li, Y. H. Du, D. P. Wang, S. M. Yin, W. G. Tu, Z. Chen, M. Kraft, G. Chen, R. Xu, *Adv. Funct. Mater.*, **2017**, 27, 1604328.
- [18] H. J. Yu, R. Shi, Y. X. Zhao, T. Bian, Y. F. Zhao, C. Zhou, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung, T. R. Zhang, *Adv. Mater.*, **2017**, 29, 70111.
- [19] J. S. Zhang, Y. Chen, X. C. Wang, *Energy Environ. Sci.*, **2015**, 8, 3092–3108.
- [20] S. W. Cao, J. X. Low, J. G. Yu, M. Jaroniec, *Adv. Mater.*, **2015**, 27, 2150–2176.
- [21] G. Mamba, A. K. Mishra, *Appl. Catal. B*, **2016**, 198, 347–377.
- [22] Y. H. Li, K. L. Lv, W. K. Ho, F. Dong, X. F. Wu, Y. Xia, *Appl. Catal. B*, **2017**, 202, 611–619.
- [23] X. J. She, J. J. Wu, J. Zhong, H. Xu, Y. C. Yang, R. Vajtai, J. Lou, Y. Liu, D. L. Du, H. M. Li, P. M. Ajayan, *Nano Energy*, **2016**, 27, 138–146.
- [24] S. M. Yin, J. Y. Han, T. H. Zhou, R. Xu, *Catal. Sci. Technol.*, **2015**, 5, 5048–5061.
- [25] Q. Han, B. Wang, J. Gao, Z. H. Cheng, Y. Zhao, Z. P. Zhang, L. T. Qu, *ACS Nano*, **2016**, 10, 2745–2751.
- [26] Z. W. Zhao, Y. J. Sun, F. Dong, *Nanoscale*, **2015**, 7, 15–37.
- [27] S. J. Tan, L. M. Liu, Y. N. Dai, J. D. Ren, J. Zhao, H. Petek, *J. Am. Chem. Soc.*, **2017**, 139, 6160–6168.
- [28] U. Bhattacharjee, L. Men, B. A. Rosales, S. R. Alvarado, J. Vela, J. W. Petrich, *J. Phys. Chem. C*, **2017**, 121, 676–683.
- [29] T. T. Wang, P. Raghunath, Y. G. Lin, M. C. Lin, *J. Phys. Chem. C*, **2017**, 121, 9681–9690.
- [30] Y. H. Li, K. L. Lv, W. K. He, Z. W. Zhao, Y. Huang, *Chin. J. Catal.*, **2017**, 38, 321–329.
- [31] C. C. Jia, X. X. Li, N. Xin, Y. Gong, J. X. Guan, L. N. Meng, S. Meng, X. F. Guo, *Adv. Energy Mater.*, **2016**, 6, 1600431.
- [32] M. Valenti, M. P. Jonsson, G. Biskos, A. Schmidt-Ott, W. A. Smith, *J. Mater. Chem. A*, **2016**, 4, 17891–17912.
- [33] J. W. Hong, D. H. Wi, S. U. Lee, S. W. Han, *J. Am. Chem. Soc.*, **2016**, 138, 15766–15773.
- [34] X. G. Meng, L. Q. Liu, S. X. Ouyang, H. Xu, D. F. Wang, N. Q. Zhao, J. H. Ye, *Adv. Mater.*, **2016**, 28, 6781–6803.
- [35] L. Yan, F. W. Wang, S. Meng, *ACS Nano*, **2016**, 10, 5452–5458.
- [36] J. M. Zhang, X. Jin, P. I. Morales-Guzman, X. Yu, H. Liu, H. Zhang, L. Razzari, J. P. Claverie, *ACS Nano*, **2016**, 10, 4496–4503.
- [37] S. Bai, X. Y. Li, Q. Kong, R. Long, C. M. Wang, J. Jiang, Y. J. Xiong, *Adv. Mater.*, **2015**, 27, 3444–3452.
- [38] A. Naldoni, T. Montini, F. Malara, M. M. Mróz, A. Beltram, T. Virgili, C. L. Boldrini, M. Marelli, I. Romero-Ocaña, J. J. Delgado, V. Dal Santo, P. Fornasiero, *ACS Catal.*, **2017**, 7, 1270–1278.
- [39] S. K. Cushing, N. Wu, *J. Phys. Chem. Lett.*, **2016**, 7, 666–675.
- [40] J. J. Yi, X. J. She, Y. H. Song, H. Xu, P. Zhang, Z. Mo, L. Liu, D. L. Du, H. M. Li, *RSC Adv.*, **2016**, 6, 112420–112428.
- [41] S. Tonda, S. Kumar, V. Shanker, *Mater. Res. Bull.*, **2016**, 75, 51–58.
- [42] X. J. Bai, R. L. Zong, C. X. Li, D. Liu, Y. F. Liu, Y. F. Zhu, *Appl. Catal. B*, **2014**, 147, 82–91.
- [43] L. Ge, C. C. Han, J. Liu, Y. F. Li, *Appl. Catal. A*, **2011**, 409–410, 215–222.
- [44] H. Xu, J. Yan, Y. G. Xu, Y. H. Song, H. M. Li, J. X. Xia, C. J. Huang, H. L. Wan, *Appl. Catal. B*, **2013**, 129, 182–193.
- [45] N. Y. Cheng, J. Q. Tian, Q. Liu, C. J. Ge, A. H. Qusti, A. M. Asiri, A. O. Al-Youbi, X. P. Sun, *ACS Appl. Mater. Interfaces*, **2013**, 5, 6815–6819.
- [46] X. J. She, H. Xu, H. F. Wang, J. X. Xia, Y. H. Song, J. Yan, Y. G. Xu, Q. Zhang, D. L. Du, H. M. Li, *Dalton Trans.*, **2015**, 44, 7021–7031.
- [47] Z. Mo, X. J. She, Y. P. Li, L. Liu, L. Y. Huang, Z. G. Chen, Q. Zhang, H. Xu, H. M. Li, *RSC Adv.*, **2015**, 5, 101552–101562.
- [48] H. Xu, J. Yan, X. J. She, L. Xu, J. X. Xia, Y. G. Xu, Y. H. Song, L. Y. Huang, H. M. Li, *Nanoscale*, **2014**, 6, 1406–1415.
- [49] Z. X. Zhou, J. H. Wang, J. C. Yu, Y. F. Shen, Y. Li, A. R. Liu, S. Q. Liu, Y. J. Zhang, *J. Am. Chem. Soc.*, **2015**, 137, 2179–2182.
- [50] H. Xu, Y. X. Song, Y. H. Song, J. X. Zhu, T. T. Zhu, C. B. Liu, D. X. Zhao, Q. Zhang, H. M. Li, *RSC Adv.*, **2014**, 4, 34539.
- [51] J. J. Xue, S. S. Ma, Y. M. Zhou, Z. W. Zhang, M. He, *ACS Appl. Mater. Interfaces*, **2015**, 7, 9630–9637.
- [52] K. L. He, J. Xie, X. Y. Luo, J. Q. Wen, S. Ma, X. Li, Y. P. Fang, X. C. Zhang, *Chin. J. Catal.*, **2017**, 38, 240–252.
- [53] F. Chen, H. Yang, X. F. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 296–304.

