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Article

Enhanced photocatalytic H₂ production over dual-cocatalyst-modified g-C₃N₄ heterojunctions

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ABSTRACT

Ag nanoparticles (NPs) were deposited on the surface of g-C₃N₄ (CN) by an *in situ* calcination method. NiS was successfully loaded onto the composites by a hydrothermal method. The results showed that the 10 wt%-NiS/1.0 wt%-Ag/CN composite exhibits excellent photocatalytic H₂ generation performance under solar-light irradiation. An H₂ production rate of 9.728 mmol·g⁻¹·h⁻¹ was achieved, which is 10.82-, 3.45-, and 2.77-times higher than those of pure g-C₃N₄, 10 wt%-NiS/CN, and 1.0 wt%-Ag/CN composites, respectively. This enhanced photocatalytic H₂ generation can be ascribed to the co-decoration of Ag and NiS on the surface of g-C₃N₄, which efficiently improves light harvesting capacity, photogenerated charge carrier separation, and photocatalytic H₂ production kinetics. Thus, this study demonstrates an effective strategy for constructing excellent g-C₃N₄-related composite photocatalysts for H₂ production by using different co-catalysts.

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1. Introduction

The depletion of conventional energy resources and the environmental damage associated with their use have necessitated the development of methods to exploit renewable energy resources such as solar energy. However, the poor efficiencies of current solar-to-chemical energy conversion methods is a critical obstacle to their practical application [1,2]. Accordingly, recent decades have seen considerable research effort being devoted to the development of artificial strategies for the conversion of solar energy [3–5]. Among them, photocatalytic H₂ production from water splitting utilizing solar energy as a driving force has garnered considerable attention because it is a cost-efficient, clean, and environmentally friendly strategy for

converting low-density solar energy into high-density clean H₂ energy [6–8]. Polymeric graphite-like carbon nitride (g-C₃N₄, CN) was first identified as a promising photocatalyst for H₂ generation from water splitting by Wang's group [9]. Since then, numerous theoretical and practical studies related to the application of g-C₃N₄ have been undertaken in a variety of fields. For example, g-C₃N₄ has been investigated as a means to produce high-reactivity free radicals and holes under solar irradiation for the degradation of organic pollutants, as a catalyst for the reduction of CO₂ into useful energy fuels, as a means of detecting volatile organic compounds (VOCs), and for application to organic synthesis [10–17].

g-C₃N₄ comprises only carbon and nitrogen atoms, making it an environmentally friendly and metal-free semiconduc-

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tor-based photocatalyst. Furthermore, it is suitable for water splitting under visible light owing to its appropriate bandgap (2.71 eV), visible-light harvesting capacity, and thermal/chemical stability [4,18]. In theory, compared with traditional photocatalysis such as TiO_2 [19–21] and ZnO [22–24], $\text{g-C}_3\text{N}_4$ can convert more light energy to chemical energy under visible light [18,25–27]. However, the application of $\text{g-C}_3\text{N}_4$ is impeded because of its poor absorption beyond 470 nm, low specific surface area, significant internal resistance, and rapid recombination of photoexcited charge carriers [28]. Accordingly, many studies have been performed to address these limitations. Typically, constructing heterojunctions with other semiconductors such as $\text{CdS/g-C}_3\text{N}_4$ [29], $\text{Bi}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ [30], $\text{BiVO}_4/\text{g-C}_3\text{N}_4$ [31,32], $\text{MoO}_3/\text{g-C}_3\text{N}_4$ [33], and $\text{InVO}_4/\text{g-C}_3\text{N}_4$ [34] is a promising strategy for extending the absorption edge of $\text{g-C}_3\text{N}_4$ into the visible-light region and impeding the recombination of photogenerated charge carriers therein. However, this strategy also has negative effects, such as decreasing the oxidation-reduction capacity of the photogenerated electron-hole pairs [35]. Modification with suitable co-catalysts, such as metallic oxides (e.g., NiO , CuO , and Co_2O_3) and metal sulfides (e.g., NiS , WS_2 , and MoS_2) is widely considered to be a promising solution for enhancing the photocatalytic H_2 generation capacity of $\text{g-C}_3\text{N}_4$ as it provides additional reaction sites and accelerates photocatalytic surface H_2 generation kinetics [36–41]. Among these co-catalysts, loading with NiS has received considerable attention owing to the earth-abundance of the required elements, its low cost, and its excellent H_2 -evolution performance [39,42–45]. However, no significant improvements in the photocatalytic properties of $\text{g-C}_3\text{N}_4$ upon surface-loading with NiS have been reported. Hence, the photocatalytic performance of this system can be further improved. Loading $\text{g-C}_3\text{N}_4$ with suitable noble metals such as Ag , Au , and Pt is a viable strategy for improving its visible-light harvesting capacity and photocatalytic properties [46–48]. Ag as a co-catalyst exhibits many inherent qualities for enhanced H_2 production under visible light, such as its excellent conductivity, strong surface plasmon resonance (SPR) effect, and good H_2 -evolution capacity [6,23,49]. Inspired by these advantages, we reasoned that co-decorating $\text{g-C}_3\text{N}_4$ with Ag and NiS would

enhance its surface H_2 generation kinetics and thus its photocatalytic H_2 production.

Accordingly, in the current study, dual co-catalyst (Ag and NiS)-modified $\text{g-C}_3\text{N}_4$ heterojunctions were successfully prepared by a simple and effective two-step synthesis strategy involving *in situ* calcination and hydrothermal synthesis, as outlined in Fig. 1. Compared with $\text{g-C}_3\text{N}_4$ alone and the as-prepared binary composites, the photocatalytic water splitting efficiency of the ternary composite NiS/Ag/CN was significantly improved. This enhanced photocatalytic activity can be ascribed to improved visible-light harvesting capacity, intimate interfacial contact, and effective charge transfer between Ag , NiS , and $\text{g-C}_3\text{N}_4$. Furthermore, a series of characterizations were performed as a means to elucidate the transfer mechanism for the photoexcited electron-hole pairs in the ternary composite. Overall, the present study demonstrates that decoration with dual co-catalysts is a promising strategy for improving the photocatalytic H_2 evolution activity of $\text{g-C}_3\text{N}_4$.

