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Selective adsorption of thiocyanate anions on Ag-modified g-C₃N₄ for enhanced photocatalytic hydrogen evolution

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ABSTRACT

Silver-modified semiconductor photocatalysts typically exhibit enhanced photocatalytic activity toward the degradation of organic substances. In comparison, their hydrogen-evolution rates are relatively low owing to poor interfacial catalytic reactions to producing hydrogen. In the present study, thiocyanate anions (SCN⁻) as interfacial catalytic active sites were selectively adsorbed onto the Ag surface of g-C₃N₄/Ag photocatalyst to promote interfacial H₂-evolution reactions. The thiocyanate-modified g-C₃N₄/Ag (g-C₃N₄/Ag-SCN) photocatalysts were synthesized via photodeposition of metallic Ag on g-C₃N₄ and subsequent selective adsorption of SCN⁻ ions on the Ag surface by an impregnation method. The resulting g-C₃N₄/Ag-SCN photocatalysts exhibited considerably higher photocatalytic H₂-evolution activity than the g-C₃N₄, g-C₃N₄/Ag, and g-C₃N₄/SCN photocatalysts. Furthermore, the g-C₃N₄/Ag-SCN photocatalyst displayed the highest H₂-evolution rate (3.9 μmol h⁻¹) when the concentration of the SCN⁻ ions was adjusted to 0.3 mmol L⁻¹. The H₂-evolution rate obtained was higher than those of g-C₃N₄ (0.15 μmol h⁻¹) and g-C₃N₄/Ag (0.71 μmol h⁻¹). Considering the enhanced performance of g-C₃N₄/Ag upon minimal addition of SCN⁻ ions, a synergistic effect of metallic Ag and SCN⁻ ions is proposed—the Ag nanoparticles act as an effective electron-transfer mediator for the steady capture and rapid transportation of photogenerated electrons, while the adsorbed SCN⁻ ions serve as an interfacial active site to effectively absorb protons from solution and promote rapid interfacial H₂-evolution reactions. Considering the present facile synthesis and its high efficacy, the present work may provide new insights into preparing high-performance photocatalytic materials.

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1. Introduction

Photocatalytic water splitting into hydrogen by solar energy is a promising route to address increasing global energy consumption and environmental issues [1–4]. However, developing highly efficient and low-cost visible light-driven photocatalysts to meet practical needs remains a major challenge [5–10].

In the past decades, various visible light photocatalysts, such as CdS, graphitic carbon nitride (g-C₃N₄), and TaON, have widely been developed for H₂ generation [11–16]. Among them, g-C₃N₄ has been extensively investigated toward hydrogen production under visible light owing to its unique inherent characteristics such as good visible light absorbance, strong reduction potential for H₂ evolution, and excellent photochemical stability

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[17–20]. Consequently, numerous strategies have been developed to improve its photocatalytic activity such as coupling with other semiconductors [21–26], forming mesoporous or nanosheet structures [27–34], and loading with co-catalysts [35–41]. However, the photocatalytic activity of modified g-C₃N₄ remains inadequate under visible light irradiation owing to rapid recombination of photogenerated electron–hole pairs on its surface (Fig. 1(a)). Therefore, it is of high interest to develop new strategies to improve the hydrogen-evolution performance of g-C₃N₄.

Loading with noble metals, such as Pt, is regarded as one of the most ideal strategies to enhance photocatalytic hydrogen evolution over g-C₃N₄ owing to the improved charge separation and accelerated surface catalytic reactions [42,43] that can be attained. However, the widespread application of this strategy is limited by the high cost and limited abundance of Pt metals. Noble metal Ag is an attractive alternative because of its considerably lower cost [44–46]. It has also been demonstrated that loading Ag nanoparticles on g-C₃N₄ photocatalysts can improve the photocatalytic H₂-evolution performance. For example, Ge et al. [47] demonstrated that the H₂-evolution rate of g-C₃N₄ could be enhanced by loading metallic Ag. The H₂-evolution rate of the Ag-loaded photocatalyst was ~11.7 times higher than that of pure g-C₃N₄. Bai et al. [48] reported that the H₂ evolution activity over core-shell Ag@C₃N₄ photocatalyst was 30 times higher than that over pure g-C₃N₄. Additionally, Chen et al. [49] reported the synthesis of a Ag quantum dot-modified g-C₃N₄ with improved hydrogen production rates. Although the above results clearly demonstrate the benefit of modifying g-C₃N₄ with Ag nanoparticles, Ag-modified g-C₃N₄ photocatalysts still show a considerably lower photocatalytic H₂-evolution performance when compared with Pt-modified photocatalysts. A possible reason is that the metallic Ag surface is not an effective active site for H₂ evolution owing to the weaker bond strength of Ag–H (37 kcal mol^{−1}) when compared with that of Pt–H (60 kcal mol^{−1}) [50] (Fig. 1(a)). To further improve the photocatalytic H₂-evolution activity of g-C₃N₄/Ag, it is highly