具有超快电子传输能力的金/薄层氮化碳等离子光催化剂用于光催化产氢

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摘要: 光催化产氢可以直接将太阳能转化为化学能, 是非常有前景的产氢技术之一。然而, 光催化产氢的瓶颈在于如何提高光催化产氢效率和光催化剂的稳定性, 以及降低产氢成本。因此, 开发廉价、易于制备的产氢光催化剂引起人们广泛关注。作为一种非金属半导体光催化剂, 石墨相氮化碳(g-C₃N₄)具有良好的物理化学性质, 如良好的化学和热稳定性、极佳的光电性能、强的抗氧化能力等。更为重要的是, g-C₃N₄具有合适的能带结构, 能够利用可见光。因此, g-C₃N₄已广泛应用于光催化降解、空气净化、光解水和光催化CO₂还原等领域。然而, 体相g-C₃N₄仍然暴露出一些缺点, 例如比表面积小、光生电子-空穴对的复合率高和反应动力学差等。将体相g-C₃N₄剥离成g-C₃N₄纳米薄片是提高光催化效率的有效方法。薄层g-C₃N₄纳米片具有较高的比表面积, 比体相的g-C₃N₄有更好的光生电子-空穴对分离效率。

为了进一步提高g-C₃N₄的光催化性能, 本文通过在薄层g-C₃N₄表面均匀分散Au纳米颗粒来控制电荷载流子的流动。并

通过光催化产氢和污染物降解来评估金/薄层氮化碳(Au/monolayer g-C₃N₄)复合材料的光催化性能。所有的Au/薄层g-C₃N₄复合材料均显示出优于体相g-C₃N₄的光催化性能,其中1% Au/薄层g-C₃N₄复合光催化剂具有最高的产氢速率(565 $\mu\text{mol g}^{-1} \text{h}^{-1}$),且具有最佳的污染物降解能力。这主要归结于热电子的注入,而不是肖特基结。Au纳米颗粒的成功引入带来了表面等离子共振(SPR)效应,SPR效应不仅能够提高光吸收效率,而且能够带来高效的热电子转移途径。热电子是从Au纳米颗粒表面注入到薄层g-C₃N₄纳米片的导带上。因此,Au/薄层g-C₃N₄复合光催化剂具有更高的光生电子-空穴对迁移和分离效率,以及更低的光生电子-空穴对复合几率。

采用紫外可见光谱(UV-Vis)、光致发光光谱(PL)、光电流和阻抗等表征手段研究了Au/薄层g-C₃N₄复合光催化剂性能提升的原因。结果表明,相比于薄层g-C₃N₄纳米片,Au/薄层g-C₃N₄复合光催化剂具有更好的光电性能,因而光催化活性更高。此外,与薄层g-C₃N₄纳米片的光电流强度相比,Au/薄层g-C₃N₄复合光催化剂的光电流强度没有发生改变,这表明薄层g-C₃N₄纳米片导带上的光生电子不可能转移到Au纳米颗粒的表面。也就是说,肖特基结并没有参与到电子转移过程中,因此推测出整个光催化反应是热电子注入在起作用。

关键词: 单层氮化碳; 金等离子纳米颗粒; 光催化产氢; 热电子; 金/单层氮化碳

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