2. Experimental

2.1. Preparation

$\text{g-C}_3\text{N}_4$ was prepared simply by directly calcining melamine. In detail, melamine was heated to 650°C at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ in a muffle furnace and calcined for 3 h. Then, the yellow agglomerated product was milled into powder without further processing. Binary Ag/CN composites were then synthesized via a solvent evaporation and calcination method by directly calcining mixed solutions of melamine and silver nitrate. The products are labelled $x\text{-Ag/CN}$, where x represents the mass percentage of Ag nanoparticles (NPs) in the melamine.

Samples of $\text{g-C}_3\text{N}_4$ co-decorated with Ag and NiS were prepared via a simple hydrothermal method. Specifically, a certain amount of 1.0-Ag/CN was dispersed in ethyl alcohol containing a moderate amount of $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$. After stirring for 30 min and ultrasonic treatment for 20 min, an appropriate amount of thiourea was added as a S source. Then, the above suspension was transferred into a reactor and heated for 12 h

Fig. 1. Preparation of Ag/CN , NiS/CN , and NiS/Ag/CN composites.

at 200 °C. γ -NiS/CN (where γ is the mass percent of NiS in NiS/CN) composites were synthesized by the same way using pure $g\text{-C}_3\text{N}_4$ as precursor for comparison. The ternary composites were labelled $z\text{-NiS}/1.0\text{-Ag/CN}$, where z is the mass percentage of NiS in 1.0-Ag/CN . The details of the process are outlined in Fig. 1.

2.2. Material characterization

Ultraviolet visible diffuse reflectance spectroscopy was recorded on a Shimadzu UV-3600 UV-vis/NIR spectrophotometer. Morphological and structural of the samples were characterized by transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN) and a scanning electron microscopy (SEM, Carl Zeiss SIGMA). Photoluminescence spectra (PL) were tested on a fluorescence spectrophotometer (Hitachi F-7000). The samples were illuminated with a 300W Xe lamp. The Brunauer Emmett-Teller (BET) surface area was tested with a Quantachrome NOVA2000e. X-ray photoelectron spectroscopy (XPS) was investigated by a Kratos AXIS NOVA spectrometer. The phase structure of the samples was characterized by a Shimadzu XRD-6000 power diffractometer. Photoelectrochemical (PEC) activities were measured with electrochemical system (CHI 660E, China).

2.3. Photocatalytic hydrogen evolution

The photocatalytic H_2 generation performance was implemented in a Pyrex top-irradiation reaction vessel. In a typically photocatalytic experiment process, 30 mg catalyst was dispersed in water (100 mL) containing triethanolamine (TEOA 10 vol%) as sacrificial. Before experiment, the vacuum pump was vacuumized to remove the air in instrument completely and stirred continuously under a Xe lamp (300 W) irradiation. The amounts of H_2 were detected every 60 min and the system was vacuumized again for each sample. A gas chromatograph (N_2 as carrier gas) was used to detect the H_2 -evolution on line.

The apparent quantum efficiency (QE) was measured with 420 ± 7.5 nm band-pass cut-off filter. The average intensity of irradiation was measured as 46.31 mW cm^{-2} and the irradiation

area was 24.62 cm^2 . The amounts of H_2 were tested every 1h and the reaction time was lasted for 7 h. The H_2 generation reached to $613.5 \mu\text{mol}$. The QE is calculated by the following equation:

$$\text{QE} = \frac{(2 \times \text{the number of evolved } \text{H}_2 \text{ molecules}) / (\text{the number of incident photons}) \times 100\%}{\text{the number of incident photons} = E\lambda/hc}$$

$$E = PSt$$

E represent the total energy of incident light (W), P represent the energy density of incident light (W/m^2), S represent illumination area (m^2), t represents illumination time, h represents the Planck constant, c represents the speed of light.

2.4. PEC measurement

PEC characterizations were performed in $1.0 \text{ mol/L Na}_2\text{SO}_4$ solution in a three-electrode system. The photoanode (working electrode) was prepared as follows. 5 mg photocatalyst was dispersed in 1.0 mL of ethanol and 1.0 mL of distilled water with ultraphonic dispersion for 10 min. Then the slurry was dropped onto a fluorine-doped tin oxide (FTO) glass and dried naturally. The sample thin films, Pt sheet and Ag/AgCl served as working, counter and the reference electrodes, respectively. A 300 W Xe lamp was served as light source. The PEC measurements were recorded with a CHI-660E electrochemical system.

3. Results and discussion

3.1. Morphology and structure

Fig. 2 displays the X-ray diffraction (XRD) patterns of $x\text{-Ag/CN}$ (Fig. 2(a)), $\gamma\text{-NiS/CN}$ (Fig. 2(b)), and $z\text{-NiS}/1.0\text{-Ag/CN}$ (Fig. 2(c)). Typical diffraction peaks for pure $g\text{-C}_3\text{N}_4$ are observed at 13.5° and 27.5° , which correspond to the (100) and (002) planes of $g\text{-C}_3\text{N}_4$, respectively [50]. The typical (002) peak at 27.5° is ascribed to interlayer stacking controlled by van der Waals forces and is in agreement with the literature [40]. As shown in Fig. 2(a), the peaks for the (002) planes of the composites are slightly narrower than that for $g\text{-C}_3\text{N}_4$, indicat-

Fig. 2. XRD patterns of the composites $x\text{-Ag/CN}$ (a), $\gamma\text{-NiS/CN}$ (b), and $z\text{-NiS}/1.0\text{-Ag/CN}$ (c). (1) NiS; (2) $1.0\text{-NiS}/1.0\text{-Ag/CN}$; (3) $5.0\text{-NiS}/1.0\text{-Ag/CN}$; (4) $10\text{-NiS}/1.0\text{-Ag/CN}$; (5) $20\text{-NiS}/1.0\text{-Ag/CN}$.