desirable to modify the Ag surface to promote its interfacial hydrogen-evolution reactions. Recently, it was reported that the strong affinity between Ag and thiocyanate (SCN[−]) ions could enhance the interfacial electron transfer rate and facilitate the reduction of protons on Ag/TiO₂ under UV light irradiation. Therefore, it is expected that SCN[−] ions adsorbed on a Ag surface can serve as effective interfacial active sites to improve the visible light photocatalytic performance of g-C₃N₄/Ag photocatalysts toward hydrogen production (Fig. 1(a)).

In the present study, SCN[−]-modified g-C₃N₄/Ag photocatalysts were synthesized via a two-step process: photoinduced deposition of Ag on g-C₃N₄ surface and selective loading of SCN[−] on the Ag surface by an impregnation method. The g-C₃N₄/Ag-SCN photocatalysts exhibited improved photocatalytic H₂-production performance compared with bare g-C₃N₄, g-C₃N₄/Ag, and g-C₃N₄/SCN. A possible photocatalytic mechanism was proposed to account for the improved photocatalytic performance. To our knowledge, this is the first report showing the improved photocatalytic H₂ generation of g-C₃N₄/Ag by selective loading of SCN[−] ions. Considering the low cost and high efficiency achieved by SCN[−] ions, the latter show great potential for use in the design and preparation of high-performance silver-modified photocatalysts.

2. Experimental

All chemicals were of analytical grade and supplied by Shanghai Chemical Reagent Ltd. (China) and used as received without further purification. Distilled water was used in all experiments.

2.1. Preparation of g-C₃N₄ photocatalyst

The g-C₃N₄ photocatalyst was synthesized via a simple calcination–hydrothermal procedure using melamine powder as the precursor [51]. In a typical procedure, 10 g of melamine was calcined at 550 °C in a muffle furnace for 4 h in ambient atmosphere. After cooling to room temperature, the yellow product was collected and ground into powder. To increase its specific surface area, 0.5 g of the above sample was dispersed into 70 mL of distilled water with constant stirring for 1 h. The mixture was then transferred into a Teflon-lined stainless steel autoclave at 180 °C for 2 h. After natural cooling to room temperature, the precipitation was collected by filtration, washed with distilled water, and dried at 60 °C for overnight. Finally, the product was ground into powder and labeled as g-C₃N₄. The nitrogen adsorption–desorption analysis revealed that after hydrothermal treatment, the specific surface area of the resultant g-C₃N₄ sample was 47.2 m² g^{−1}, which was much higher than that of the bulk g-C₃N₄ sample (2.3 m² g^{−1}) prepared in the absence of a hydrothermal treatment [52].

2.2. Preparation of the g-C₃N₄/Ag photocatalyst

Silver nanoparticles were loaded onto the g-C₃N₄ surface via a photodeposition method. Briefly, 0.05 g of the as-prepared g-C₃N₄ powder was uniformly dispersed into 10 mL of distilled

Fig. 1. Schematic illustration of the strategy for developing highly efficient g-C₃N₄/Ag-SCN photocatalysts (a), synthetic route of g-C₃N₄/Ag-SCN photocatalysts (b), and corresponding materials at the different synthesis stages (c). (1) g-C₃N₄; (2) g-C₃N₄/Ag; (3) g-C₃N₄/Ag-SCN.

water and stirred at room temperature for 10 min. Subsequently, 1.38 mL of AgNO_3 solution (0.01 mol L^{-1}) and 0.3 mL of lactic acid solution (10 vol%), as an electron donor, were injected into the above suspension. After visible light irradiation using four low-power LEDs (3 W, 420 nm, Shenzhen Lamplic Science Co. Ltd.) for 30 min, the resultant sample was filtered and washed with distilled water for several times to obtain the $\text{g-C}_3\text{N}_4/\text{Ag}$ photocatalyst.

