Exploration of the g-C₃N₄ Heterostructure with Ag–In Sulfide Quantum Dots for Enhanced Photocatalytic Activity

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ABSTRACT: Photocatalysis is an effective technology to convert solar energy into chemical energy, which has attracted great attention for the degradation of water pollutants and the hydrogen production by water splitting. The nonmetallic polymer $g_{\rm c}$. N	Ag-In-S quantum dots (AIS-QDs)	degraded products GCN AIS-QDs TC O_2 C_B $e^- C_B$ O_2O_2 $C_B e^- e^- C_B$ O_2O_2 O_2O_2 $O_2O_$

attention for the degradation of water pollutants and the hydrogen production by water splitting. The nonmetallic polymer g- C_3N_4 (GCN) can meet the thermodynamic conditions of photocatalytic water splitting, but its performances are not satisfying due to its narrow light absorption range and high recombination rate of photogenerated charge carriers. Among metal sulfide semiconductors, Ag–In sulfide quantum dots (AIS QDs), such as AgInS₂, show excellent visible light absorption and promising



photoactivity. In this work, AIS QDs-modified GCN is synthesized by an in situ growth method in mild conditions. The photocatalytic activity of the AIS-QDs/GCN nanocomposite is notably higher than that of the pure phase g-C₃N₄. Especially, the sample containing 10 wt % AIS QDs has the best activity in both tetracycline degradation and hydrogen generation, reaching 48.5% degradation efficiency in 1 h of visible light exposure (3.2 times that of GCN) and a hydrogen evolution rate of 62.3 μ mol·g⁻¹·h⁻¹ (that of bare GCN being negligible). The optical and photoelectrochemical characterization highlights the interplay between the two components, suggesting that the enhanced photocatalytic activity of AIS-QDs/GCN is mainly due to the broadening of the light absorption range, the acceleration of charge transfer, and the reduction of the carrier pair recombination rate due to the formation of a type-II heterojunction inside the composite catalyst. This work is among the first attempts to modify g-C₃N₄ with polysulfide quantum dots to improve its catalytic performance, and the results provide an important step for advances in the application of these systems.

KEYWORDS: Ag-In-S quantum dots, graphitic carbon nitride, heterojunction, photocatalytic degradation, tetracycline, H_2 production

1. INTRODUCTION

With the rapid development of social economy and industrialization, environmental pollution and energy shortage are becoming increasingly serious problems. Anthropic activities cause the release in the environment of a variety of potentially harmful substances, including different pharmaceuticals. Antibiotics are widely used (and sometimes overused) in the prevention and treatment of human and animal diseases and even as a promoter of animal growth. However, only a small portion of antibiotics can actually exert their medical role in the body, and the rest of them will be excreted into the environment together with the metabolites. For instance, tetracycline (TC), a common low-cost and effective antibacterial agent, is widely accumulated in the water environment, leading to bacterial resistance and unexpected adverse effects on ecosystems and public health.¹ Various traditional methods, such as adsorption,² sonocatalysis degradation,³ and biodegradation,⁴ have been proven capable to remove TC from water; however, their use has been limited by low removal efficiencies and long treatment times. Now, photocatalytic oxidation has arisen as a cost-effective, highperformance, and environmentally sustainable alternative to

wastewater treatments mentioned above.⁵ In addition, photocatalysis shows great promise for the crucial challenge of clean energy production: in response to the over-development and serious pollution from fossil fuel combustion, hydrogen is regarded as the ideal clean energy vector for the 21st century.⁶ Therefore, photocatalysis, having the great advantage of direct utilization of sunlight and water resources, is expected to robustly contribute to solving the problems of environmental pollution and energy shortage.^{7,8} The development of highly active photocatalytic materials is the key to promote the advancement of this technology.