Fig. 3. FT-IR spectra of g-C₃N₄, 1.0-Ag/CN, 10-NiS/CN, and 10-NiS/1.0-Ag/CN.

ing an enhancement of crystallinity upon Ag introduction. Moreover, the intensity of the peak for the (002) plane becomes weaker with increasing Ag mass content, implying that loading the g-C₃N₄ with Ag NPs reduces its interlayer spacing and disrupts its porous layer structure [51]. For *x*-Ag/CN, the peak intensity for Ag increases gradually with increasing Ag content. The peaks observed for 1.0-Ag/CN and 1.5-Ag/CN around 38.2°, 44.2°, 64.3°, 77.1°, and 81.5° are assigned to the (111), (200), (220), (311), and (222) planes of Ag, respectively [49]. In Figs. 2(b) and 2(c), the characteristic peaks at 18.2°, 30.1°, 31.8°, 35.6°, 40.2°, 48.6°, 50.1°, 52.3°, 56.3°, 57.2°, 66.5°, 67.9°, 72.8°, and 76.1° are ascribed to the (110), (101), (300), (021), (211), (131), (410), (401), (321), (330), (241), (600), (312), and (431) planes, respectively, of hexagonal NiS (JCPDS #86-2281). These peaks are also observed for binary NiS/CN (Fig. 2(b)) and ternary NiS/Ag/CN (Fig. 2(c)) [42,43]. The above results indicate that the g-C₃N₄ was successfully co-decorated with Ag and NiS. In addition, no peak shift is observed in the composites, indicating that the crystalline structure of g-C₃N₄ is not affected by the introduction of Ag and NiS [52,53].

FT-IR spectra of g-C₃N₄, 1.0-Ag/CN, 10-NiS/CN, and 10-NiS/Ag/CN are presented in Fig. 3. The peaks around 807 cm⁻¹ originate from the typical breathing vibration of the tri-s-triazine cycles in g-C₃N₄ [4,54]. The peaks at 1238, 1319, 1455, 1570, and 1632 cm⁻¹ are assigned to the aromatic C–N stretching of the g-C₃N₄, including the *sp*² C=N and the *sp*³ C–N bond stretching modes. The broad peaks around 3000 to 3500 cm⁻¹ are ascribed to the –NH and hydroxyl stretching vibrations [41]. All the characteristic peaks related to g-C₃N₄ are clearly observed for 1.0-Ag/CN, 10-NiS/CN, and 10-NiS/1.0-Ag/CN. No peaks for the bonding of sulfur with other elements are observed, indicating that the sulfur exists mainly as NiS rather than doping the g-C₃N₄ [52]. Therefore, the results of the FT-IR and XRD analyses demonstrate that the overall structure of g-C₃N₄ remains intact after loading with Ag and NiS.

XPS was employed to investigate the local electronic structures and elementary compositions of the composites. As shown in Fig. 4(a), the ternary composites consist mainly of C,

Fig. 4. XPS spectra for 10-NiS/1.0-Ag/CN. (a) Survey; (b) C 1s; (c) N 1s; (d) Ag 3d; (e) S 2p; (f) Ni 2p.

N, Ag, Ni, and S, demonstrating that g-C₃N₄, Ag NPs, and hexagonal NiS are hybridized in 10-NiS/1.0-Ag/CN. The presence of O might be due to surface adsorption under the experimental conditions employed. The characteristic peaks for C 1s in 10-NiS/1.0-Ag/CN at 284.6 and 288.2 eV can be attributed to the *sp*² C atoms in C=C and C–C as well as to the C–(N)₃ groups of g-C₃N₄ (Fig. 4(b)) [55]. Furthermore, the C 1s XPS spectra show no additional diffraction peaks, indicating that the structure of g-C₃N₄ is not changed during preparation [56]. Peaks at 398.8, 401.0, and 404.6 eV corresponding to C=N–C, N–(C)₃, and π -excitations in g-C₃N₄ can be observed in Fig. 4(c) [57]. In Fig. 4(d), the two peaks at 367.6 and 373.6 eV originate from Ag 3d_{5/2} (Ag⁰) and Ag 3d_{3/2} (Ag⁰), respectively [58]. In Fig. 4(e), the peaks around 163.8 and 168.6 eV are related to the sulfur in NiS (S²⁻ ions). In the Ni XPS spectrum shown in Fig. 4(f), peaks at 854.2 and 871.5 eV, which correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, are observed, while the peaks around 859.8 and 878.7 eV are their satellite peaks [42]. The S 2p and Ni 2p results are in good accord with previous reports [43,59,60]. Thus, the XRD, FT-IR, and XPS results demonstrate that the dual co-catalysts Ag and NiS were successfully loaded onto the surface of g-C₃N₄.

3.2. Morphology analysis

TEM images of 1.0-Ag/CN are presented in Fig. 5(a). It is evident that, in the 1.0-Ag/CN composite, Ag NPs with diameters ranging 10 to 15 nm (indicated by red dotted lines) are well dispersed on the g-C₃N₄ [46,61]. The clear lattice fringe is determined to have a spacing of 0.236 nm, which corresponds to the (111) crystallographic plane of Ag⁰. In addition, a TEM image of 10-NiS/CN is shown in Fig. 5(b). The results show that the NiS has been deposited on the surface of g-C₃N₄ and the lattice distance is approximately 0.478 nm, which is in good accordance with the (110) crystallographic plane of NiS (JCPDS #86-2281) [39,43]. TEM images of 10-NiS/1.0-Ag/CN are displayed in Fig. 5(c)–(e). It can be seen that the Ag and NiS are closely connected with the g-C₃N₄. In Fig. 5(d), the NiS dispersed on the surface of the g-C₃N₄ is marked with a gray dot-

ted line. The high-resolution (HR)-TEM image in Fig. 5(e) further confirms the presence of Ag and NiS on the g-C₃N₄ surface. As expected, three kinds of lattice fringes can be observed. The clear lattice spacing of approximately 0.33 nm is assigned to the (002) planes of g-C₃N₄. The lattice spacings of 0.236 and 0.225 nm are ascribed to the (111) planes of Ag⁰ and the (211) planes of NiS (JCPDS #86-2281), respectively [39]. Energy dispersive spectroscopy (EDS) mapping images of 10-NiS/1.0-Ag/CN are shown in Figs. 6(a)–(g), showing that C, N, Ag, S, and Ni are uniformly distributed on the surface of the as-prepared catalyst [60]. The weight percentages of Ag and NiS in 10-NiS/1.0-Ag/CN are approximately 2.48% and 7.64%, respectively. Thus, the XRD, XPS, and TEM results confirm that heterojunction photocatalysts co-decorated with Ag NPs and NiS were successfully fabricated.