2.3. Preparation and photocatalytic H_2 -evolution reaction of $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalyst

Both the preparation of the $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalysts and their photocatalytic hydrogen-production experiments were conducted in a 100-mL three-neck Pyrex flask at ambient temperature and atmospheric pressure. In a typical experiment, 0.05 g of $\text{g-C}_3\text{N}_4/\text{Ag}$ was dispersed into 80 mL of lactic acid solution (10 vol%) under continuous stirring for 10 min followed by injection of a known volume of potassium thiocyanate solution (0.1 mol L^{-1}).

For the photocatalytic runs, prior to irradiation, the above suspension solution was bubbled with nitrogen for 30 min to remove dissolved oxygen. Four low-power LEDs (3 W, 420 nm, Shenzhen Lamplic Science Co. Ltd) were used as the light source to trigger the photocatalytic reaction. The LEDs were positioned radially 1 cm away from the reactor. During visible light irradiation, continuous stirring was applied to keep the photocatalyst particles in a suspension state. To measure the H_2 amount, 0.4 mL of gas was intermittently sampled through a septum, and its composition was analyzed on a gas chromatograph (Shimadzu GC-2014C, Japan, with nitrogen as the carrier gas) equipped with a 5-Å molecular sieve column and a thermal conductivity detector. The final concentrations of SCN^- in the suspension solution were adjusted to 0, 0.1, 0.2, 0.3, 0.5, 0.7, 1.0 mmol L^{-1} . After the photocatalytic reaction, the precipitation was filtered, washed with deionized water several times, and finally dried at 60 °C for 12 h to obtain the $\text{g-C}_3\text{N}_4/\text{Ag-SCN}(X \text{ mM})$ samples, where X represents the final concentration (mmol L^{-1}) of the SCN^- anions.

2.4. Characterization

X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima III X-ray diffractometer (Japan) using $\text{Cu K}\alpha$ radiation. The morphology of the materials prepared was analyzed via field-emission scanning electron microscopy (FESEM) on a JEOL JEM-7500F microscope (Japan). Further morphological and structural characterizations were performed via transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using a JEOL JEM-2100F microscope. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a KRATOA XSAM800 XPS system with $\text{Mg K}\alpha$ source. All of the binding energies were referenced to the C 1s peak at 284.8 eV for the surface adventitious carbon. UV-visible (UV-vis) absorption spectra were obtained using a UV-visible spectrophotometer (UV-2450, Shimadzu, Japan). For the UV-vis diffuse reflectance studies, BaSO_4 was used as the

reflectance standard.

2.5. Photoelectrochemical measurements of photocatalysts

Photoelectrochemical measurements were performed in a standard three-electrode system with platinum wire as the counter electrode, saturated $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (in saturated KCl) as the reference electrode, and Na_2SO_4 aqueous solution (0.5 mol L^{-1}) as the electrolyte. The results were recorded at an electrochemical workstation (CHI660E). The visible light irradiation was provided by one 3 W LED (420 nm light source with a 90 mW cm^{-2} power). A fluorine-doped tin oxide (FTO) conductor glass was used as the working electrode. To prepare the working electrode, typically, 10 mg of the sample powders was added to 1 mL of anhydrous ethanol and 1 mL of Nafion D-520 dispersion (5%, w/w, in water and 1-propanol, Alfa Aesar) and then evenly dispersed by ultrasound to obtain a suspension. The suspension was spread onto a $1 \text{ cm} \times 1 \text{ cm}$ FTO glass with the sides protected by Scotch tape and then dried at 60 °C for 1 h. Last, linear sweep voltammetry (LSV) curves were measured at potentials ranging from 0.1 to -0.5 V and a scan rate of 10 mV s^{-1} .