Graphitic carbon nitride $(g-C_3N_4, GCN)$ is a novel nonmetallic polymer semiconductor with a band gap of around 2.7 eV, appropriate to respond to a relatively broad range of the solar radiation spectrum. As a consequence, GCN breaks the

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Scheme 1. Synthesis Procedure of g-C₃N₄-based Composites with In Situ Grown AIS QDs



barrier of traditional photocatalytic materials (such as TiO₂ and ZnO), i.e., their ability to exploit only ultraviolet light energy,⁹ and shows a valuable potential also for electrocatalytic and photoelectrochemical processes such as water splitting, water remediation, and sensing.¹⁰ Its other unique characteristics, including simple preparation, environmental friendliness, and high stability, have attracted increasing attention in the environmental, energy, and industrial fields. However, the catalytic activity of GCN is still not satisfactory in practical applications. The rather narrow visible light response range, easy recombination of photogenerated charges, small specific surface area, and few active sites negatively affect its photocatalytic performance.¹¹ In order to improve its photocatalytic activity, some methods have been carried out, including doping, coating, and preparing composites with other materials.^{12,13} Several studies have shown encouraging results by constructing heterojunction composites of GCN with other semiconductors such as Sn_3O_4 ¹⁴ MoS₂ ¹⁵ WO₃ ¹⁶ and Cu₃P.¹⁷

In recent years, the modification of GCN by quantum dots (QDs) has received a growing research interest.¹⁸ Compared with bulk materials, "zero dimensional" QDs exhibit a unique size effect, a quantum confinement effect, and an edge effect, besides other advantages, such as a wide visible light absorption range, large specific surface area, strong photoelectric conversion ability, etc.¹⁹ In the composite constructed by QDs and GCN, the absorption range of the material in the visible light region is broadened, the altered band structure accelerates the separation and transmission of photogenerated charge carrier pairs, and the reactive surface sites increase, thus enhancing its photocatalytic activity.²⁰ It has been reported that the GCN composites co-built with QDs, such as TiO₂, carbon, and SbVO₄ QDs, have shown excellent activity in the application of photocatalytic hydrogen production and pollutant degradation.²¹⁻²³

Semiconducting metal sulfides, especially I-III-VI polysulfides, have many advantages, such as strong visible light absorption, narrow band gap, excellent conductivity, chemical stability, and light corrosion resistance.^{24,25} Indium sulfide (In_2S_3) is an n-type semiconductor with a band gap energy of 2.0-2.3 eV, high photosensitivity, and low toxicity, and it has been studied in a heterostructure with other semiconductors, including GCN, in a few reports.²⁶⁻²⁹ The photochemical properties of indium sulfide can be enhanced by the introduction of silver, obtaining I-III-VI sulfides with a range of stoichiometry, from doping levels to AgIn₅S₈ and AgInS₂.³⁰⁻³² Silver indium sulfides (AIS) possess a narrower band gap energy (\sim 1.7 eV), which allows for a higher sunlight capture ability, favoring promising results in the research of photocatalytic degradation and hydrogen production by water splitting.^{33–35} Heterojunction composites containing AIS were successfully proposed, for example, between AgInS₂ nanosheets and TiO₂, exhibiting an enhanced absorption of visible light and a promoted separation of photoinduced charge carrier pairs in the system,³⁶ or zero-dimensional AgInS₂ QDs loaded on two-dimensional MXene nanosheets to construct a Z-type heterojunction with excellent interfacial charge transfer capability.³⁷ After all, in view of the shortcomings of GCN, it is of practical significance to build a composite system of AIS QDs and GCN and optimize its optoelectronic properties by taking advantage of the unique properties of QDs. To the authors' knowledge, the only studies about photocatalytic composite systems including AIS and GCN reported the hydrogen production performances of Zn-AgIn₅S₈ QDs with a low GCN content of 10 wt %³⁸ or large nanoparticles of AgIn₅S₈ co-precipitated on mesoporous GCN with Pt deposited as a co-catalyst.³⁹

In this work, AIS QDs with a 1:8 Ag/In molar ratio are grown on GCN by the heating-up method in different proportions (from 5 to 15 wt % AIS). The photocatalytic performance of the synthesized composites is studied through the degradation of antibiotic TC and hydrogen production from water splitting. The results show that the AIS-QDs/GCN composite has an enhanced photocatalytic activity compared with that of GCN. The loading of AIS-QDs broadens the visible light absorption range and forms a type-II heterojunction that accelerates the charge carrier pair separation and migration rate, reducing their recombination, as revealed by the optical and photoelectrochemical characterization. It is shown that the modification of GCN with a narrow band gap polysulfide has significant advantages, providing a viable method for efficient photocatalytic and photoelectrocatalytic applications.