3.3. Optical properties

UV-Vis diffuse reflectance spectra were obtained to assess the light absorption performance of the resulting samples. As illustrated in Fig. 7, the characteristic absorption edge of g-C₃N₄ originating from its inherent band gap (2.71 eV) is approximately 470 nm [42,62]. Interestingly, there is an apparent red shift in the range 450–550 nm for g-C₃N₄, which may be caused by increases in polymerization degree and p-plane conjugation [63]. After loading Ag NPs onto the surface of the g-C₃N₄, its visible-light harvesting capacity is significantly enhanced and a red shift of approximately 50 nm due to the SPR effect can be observed [64–66]. In addition, Ag NPs can act as an efficient electronic transmission channel, significantly enhancing the separation of the photoexcited charge carriers produced by g-C₃N₄ [67]. Moreover, upon loading with NiS, the light absorption intensity in the range 500–700 nm is clearly improved, which is in good accord with the change in sample color from canary yellow to dark grey (1.0, 5.0, and 10 to 20 wt% NiS). Furthermore, the absorption edge of g-C₃N₄ does not obviously shift, demonstrating that the NiS is in contact with the g-C₃N₄ instead of doping it [39]. Therefore, we believe that the en-

Fig. 5. TEM images of 1.0-Ag/CN (a), 10-NiS/CN (b), and 10-NiS/1.0-Ag/CN (c–e).

Fig. 6. EDS spectrum and mapping images of 10-NiS/1.0-Ag/CN.

hanced visible-light harvesting capacity is caused by the simultaneous introduction of Ag NPs and NiS. This improved light-harvesting capacity of the ternary composites is beneficial for the photogeneration of electron-hole pairs, thus promoting photocatalytic water splitting for H_2 evolution.

3.4. Photocatalytic H_2 -production performance

Photocatalytic H_2 production was evaluated in triethanolamine (TEOA) solution under solar-light irradiation. Fig. 8(a) shows plots of H_2 generation with time for the different photocatalysts. For all the samples, the H_2 -evolution rate is stable throughout the course of the experiments. No observable deac-

tivation of photocatalytic H_2 -evolution rate can be observed, indicating that the photocatalysts exhibit considerable stability. Fig. 8(b) shows the average H_2 -evolution rate values. Clearly, the H_2 -evolution rate of g- C_3N_4 is significantly improved upon loading with Ag NPs and NiS, indicating that the Ag and NiS as H_2 -evolution co-catalysts promote the migration of photogenerated electrons and enhance photocatalytic water reduction. The binary 1.0-Ag/CN and 10-NiS/CN samples exhibit photocatalytic activity with H_2 -evolution rates of 3.508 and 2.816 $mmol \cdot h^{-1} \cdot g^{-1}$, respectively, which are 3.90- and 3.13-fold higher than that of pure g- C_3N_4 [68]. Additionally, the 1.0, 5.0, 10, and 20 wt% NiS ternary samples show higher H_2 -evolution rates of 5.208, 8.358, 9.728, and 8.937 $mmol \cdot h^{-1} \cdot g^{-1}$, respectively. The 10-NiS/1.0-Ag/CN sample exhibits the highest activity of 9.728 $mmol \cdot h^{-1} \cdot g^{-1}$, which is 10.82-, 3.45-, and 2.77-times higher than those of g- C_3N_4 , 10-NiS/CN, and 1.0-Ag/CN, respectively. Furthermore, the apparent quantum efficiency of 10-NiS/1.0-Ag/CN is 1.21% at 420 nm, as shown in Fig. S1. These results indicate that co-decoration with Ag and NiS provides more active sites, retarding the recombination of photoexcited charge carriers and intensifying the reaction kinetics of the H_2 evolution. However, a decrease in the photocatalytic H_2 evolution is observed upon a further increase in the content of NiS, indicating that, in this case, excess NiS covers the surface-active sites on the g- C_3N_4 , negatively affecting the reaction kinetics [42].

In order to investigate the photocatalytic stability of the 10-NiS/1.0-Ag/CN catalyst, cycling tests were performed and the XRD pattern of the catalyst was obtained after four cycles. As shown in Figs. 8(c) and (d), the XRD pattern and photocatalytic H_2 production rate hardly change, indicating that the as-prepared sample is stable.

Fig. 7. UV-Vis diffuse reflectance spectra of g- C_3N_4 , 1.0-Ag/CN, 10-NiS/CN, and z-NiS/1.0-Ag/CN. (a) g- C_3N_4 ; (b) 1.0-NiS/1.0-Ag/CN; (c) 5.0-NiS/1.0-Ag/CN; (d) 10-NiS/1.0-Ag/CN; (e) 20-NiS/1.0-Ag/CN; (f) 1.0-Ag/CN; (g) 10-NiS/CN.

Fig. 8. Photocatalytic performance under solar light irradiation. (a) H₂ evolution with time for different photocatalysts; (b) H₂-evolution rates; (c) Recycling experiment results for 10-NiS/1.0-Ag/CN; (d) XRD patterns of 10-NiS/1.0-Ag/CN before and after four reaction cycles.