3. Results and discussion

3.1. Synthesis of the $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalyst

Fig. 1(b) illustrates the synthesis of the $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalysts via a facile photodeposition process of metallic Ag on $\text{g-C}_3\text{N}_4$ followed by selective adsorption of SCN^- ions on the Ag surface by an impregnation method. First, $\text{g-C}_3\text{N}_4$ was prepared via a simple calcination-hydrothermal procedure, as reported in our previous report. The resulting $\text{g-C}_3\text{N}_4$ powder was pale yellow. To prepare $\text{g-C}_3\text{N}_4/\text{Ag}$, $\text{g-C}_3\text{N}_4$ powder was uniformly dispersed into an AgNO_3 aqueous solution with lactic acid solution as an electron donor. After visible light irradiation for 30 min, Ag^+ ions were reduced on the $\text{g-C}_3\text{N}_4$ surface to form Ag^0 nanoparticles. The resulting sample was dark brown, indicating successful deposition of Ag nanoparticles. To prepare $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalyst, KSCN solution was injected into a $\text{g-C}_3\text{N}_4/\text{Ag}$ suspension under nitrogen atmosphere. The SCN^- ions selectively adsorbed on the Ag nanoparticle surface owing to the strong affinity between silver and sulfur [53], as shown in Fig. 1(b). Thus, owing to the adsorption of SCN^- ions on the Ag surface, the prepared $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalyst (Fig. 1(c)) was slightly less brown than the $\text{g-C}_3\text{N}_4/\text{Ag}$ sample. The above results indicate the successful preparation of the $\text{g-C}_3\text{N}_4/\text{Ag}$ and $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalysts.

3.2. Morphologies and microstructures of the $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$ photocatalysts

The phase structure and composition of the as-prepared $\text{g-C}_3\text{N}_4/\text{Ag-SCN}$, $\text{g-C}_3\text{N}_4/\text{Ag}$, and pure $\text{g-C}_3\text{N}_4$ photocatalysts were first analyzed by XRD (Fig. 2(a)). The XRD pattern of the pure $\text{g-C}_3\text{N}_4$ displayed two characteristic diffraction peaks, which can be well indexed to the hexagonal phase of $\text{g-C}_3\text{N}_4$

Fig. 2. XRD patterns (a) and diffraction peaks of metallic Ag (b) in the samples prepared. (1) g-C₃N₄; (2) g-C₃N₄/Ag; (3) g-C₃N₄/Ag-SCN(0.1 mM); (4) g-C₃N₄/Ag-SCN(0.3 mM); (5) g-C₃N₄/Ag-SCN(1.0 mM); (6) g-C₃N₄/SCN(0.3 mM).

(JCPDS 87-1526) [54]. Specifically, the weak peak at 13.2° is typically oriented melons, which can be indexed to (100) facets and the strong peak at 27.6° represents the interplanar stacking of aromatic units, corresponding to (002) facets [55]. For the Ag-modified g-C₃N₄ photocatalysts, only weak diffraction peaks of metallic Ag could be detected in addition to the diffraction peaks of g-C₃N₄ owing to the small deposition amounts (~3 wt%) and high dispersion of the Ag species. To further observe the characteristic diffraction peak of metallic Ag, their slow-scan spectra are shown in Fig. 2(b). The g-C₃N₄/Ag and g-C₃N₄/Ag-SCN photocatalysts displayed comparable peak diffraction intensities owing to the similar amount of metallic Ag phase incorporated in the photocatalyst.

To further demonstrate the successful loading of Ag nanoparticles on the g-C₃N₄ surface and the selective adsorption of SCN⁻ on the surface of Ag nanoparticles, the morphology and microstructures of the prepared samples were investigated by SEM and TEM, and the results are shown in Fig. 3. As observed, the g-C₃N₄ sample (Fig. 3(a)) was composed of many agglomerates of several micrometers in size. The g-C₃N₄/Ag, g-C₃N₄/Ag-SCN, and g-C₃N₄/SCN samples retained the same morphology as that of the g-C₃N₄ sample owing to the mild modification process used and minimal amounts of Ag and SCN ions deposited (Fig. 3(b)–(d)). According to the energy-dispersive X-ray spectroscopy (EDS) results (insets in Fig. 3(b) and (c)), the amount of metallic Ag incorporated was ~0.2

Fig. 3. FESEM images of the prepared samples. (a) g-C₃N₄; (b) g-C₃N₄/Ag; (c) g-C₃N₄/Ag-SCN(0.3 mM); (d) g-C₃N₄/SCN(0.3 mM); (e, f) TEM images of g-C₃N₄/Ag-SCN(0.3 mM).