2. EXPERIMENTAL SECTION

2.1. Materials. All reagents used in the experiments are of analytical grade, without secondary treatment. The water used to prepare the solution in the experiment is ultrapure water. AgNO₃ (silver nitrate), NaOH, anhydrous Na₂SO₄, and BaSO₄ are purchased from Sinopharm Chemical Reagent Co., Ltd.; urea $[CO(NH_2)_2]$ is purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd.; reduced glutathione (GSH, C₁₀H₁₇N₃O₆S), indium nitrate hexahydrate (InN₃O₉·xH₂O), and TC (C₂₂H₂₄N₂O₈) are purchased from McLean Reagent Co., Ltd.; sodium sulfide hydrate (Na₂S·9H₂O) is purchased from Nanjing Chemical Reagent Co., Ltd.; and isopropanol is purchased from Xilong Scientific Chemical Reagent Co., Ltd.

2.2. Preparation of the Catalysts. The preparation of graphitic carbon nitride (GCN) is performed by a typical calcination process: 10.0 g of urea is put into an aluminum oxide crucible with a cover, heated to 520 °C in a muffle furnace at a heating rate of 10 °C/min, kept at 520 °C for 4 h, and then cooled to room temperature at a rate of 10 °C/min. The product is collected as a pale yellow powder for later use.

The synthesis of Ag-modified indium sulfide quantum dots (AIS QDs) is performed by the following procedure: 0.1 mmol AgNO₃, 0.8 mmol InN_3O_9 :xH₂O, and 2 mmol GSH are successively added into a

beaker containing 40 mL of deionized water. After ultrasonic treatment for 10 min, they are fully mixed. Then, under magnetic stirring, 0.05 mol/L NaOH solution is added dropwise to adjust the pH to 8.5. After that, the above mixed solution is transferred to a three-necked flask and put into an oil bath equipped with a condensation reflux device. The temperature is raised to 90 °C under a N₂ atmosphere and stirring, and 0.6 mmol Na₂S solution is quickly added. The reaction is conducted at 90 °C for 1 h; then, heating is stopped, and the system is allowed to naturally cool to room temperature. Finally, the solution is washed with isopropyl alcohol and centrifuged, and the precipitate is dried in vacuum at room temperature to obtain an orange powder, namely, AIS QDs.

For the synthesis of AIS-QDs/GCN, an in situ growth method is adapted, which is the same as the preparation procedure of AIS QDs, except a certain amount of GCN powder is first added into 40 mL of deionized water according to the calculated value, and ultrasonic treatment is carried out for 10 min (Scheme 1). Finally, a series of composites with different weight ratios are synthesized, including 5 wt % AIS-QDs/GCN, 8 wt % AIS-QDs/GCN, 10 wt % AIS-QDs/GCN, 12 wt % AIS-QDs/GCN, 15 wt % AIS-QDs/GCN, abbreviated as follows: 5%-AIS-QDs/GCN, 8%-AIS-QDs/GCN, 10%-AIS-QDs/ GCN, 12%-AIS-QDs/GCN and 15%-AIS-QDs/GCN, respectively.

2.3. Characterization. The samples are tested by X-ray powder diffraction (XRD) using a Bruker X-ray powder diffractometer to analyze their crystal structure and crystallinity. The surface element composition and valence state of the samples are analyzed by X-ray photoelectron spectroscopy (XPS), which is carried out by an Escalab 250Xi X-ray photoelectron spectrometer with Al K α radiation. The microstructure of samples is analyzed by transmission electron microscopy (TEM, Talos F200X). The detection of the molecular structure and functional groups of the sample is carried out by Fourier transform infrared (FTIR) spectroscopy using a Nicolet Magna-IR spectrometer 560. The UV-visible diffuse reflectance spectra (UVvis DRS) are recorded by a TU-1901 UV-vis spectrophotometer. The steady-state photoluminescence (PL) spectra of the prepared samples are measured by an RF-5301PC fluorescence spectrometer at 325 nm excitation wavelength. The time-resolved PL (TRPL) spectra of the prepared samples are measured by an FLS1000 fluorescence lifetime spectrophotometer.