3.5. Feasible mechanism for photocatalytic H₂ production

In order to further investigate the separation and migration of charge carriers during photocatalytic water splitting, we performed Brunauer-Emmett-Teller (BET), PL, and PEC analyses. The N₂ adsorption-desorption isotherms of the catalysts were obtained in order to evaluate the surface area and porous structures of the materials. As depicted in Fig. 9, it is quite clear that all the composites exhibit classical type-IV curves with H₃ adsorption hysteresis loops, demonstrating the presence of mesopores in the composites. Table 1 shows the corresponding surface area and porous structure parameters. Compared with g-C₃N₄, the 1.0-Ag/CN and 10-NiS/CN composites have larger specific surface areas (*S*_{BET}) [3]. This may be caused by Ag and NiS decorating the g-C₃N₄, resulting in nanolayer and porous structures [69]. However, the 10-NiS/1.0-Ag/CN composite has a smaller surface area and pore volume than the binary composites. It is evident that the surface area, total pore volume, and pore size decrease because NiS may partially fill the pores in 1.0-Ag/CN [42,43,60]. These data clearly demonstrate that

surface area does not play a key role in the improved photocatalytic activity observed in this study.

The migration and recombination processes of charge carriers can be revealed by PL spectra. The spectra for 1.0-Ag/CN, 10-NiS/CN, and 10-NiS/1.0-Ag/CN and that of g-C₃N₄ for comparison are shown in Fig. 10 (excitation wavelength: 270 nm). The pure g-C₃N₄ possesses the highest emission peak at approximately 480 nm. The emission intensity decreases significantly after loading with Ag, indicating that the recombination of photoexcited charge carriers is efficiently restrained. This is because Ag can act as an electronic sink to allow the rapid migration of the charge carriers over the interface between the Ag NPs and g-C₃N₄. Note that the intensity of the emission peak is also distinctly decreased after loading NiS on g-C₃N₄. Therefore, these results show that the dual co-catalysts Ag and NiS on the g-C₃N₄ effectively restrain the recombination of photogenerated electron-hole pairs, and are thus beneficial for photocatalytic H₂ evolution [69].

The generation and separation behaviors of photoexcited charge carriers can be explained by photocurrent response. As shown in Fig. 11, prompt photocurrent responses are exhibited

Fig. 9. N₂ adsorption-desorption isotherms (a) and the corresponding pore-size distribution curves (b) for the as-obtained samples.

by g-C₃N₄, 1.0-Ag/CN, 10-NiS/CN, and 10-NiS/1.0-Ag/CN. Thus, the photocurrent intensity rapidly responds and stabilizes at a maximum value during the illumination process. Moreover, the photocurrents for the 1.0-Ag/CN composites are much higher than those of 10-NiS/CN and g-C₃N₄, implying that the Ag NPs on the g-C₃N₄ effectively enhance its visible-light absorbance, which is due to the SPR effect of Ag [50]. Thus, the migration of charge carriers is effectively promoted. In addition, 10-NiS/1.0-Ag/CN exhibits the highest photocurrent density, demonstrating that the co-decoration of g-C₃N₄ with Ag and NiS retards the recombination of photoexcited electrons and holes, resulting in improved photocatalytic H₂ generation. These results also correspond well with the PL results (Fig. 10).

To further investigate the enhanced charge carrier separation and transfer ability, four representative samples were subjected to electrochemical impedance spectroscopy (EIS), and the results are presented in Figs. 12(a) and 12(b). The EIS Nyquist plot for 10-NiS/1.0-Ag/CN exhibits a smaller semicircle diameter than those of g-C₃N₄, 10-NiS/CN, and 1.0-Ag/CN, demonstrating the lower interfacial resistance and more efficient electron transfer in the ternary 10-NiS/1.0-Ag/CN sample. It is believed that the dual co-catalysts Ag and NiS accelerate charge transport and separation, leading to markedly enhanced photocatalytic H₂-evolution performance. The results are also in good accord with the PL results (Fig. 10) and the transient photocurrent responses (Fig. 11).

According to these results, a mechanism for the photoexcited electron-hole transfer in ternary NiS/Ag/CN samples can be proposed, as illustrated in Fig. 13. The conduction band (CB) and valence band (VB) potentials can be calculated using the following empirical formulae:

$$E_{VB} = X - E_e + 0.5 \times E_g$$

$$E_{CB} = E_{VB} - E_g$$

The absolute electronegativity (X) of g-C₃N₄ is approximately 4.71 eV [47,48]. The energy of the free electrons (E_e) is ap-

Fig. 10. PL spectra of different samples.

Fig. 11. Transient photocurrent responses of different samples.

Table 1

Pore structure parameters of the samples.

Sample	S_{BET} (m ² ·g ⁻¹)	Pore size (nm)	Pore volume (cm ³ ·g ⁻¹)
g-C ₃ N ₄	42.80	3.759	0.277
1.0-Ag/CN	62.87	7.183	0.113
10-NiS/CN	56.31	3.830	0.329
10-NiS/1.0-Ag/CN	33.07	4.728	0.110

Fig. 12. EIS spectra of different samples.