at% in the g-C₃N₄/Ag and g-C₃N₄/Ag-SCN photocatalysts. A new S signal could be observed in the EDS pattern of the g-C₃N₄/Ag-SCN(0.3 mM) sample [Fig. 3(c)], suggesting that the SCN⁻ ions were loaded on the g-C₃N₄/Ag surface. To observe the morphology and phase structure of the Ag nanoparticles, TEM analysis was conducted. The TEM images of g-C₃N₄/Ag-SCN(0.3 mM) are shown in Fig. 3(e) and (f). As indicated by the red circles, the Ag nanoparticles (<20 nm in size) were homogeneously dispersed on the g-C₃N₄ surface. The above results confirm the successful synthesis of the g-C₃N₄/Ag-SCN photocatalysts.

XPS was used to further confirm the chemical states of Ag and SCN⁻ on the g-C₃N₄ surface. Fig. 4(a) shows the XPS survey spectra of the pure g-C₃N₄, g-C₃N₄/Ag-SCN, and g-C₃N₄/SCN samples. All samples displayed the main peaks of C and N elements from g-C₃N₄ [56]. Small XPS peaks of Ag and S elements could also be found in the g-C₃N₄/Ag-SCN samples. More detailed information of the elements in the samples could be obtained from the corresponding high-resolution XPS spectra in Fig. 4(b)–(e). The C 1s XPS spectra displayed two distinct peaks at about 284.8 and 288.2 eV, which can be attributed to the pollutant from the XPS equipment and the triazine rings (N=C=N), respectively [Fig. 4(b)]. The N 1s XPS spectra [Fig. 4(c)] displayed three main peaks at about 398.8, 400.4, and 401.8 eV, which can be ascribed to the *sp*²-bonded nitrogen in N-containing aromatic rings (C=N=C), tertiary nitrogen (N-(C)₃), and the amino functional groups (C-N-H) on the fringes of g-C₃N₄ [57,58], respectively. The Ag 3d XPS spectra [Fig. 4(d)] displayed peaks with binding energies of 367.6 eV (Ag 3d_{5/2}) and 373.9 eV (Ag 3d_{3/2}), which can be ascribed to Ag⁰ [59]. The S 2p XPS spectra of g-C₃N₄/Ag-SCN and g-C₃N₄/SCN showed weak peaks at 161.4 eV [Fig. 4(e)], which can be attributed to adsorbed SCN⁻. According to the element compo-

Table 1

Element component analysis (at%) of the prepared photocatalysts determined from the XPS results.

Sample	C	N	Ag	S
g-C ₃ N ₄	41.25	55.76	0	0
g-C ₃ N ₄ /Ag	43.15	56.49	0.37	0
g-C ₃ N ₄ /Ag-SCN(0.3 mM)	42.77	56.57	0.45	0.22
g-C ₃ N ₄ /Ag-SCN(1.0 mM)	42.80	56.60	0.48	0.22
g-C ₃ N ₄ /SCN(0.3 mM)	43.98	55.90	0	0.08

nent analysis based on the XPS results (Table 1), the calculated amounts of Ag and S in g-C₃N₄/SCN(0.3 mM) were ~0.45 and 0.22 at%, respectively. The XPS results further proved that Ag and SCN⁻ were successfully incorporated on the g-C₃N₄ surface.

The light absorption properties of the pure g-C₃N₄, g-C₃N₄/Ag, and g-C₃N₄/Ag-SCN photocatalysts were characterized by UV-vis diffuse reflectance spectroscopy (Fig. 5). The g-C₃N₄ sample featured an absorption edge of ~460 nm, corresponding to a band gap of ~2.7 eV. After surface deposition of Ag nanoparticles, the resultant g-C₃N₄/Ag showed strong visible light absorption features in the range of 460–800 nm, which can be attributed to the localized surface plasmon resonance (LSPR) effect of metallic Ag nanoparticles. Modification of g-C₃N₄/Ag with SCN⁻ to form g-C₃N₄/Ag-SCN resulted in a slight decrease in visible light absorption, and the corresponding sample was of a lighter brown (inset of Fig. 5). The above results suggest that the LSPR effect of the Ag nanoparticles can be slightly influenced by the addition of SCN⁻, further confirming the formation of a strong coupling interface between Ag and SCN⁻. The g-C₃N₄/SCN photocatalyst exhibited a comparable UV-vis spectrum to that of pure g-C₃N₄, indicating that the adsorption of SCN⁻ alone on the g-C₃N₄ surface cannot cause the change observed in visible light absorption. The above results