proximately 4.62 eV. The band gap energy (E_g) of g-C₃N₄ is 2.71 eV based on the calculated band gap (Fig. S2). These results show that the CB and VB are approximately -1.27 and 1.45 eV, respectively. The photogenerated electron-hole pairs are generated in the CB and VB of g-C₃N₄ under light irradiation. Then, the photogenerated charge carriers quickly transfer to the Ag NPs, and a Schottky barrier between Ag and g-C₃N₄ is formed as the electrons accumulate on the Ag NPs, promoting the migration and separation of photoinduced electrons and holes [70,71]. Meanwhile, the SPR effect of the Ag NPs induced by the visible light forms a strong local electromagnetic field, enhancing the energy of the electrons. Therefore, Ag NPs act as electronic sinks to allow rapid electron migration and their reaction with electron acceptors (H^+) more easily, leading to enhanced H_2 production activity [72]. Furthermore, according to a previous report, NiS can act as an active site to enhance H_2 -evolution kinetics. An intermediate (HNiS) is formed upon absorption of H^+ on the surface of the NiS, and H_2 is then generated upon the reduction of another H^+ ion [43,73]. Furthermore, NiS can also enhance charge separation, improving H_2 generation [39,74]. In addition, the TEOA can act as sacrificial

reagent, being directly oxidized by the photoinduced holes on g-C₃N₄. Based on these experiment results, the improved photocatalytic H_2 -production activity can be ascribed to the co-decoration of Ag and NiS owing to the following factors: (1) the light harvesting capacity is intensified with the help of the Ag SPR effect and NiS; (2) the SPR effect induced by visible light provides a strong local electromagnetic field leading to improvement of the captured electron energy, allowing them to react with H^+ more easily; and (3) NiS can act as an effective co-catalyst to capture photoexcited electrons and then promote H_2 -generation kinetics by forming HNiS intermediates. Therefore, g-C₃N₄ co-decorated with Ag and NiS exhibits effectively enhanced light utilization, rapid migration of charge carriers, and accelerated surface H_2 -generation kinetics.

4. Conclusions

NiS/Ag/CN composites were successfully prepared by a facile method involving the deposition of Ag through *in situ* calcination and NiS by a hydrothermal method. The ternary composite 10-NiS/1.0-Ag/CN exhibited the highest photocatalytic H_2 -evolution activity with a rate of 9.728 mmol·g⁻¹·h⁻¹, which is 10.8-fold higher than that of g-C₃N₄. We verified that the enhancement of light-harvesting capacity, rapid photoinduced electron transfer, and enhanced surface H_2 -evolution kinetics are key factors in the improvement of photocatalytic properties. Thus, this study demonstrated a promising strategy for constructing excellent g-C₃N₄-related photocatalysts as well as valuable information for the construction of other semiconductor photocatalysts modified with different co-catalysts for photocatalytic water splitting.

References

- [1] C. L. Muhich, B. D. Ehrhart, I. Al-Shankiti, B. J. Ward, C. B. Musgrave, A. W. Weimer, *Wires Wiley Interdis. Rev. Energy Environ.*, **2016**, 5, 261–287.
- [2] X. Li, J. G. Yu, J. X. Low, Y. P. Fang, J. Xiao, X. B. Chen, *J. Mater. Chem. A*, **2015**, 3, 2485–2534.

Fig. 13. Schematic of the proposed mechanism for photocatalytic H_2 production over NiS/Ag/CN.

Graphical Abstract

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Enhanced photocatalytic H₂ production over dual-cocatalyst-modified g-C₃N₄ heterojunctions

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g-C₃N₄ co-decorated with Ag nanoparticles and NiS co-catalysts exhibits enhanced migration and separation of photoexcited charge carriers and, thus, improved photocatalytic H₂ generation owing to Ag and NiS serving as electron acceptors, surface-active sites, and H₂-evolution co-catalysts.

- [3] W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.*, **2016**, 116, 7159–7329.
- [4] K. Chen, Z. G. Chai, C. Li, L. R. Shi, M. X. Liu, Q. Xie, Y. F. Zhang, D. S. Xu, A. Manivannan, Z. F. Liu, *ACS Nano*, **2016**, 10, 3665–3673.
- [5] Q. Li, X. Li, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, *Adv. Energy. Mater.*, **2015**, 5, 1500010.
- [6] J. Q. Wen, J. Xie, X. B. Chen, X. Li, *Appl. Surf. Sci.*, **2017**, 391, 72–123.
- [7] S. W. Cao, H. Li, Y. Li, B. C. Zhu, J. G. Yu, *ACS Sustain. Chem. Eng.*, **2018**, 6, 6478–6487.
- [8] W. H. Xue, X. Y. Hu, E. Z. Liu, J. Fan, *Appl. Surf. Sci.*, **2018**, 447, 783–794.
- [9] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2008**, 8, 76–80.
- [10] J. Zhang, X. H. Mao, W. Xiao, Y. F. Zhuang, *Chin. J. Catal.*, **2017**, 38, 2009–2020.
- [11] P. Kumar, R. Boukherroub, K. Shankar, *J. Mater. Chem. A*, **2018**, 6, 12876–12931.
- [12] Z. Zhao, Y. Sun, F. Dong, *Nanoscale*, **2015**, 7, 15–37.
- [13] J. Luo, X. Zhang, J. Zhang, *ACS Catal.*, **2015**, 5, 2250–2254.
- [14] M. Marszewski, S. W. Cao, J. G. Yu, M. Jaroniec, *Mater. Horiz.*, **2015**, 2, 261–278.
- [15] D. Xu, B. Cheng, W. K. Wang, C. J. Jiang, J. G. Yu, *Appl. Catal. B*, **2018**, 231, 368–380.
- [16] N. Nie, L. Y. Zhang, J. W. Fu, B. Cheng, J. G. Yu, *Appl. Surf. Sci.*, **2018**, 441, 12–22.
- [17] S. Chandrasekaran, C. Bowen, P. X. Zhang, Z. L. Li, Q. H. Yuan, X. Z. Ren, L. B. Deng, *J. Mater. Chem. A*, **2018**, 6, 11078–11104.
- [18] J. W. Fu, J. G. Yu, C. J. Jiang, B. Cheng, *Adv. Energy. Mater.*, **2018**, 8, 1701503.
- [19] J. B. Fei, J. B. Li, *Adv. Mater.*, **2015**, 27, 314–319.
- [20] C. Liu, F. Raziq, Z. J. Li, Y. Qu, A. Zada, L. Q. Jing, *Chin. J. Catal.*, **2017**, 38, 1072–1078.
- [21] J. X. Low, L. Y. Zhang, T. Tong, B. J. Shen, J. G. Yu, *J. Catal.*, **2018**, 361, 255–266.
- [22] S. Wang, P. Y. Kuang, B. Cheng, J. G. Yu, C. J. Jiang, *J. Alloys Compd.*, **2018**, 741, 622–632.
- [23] J. J. Yu, D. P. Sun, T. H. Wang, F. Li, *Chem. Eng. J.*, **2018**, 334, 225–236.
- [24] J. Cheng, Y. Shen, K. Chen, X. Wang, Y. F. Guo, X. J. Zhou, R. B. Bai, *Chin. J. Catal.*, **2018**, 39, 810–820.
- [25] P. Zhang, T. Wang, J. Gong, *Adv. Mater.*, **2015**, 27, 5328–5342.
- [26] R. O. Reithmeier, S. Meister, A. Siebel, B. Rieger, *Dalton Trans.*, **2015**, 44, 6466–6472.
- [27] Q. Sun, P. Wang, H. G. Yu, X. F. Wang, *J. Mol. Catal. A*, **2016**, 424, 369–376.
- [28] Z. Wang, W. Guan, Y. Sun, F. Dong, Y. Zhou, W. K. Ho, *Nanoscale*, **2015**, 7, 2471–2479.
- [29] Z. L. Fang, H. F. Rong, Z. L. Ya, P. Qi, *J. Mater. Sci.*, **2015**, 50, 3057–3064.
- [30] W. Mao, T. Y. Wang, H. Y. Wang, S. Zou, S. X. Liu, *J. Mater. Sci-Mater. EL*, **2018**, 29, 15174–15182.
- [31] M. Ou, Q. Zhong, S. L. Zhang, L. M. Yu, *J. Alloys Compd.*, **2015**, 626, 401–409.
- [32] G. Miao, D. S. Huang, X. L. Ren, X. Li, Z. Li, J. Xiao, *Appl. Catal. B*, **2016**, 192, 72–79.
- [33] S. Patnaik, G. Swain, K. M. Parida, *Nanoscale*, **2018**, 10, 5950–5964.
- [34] W. L. Shi, F. Guo, J. B. Chen, G. B. Che, X. Lin, *J. Alloys Compd.*, **2014**, 612, 143–148.
- [35] J. X. Low, C. J. Jiang, B. Cheng, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, *Small Methods*, **2017**, 1, 1700080/1–1700080/21.
- [36] X. T. Xu, Y. Z. Liu, Y. Z. Zhu, X. B. Fan, Y. Li, F. B. Zhang, G. L. Zhang, W. C. Peng, *ChemElectroChem*, **2017**, 4, 1498–1502.
- [37] H. G. Yu, P. Xiao, P. Wang, J. G. Yu, *Appl. Catal. B*, **2016**, 193, 217–225.