Fig. 4. XPS survey spectra (a) and high-resolution XPS C 1s (b), N 1s (c), Ag 3d (d), and S 2p (e) spectra of g-C₃N₄ (1), g-C₃N₄/Ag (2), g-C₃N₄/Ag-SCN(0.3 mM) (3), g-C₃N₄/Ag-SCN(1.0 mM) (4), and g-C₃N₄/SCN(0.3 mM) (5).

Fig. 5. UV-vis spectra and corresponding photographs of the prepared samples. (1) g-C₃N₄; (2) g-C₃N₄/Ag; (3) g-C₃N₄/Ag-SCN(0.1 mM); (4) g-C₃N₄/Ag-SCN(0.3 mM); (5) g-C₃N₄/Ag-SCN(1.0 mM); (6) g-C₃N₄/SCN(0.3 mM).

confirm the successful preparation of the g-C₃N₄/Ag-SCN photocatalysts.

3.3. Photocatalytic performance and mechanism

The photocatalytic performance of the samples prepared was evaluated by monitoring the hydrogen evolution under visible light irradiation; the results are shown in Fig. 6(a). The pure g-C₃N₄ sample displayed a very low photocatalytic H₂-evolution activity ($\sim 0.15 \mu\text{mol h}^{-1}$), as consistent with the previously reported results [60]. However, upon modification with Ag co-catalyst, the photocatalytic H₂-evolution activity of the resultant g-C₃N₄/Ag sample showed a slight improvement ($\sim 0.71 \mu\text{mol h}^{-1}$) owing to effective separation of the photo-generated electrons from the g-C₃N₄ surface to the Ag nanoparticles. When KSCN selectively adsorbed onto the Ag surface, all resulting g-C₃N₄/Ag-SCN samples exhibited remarkably higher photocatalytic H₂-evolution activities than g-C₃N₄/Ag. Particularly, g-C₃N₄/Ag-SCN(0.3 mM) displayed the highest photocatalytic activity ($\sim 3.89 \mu\text{mol h}^{-1}$), which is higher than that of

pure g-C₃N₄ by a factor of 25.5. However, further increasing the amount of SCN⁻ ions led to a slight decrease in the photocatalytic performance, as consistent with the performance of widely reported co-catalyst-modified photocatalysts [61]. Furthermore, g-C₃N₄/SCN(0.3 mM) displayed comparable photocatalytic H₂-evolution activity ($\sim 0.15 \mu\text{mol h}^{-1}$) to that of pure g-C₃N₄, indicating that the SCN⁻ ions alone on the g-C₃N₄ surface (without metallic Ag) have a negligible effect on the photocatalytic H₂-evolution activity. To evaluate the H₂-evolution stability of the g-C₃N₄/Ag-SCN photocatalysts, g-C₃N₄/Ag-SCN(0.3 mM) was subjected to repeated photocatalytic runs. The results are shown in Fig. 6(b). As observed, the g-C₃N₄/Ag-SCN photocatalyst could maintain a stable and effective photocatalytic performance under visible light irradiation during repeated tests. Hence, the g-C₃N₄/Ag-SCN photocatalyst can be regarded as a highly efficient visible light photocatalyst for H₂ production.