- [38] Y. H. Fu, Z. J. Li, Q. Q. Liu, X. F. Yang, H. Tang, *Chin. J. Catal.*, **2017**, 38, 2160–2170.
- [39] K. He, J. Xie, M. L. Li, X. Li, *Appl. Surf. Sci.*, **2018**, 430, 208–217.
- [40] H. Zhu, F. Lyu, M. Du, M. Zhang, Q. Wang, J. Yao, B. Guo, *ACS Appl. Mater. Interfaces*, **2014**, 6, 22126–22137.
- [41] J. W. Fu, C. B. Bie, B. Cheng, C. J. Jiang, J. G. Yu, *ACS Sustain. Chem. Eng.*, **2018**, 6, 2767–2779.
- [42] X. J. Lu, Y. Wang, X. Y. Zhang, G. Q. Xu, D. M. Wang, J. Lv, Z. X. Zheng, Y. C. Wu, *J. Hazard. Mater.*, **2018**, 341, 10–19.
- [43] J. Wen, J. Xie, H. Zhang, A. Zhang, Y. Liu, X. Chen, X. Li, *ACS Appl. Mater. Interfaces*, **2017**, 9, 14031–14042.
- [44] J. Q. Wen, X. Li, H. Q. Li, S. Ma, K. He, Y. H. Xu, Y. P. Fang, W. Liu, Q. Z. Gao, *Appl. Surf. Sci.*, **2015**, 358, 204–212.
- [45] K. 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.
- [46] T. Tong, B. C. Zhu, C. J. Jiang, B. Cheng, J. G. Yu, *Appl. Surf. Sci.*, **2018**, 433, 1175–1183.
- [47] X. F. Wang, D. Liao, H. G. Yu, J. G. Yu, *Dalton Trans.*, **2018**, 47, 6370–6377.
- [48] F. Chen, H. Yang, W. Luo, P. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 1990–1998.
- [49] Z. Zhu, Z. Y. Lu, D. D. Wang, X. Tang, Y. S. Yan, W. D. Shi, Y. Wang, N. L. Gao, X. Yao, H. J. Dong, *Appl. Catal. B*, **2016**, 182, 115–122.
- [50] Y. Chen, W. Huang, D. He, Y. Situ, H. Huang, *ACS Appl. Mater. Interfaces*, **2014**, 6, 14405–14414.
- [51] F. Chen, H. Yang, W. Luo, P. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 1990–1998.
- [52] X. L. Luo, G. L. He, Y. P. Fang, Y. H. Xu, *J. Colloid Interface Sci.*, **2018**, 518, 184–191.
- [53] H. G. Yu, W. Y. Chen, X. F. Wang, Y. Xu, J. G. Yu, *Appl. Catal. B*, **2016**, 187, 163–170.
- [54] W. Zhao, Y. Guo, S. M. Wang, H. He, C. Sun, S. G. Yang, *Appl. Catal. B*, **2015**, 165, 335–343.
- [55] F. F. Liang, Y. F. Zhu, *Appl. Catal. B*, **2016**, 180, 324–329.
- [56] R. C. Shen, J. Xie, H. D. Zhang, A. P. Zhang, X. B. Chen, X. Li, *ACS Sustain. Chem. Eng.*, **2017**, 6, 816–826.
- [57] X. Du, G. Zou, Z. Wang, X. Wang, *Nanoscale*, **2015**, 7, 8701–8706.
- [58] Y. N. Ma, J. Li, E. Z. Liu, J. Wan, X. Y. Hu, J. Fan, *Appl. Catal. B*, **2017**, 219, 467–478.
- [59] J. Chen, S. H. Shen, P. H. Guo, M. Wang, P. Wu, X. X. Wang, L. J. Guo, *Appl. Catal. B*, **2014**, 152–153, 335–341.
- [60] Z. H. Chen, P. Sun, B. Fan, Z. Zhang, X. M. Fang, *J. Phys. Chem. C*, **2014**, 118, 7801–7807.
- [61] J. Wang, H. Xu, S. M. Li, B. Yan, Y. T. Shi, C. Q. Wang, Y. K. Du, *Analyst*, **2017**, 142, 4852–4861.
- [62] J. X. Low, J. G. Yu, M. Jaroniec, S. Wageh, A. A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [63] 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.
- [64] S. Patnaik, D. P. Sahoo, K. Parida, *Renew. Sust. Energy Rev.*, **2018**, 82, 1297–1312.
- [65] Y. F. Ma, L. L. Yang, Y. Yang, Y. S. Peng, Y. Q. Wei, Z. R. Huang, *RSC Adv.*, **2018**, 8, 22095–22102.
- [66] D. Z. Lu, H. M. Wang, X. N. Zhao, K. K. Kondamareddy, J. Q. Ding, C. H. Li, P. F. Fang, *ACS Sustainable Chem. Eng.*, **2017**, 5, 1436–1445.
- [67] J. Qin, J. Huo, P. Zhang, J. Zeng, T. Wang, H. Zeng, *Nanoscale*, **2016**, 8, 2249–2259.
- [68] J. Q. Wen, J. Xie, Z. H. Yang, R. C. Shen, H. Y. Li, X. Y. Luo, X. B. Chen, X. Li, *ACS Sustain. Chem. Eng.*, **2017**, 5, 2224–2236.
- [69] T. Xiong, W. G. Cen, Y. X. Zhang, F. Dong, *ACS Catal.*, **2016**, 6, 2462–2472.
- [70] H. G. Yu, G. Q. Cao, F. Chen, X. F. Wang, J. G. Yu, M. Lei, *Appl. Catal. B*, **2014**, 160–161, 658–665.
- [71] J. Fei, J. Li, *Adv. Mater.*, **2015**, 27, 314–319.
- [72] S. Patnaik, D. P. Sahoo, K. Parida, *Renew. Sust. Energy Rev.*, **2018**, 82, 1297–1312.
- [73] W. Zhao, Y. Wang, Z. Wang, Z. Zhong, R. Xu, *Chem. Commun.*, **2010**, 46, 7631–7633.
- [74] Y. Zhong, J. Yuan, J. Wen, X. Li, Y. Xu, W. Liu, S. Zhang, Y. Fang, *Dalton Trans.*, **2015**, 44, 18260–18269.