Based on the results obtained, a mechanism for the photocatalytic H₂-evolution over g-C₃N₄/Ag-SCN photocatalysts is proposed and schematically illustrated in Fig. 7(a). In the g-C₃N₄/Ag-SCN photocatalyst, the SCN⁻ anions with strong electronegativity can be selectively adsorbed on the metallic Ag surface owing to its strong affinity for sulfur to form Ag–SCN⁻ bond [53]. The sulfur atoms in the SCN⁻ ions can effectively capture positive H⁺ ions from solution owing to their strong nucleophilicity [62], while the SCN⁻ ions with a strong electronegativity can facilitate electron transfer from the Ag surface [45], subsequently promoting the direct reduction of protons to hydrogen. A more detail photocatalytic mechanism of g-C₃N₄/Ag-SCN photocatalyst is proposed in Fig. 7(b). After band gap excitation of bulk g-C₃N₄, the Ag nanoparticles first act as an electron sink to rapidly capture photogenerated electrons from the conduction band of g-C₃N₄ and then serve as an electron-transfer mediator to steadily transport photogenerated electrons to the adsorbed SCN⁻ ions. The SCN⁻ anions serve as interfacial active sites to effectively absorb protons from solution and then promote the subsequent interfacial H₂-evolution reaction. Furthermore, the higher photocatalytic H₂-evolution activity of g-C₃N₄/Ag-SCN when compared with

Fig. 6. (a) Photocatalytic H₂-evolution activities of g-C₃N₄ (1), g-C₃N₄/Ag (2), g-C₃N₄/Ag-SCN(0.1 mM) (3), g-C₃N₄/Ag-SCN(0.2 mM) (4), g-C₃N₄/Ag-SCN(0.3 mM) (5), g-C₃N₄/Ag-SCN(0.5 mM) (6), g-C₃N₄/Ag-SCN(0.7 mM) (7), g-C₃N₄/Ag-SCN(1.0 mM) (8), and g-C₃N₄/SCN(0.3 mM) (9) samples. (b) H₂ evolution over g-C₃N₄/Ag-SCN(0.3 mM) photocatalyst subjected to repeated photocatalytic runs.

Fig. 7. Schematic diagram illustrating the photocatalytic H₂-evolution mechanism. (a) Photocatalytic H₂ evolution over g-C₃N₄/Ag-SCN photocatalyst; (b) General synergistic effect mechanism of electron-transfer mediator and interfacial catalytic active sites.

that of the single-component-modified g-C₃N₄/Ag and g-C₃N₄/SCN photocatalysts indicates the synergistic effect of Ag as an electron-transfer mediator and SCN⁻ as an interfacial catalytic active site. Therefore, it is apparent that the synergistic effect between Ag and SCN⁻ accounts for the greatly improved photocatalytic H₂-evolution performance of the g-C₃N₄/Ag-SCN photocatalyst.

To further understand the role of metallic Ag and SCN⁻ co-catalysts in the photocatalytic H₂-evolution reaction over g-C₃N₄/Ag-SCN photocatalyst, the photoelectrocatalytic activities of the various samples were investigated. Fig. 8 displays the polarization curves of the g-C₃N₄, g-C₃N₄/Ag, g-C₃N₄/Ag-SCN, and g-C₃N₄/SCN samples. As observed, the Ag loading onto g-C₃N₄ surface enhanced the current density, indicating that Ag functions as a co-catalyst to rapidly capture electrons from the g-C₃N₄ surface. Upon further selective adsorption of SCN⁻ on the Ag surface, the prepared g-C₃N₄/Ag-SCN sample displayed a further improved current density, which can be attributed to the fact that the adsorbed SCN⁻ can serve as an interfacial catalytic active site to effectively adsorb H⁺ ions from

Fig. 8. LSV curves of the prepared samples. (1) g-C₃N₄; (2) g-C₃N₄/Ag; (3) g-C₃N₄/Ag-SCN(0.3 mM); (4) g-C₃N₄/SCN(0.3 mM).

solution, thereby promoting the effective reduction of H⁺ to H₂.

4. Conclusions

g-C₃N₄/Ag-SCN photocatalysts were synthesized via facile photodeposition of metallic Ag on g-C₃N₄ and subsequent selective adsorption of SCN⁻ ions on the Ag surface by an impregnation method. The resulting g-C₃N₄/Ag-SCN photocatalysts showed a higher photocatalytic H₂-evolution performance than g-C₃N₄, g-C₃N₄/Ag, and g-C₃N₄/SCN under visible light irradiation. In particular, g-C₃N₄/Ag-SCN(0.3 mM) achieved the highest photocatalytic activity (3.89 μmol h⁻¹), which is higher than that of pure g-C₃N₄ by a factor of 25.5. The improved photocatalytic performance of the g-C₃N₄/Ag-SCN photocatalyst can be attributed to the synergistic effect of metallic Ag and SCN⁻ ions, whereby the Ag nanoparticles function as an effective electron-transfer mediator for the steady capture and rapid transportation of photogenerated electrons, while the adsorbed SCN⁻ serves as an interfacial active site to effectively absorb protons from solution and promote rapid interfacial H₂-evolution reaction. Considering the present facile synthesis and its high efficacy, the present work may provide new insights into preparing high-performance photocatalytic materials.