双助剂促进g-C₃N₄光解水制氢性能

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摘要: 氢能是最具应用前景的清洁能源之一, 利用太阳能作为驱动力光催化水分解制取氢气已被广泛研究. 作为非金属半导体光催化剂, g-C₃N₄具有合适的能带结构(2.71 eV), 良好的可见光捕获能力和物理化学稳定性, 因而有一定的光催化产氢能力; 但是它具有可见光吸收能力(<470 nm)不够、光生电子空穴容易复合等缺点, 使其光催化制氢能力受到了极大限制. 通过助剂修饰可有效促进载流子分离, 增加反应活性位点及加速产氢动力学. 因此, 本文采用双助剂改性以提高g-C₃N₄的光催化制氢性能.

本文首先采用原位煅烧法将银纳米粒子(Ag NPs)沉积在g-C₃N₄表面(Ag/g-C₃N₄), 随后利用水热法成功地将硫化镍(NiS)负载在Ag/g-C₃N₄复合材料表面. XRD, FT-IR, XPS和TEM结果表明, 通过原位煅烧和水热合成法可以成功地将Ag和NiS均匀、稳定沉积在g-C₃N₄表面, 并且g-C₃N₄保持原有结构不变. 紫外可见吸收光谱(UV-Vis)、瞬态光电流、阻抗(EIS)和光致发光谱(PL)分析表明, Ag NPs和NiS的引入不仅改善了体系的光吸收范围和强度, 而且显著提高了体系光生电子和空穴的产生、分离性能, 有助于提高光子利用效率. 其中三元样品的最高光电流可以达到 $2.94 \times 10^{-7} \text{ A} \cdot \text{cm}^{-2}$, 是纯g-C₃N₄的3.1倍.

对系列光催化剂的分解水制氢性能测试发现(采用300 W氙灯作为光源, 三乙醇胺作为牺牲剂), 10 wt%-NiS/1.0 wt%-Ag/CN样品具有最优异的光催化分解水制氢性能, 产氢速率可达 $9.728 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, 是纯g-C₃N₄的10.82倍, 二元10

wt%-NiS/CN的3.45倍, 1.0 wt%-Ag/CN的2.77倍. 三元样品反应前后的XRD特征峰位置没有发生变化, 循环四次后样品仍具有83%的催化活性, 证明其具有良好的制氢稳定性. 10 wt%-NiS/1.0 wt%-Ag/CN样品在可见光下($\lambda > 420$ nm)的制氢量子效率为1.21%. 三元体系光催化产氢性能增强的原因在于: (1)Ag纳米颗粒的局域表面等离子体效应使得三元体系的光捕获能力得到提高; (2)Ag NPs和NiS负载在g-C₃N₄上共同促进了光生电子空穴的产生和分离; (3)Ag NPs和NiS作为优良的析氢助催化剂沉积在g-C₃N₄表面上可以有效地提高产氢动力学. 本文构建的NiS/Ag/g-C₃N₄复合体系为g-C₃N₄基复合光催化剂的设计及制备提供了新的思路.

关键词: 光催化; 光催化制氢; 氮化碳; 银; 硫化镍

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