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Graphical Abstract

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Selective adsorption of thiocyanate anions on Ag-modified g-C₃N₄ for enhanced photocatalytic hydrogen evolutionFeng Chen, Hui Yang, Wei Luo, Ping Wang, Huogen Yu *
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g-C₃N₄/Ag-SCN showed remarkably improved photocatalytic H₂-evolution activity owing to the synergetic effect of Ag nanoparticles as electron-transfer mediator and SCN⁻ as effective interfacial active sites.

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硫氰根选择性吸附在g-C₃N₄/Ag表面增强其光催化制氢性能

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摘要: 作为一种无金属的新型半导体材料, g-C₃N₄因具有稳定的物理化学性质及合适的能带结构而引起人们的关注. 理论上g-C₃N₄完全满足水分解的电势条件. 然而研究发现, g-C₃N₄材料本身的光催化性能并不好, 这主要是由于半导体材料被光激发后生成的自由电子和空穴还没来得及到达材料表面参与反应, 就在材料体相内发生复合, 导致电子参与有效光催化制氢反应的几率大大降低. 同时还发现, 将少量的贵金属, 如Pt, Au, Pd作助催化剂修饰在该半导体表面, 其光催化性能明显提高. 但由于这些贵金属储量非常稀少, 价格昂贵, 导致它们的使用受到一定限制. 而Ag作为一种价格远低于Pt, Au, Pd的贵金属, 也得到了广泛的研究. 研究表明, 金属Ag储存电子的能力很好, 因此可以有效地将半导体上生成的光生电子快速转移到Ag上面去, 从而达到电子空穴快速分离的目的. 但是在光催化制氢过程中, Ag吸附H⁺的能力较弱, 致使电子与H⁺反应的诱导力较弱, 使得Ag释放电子的能力较差. 因此可以通过提高Ag表面对H⁺的吸附强度, 以加速Ag的电子释放, 通过表面修饰来提高Ag助剂的光催化活性. 研究发现, Ag纳米粒子表面与含硫化合物之间存在很强的亲和力. 硫氰根离子(SCN⁻)具有很强的电负性, 容易吸附溶液中H⁺离子, 并且也易吸附在Ag纳米粒子的表面. 因此可以利用Ag与SCN⁻的作用来增强Ag释放电子的能力.

本文采用光还原法将Ag沉积在g-C₃N₄半导体材料表面, 然后通过在制氢牺牲剂中加入KSCN溶液, 利用SCN⁻与Ag的亲和力来提高光生电子参与光催化反应的效率. 结果表明, 在SCN⁻存在的情况下, g-C₃N₄/Ag的光催化制氢性能显著提高. 当制氢溶液中SCN⁻浓度为0.3 mmol L⁻¹时, 材料的光催化制氢性能达最大, 为3.89 μmol h⁻¹, 比g-C₃N₄/Ag性能提高5.5倍. 基于少量的SCN⁻就能明显提高g-C₃N₄/Ag材料的光催化性能, 我们提出了一个可能性的作用机理: 金属银和SCN⁻协同作用, 即银纳米粒子作为光生电子的捕获和传输的一种有效的电子传递介质, 而选择性吸附在银表面的SCN⁻作为界面活性位点有效地吸附溶液中的质子以促进产氢反应, 二者协同作用, 加速了g-C₃N₄-Ag-SCN⁻三物种界面之间电荷的传输、分离及界面催化反应速率, 有效抑制了g-C₃N₄主体材料光生电子和空穴的复合, 因而g-C₃N₄/Ag-SCN复合材料的光催化制氢性能提高. 考虑到其成本低、效率高, SCN⁻助催化剂有很大的潜力广泛应用于制备高性能的银修饰光催化材料.

关键词: 光催化; g-C₃N₄/Ag; 选择性吸附; 界面活性位; 光催化制氢

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