2.4. Photocatalytic Activity. The photocatalytic activity of the synthesized catalysts is studied taking TC as the model pollutant. The photodegradation experiment is carried out in a self-made photocatalytic reaction device, using a 1000 W halogen lamp equipped with a 420 nm filter as the light source, where the quartz beaker containing the polluted solution is fixed at a distance of 10 cm from the light source. The volume of TC solution (40 mg/L) is 100 mL, and the dosage of the photocatalyst is 50 mg (0.5 g/L). In short, before the experiment, 100 mL of TC solution containing 50 mg of the catalyst is ultrasonically treated for 3 min to make the catalyst disperse evenly. After adding the catalyst, first, the suspension is stirred in the dark for 30 min to reach the adsorption-desorption equilibrium of TC on the photocatalyst surface, and then, the light is switched on for 1 h. The suspension is centrifuged before passing a 0.22 μ m microporous membrane used to filter the supernatant in order to remove the photocatalyst, and then, the absorbance of the solution is measured at the wavelength of 357 nm by a TU-1901 ultraviolet-visible spectrophotometer, and the degradation efficiency (D) is calculated according to formula 1

$$D\% = \frac{(A_0 - A_t)}{A_0} \times 100\%$$
(1)

where A_0 is the absorbance of TC solution before light exposure and A_t is the absorbance of TC in solution after a certain time of light exposure.

The test of hydrogen generation from photocatalytic water splitting is also carried out. A 350 W xenon lamp (Beijing NBET Co. Ltd) with a 365 nm filter is used as the sunlight simulation light source, a 100 mL three-necked flask is used as the reaction vessel, and the port is sealed with a silicone rubber diaphragm. 20 mg of the photocatalyst and 10 mL of triethanolamine (TEOA) are added to 80 mL of water to test the rate of hydrogen production by photocatalytic water splitting, in which TEOA is used as a sacrificial agent to consume photogenerated holes. Before the reaction, the solution is bubbled with nitrogen gas for 30 min to remove the dissolved oxygen, and then, the photolytic test is conducted and examined by a Shimadzu GC-14C gas chromatograph.

2.5. Photoelectrochemical Tests. In order to further explore the reasons for the enhanced photocatalytic activity of AIS-QDs/GCN composites, the photoelectric properties of GCN, AIS QDs, and 10%-AIS-QDs/GCN are tested, including tests of Mott-Schottky, chronoamperometry (I-t), and electrochemical impedance spectroscopy (EIS). All of them are carried out via CHI660D electrochemical workstation (Shanghai Chenhua Company). The standard threeelectrode system is used in the experiment, i.e., working electrode, counter electrode (Pt electrode), and reference electrode (saturated calomel electrode, SCE). Preparation of the working electrode: firstl, the ITO conductive glass (10 mm \times 20 mm) is washed with acetone, anhydrous ethanol, and deionized water for 30 min in turn and then dried. 16 mg of the sample to be tested is dispersed in a mixture of 3.6 mL of absolute ethanol and 0.4 mL of 5% Nafion solution to obtain a suspension (4 mg/mL). After ultrasonic treatment for 30 min, it is magnetically stirred for 4 h to get a homogeneous dispersion. 30 μ L of the suspension is evenly applied to the conductive surface of ITO glass, with an area of 10 mm \times 10 mm, and after leaving standing for 1 h, an infrared lamp is used to dry it and obtain the working electrode.

The Mott–Schottky curve is plotted based on the capacitance data measured by the impedance potential method. The electrolyte solution is 0.1 M Na₂SO₄ solution (nitrogen charging for 30 min before the experiment to remove O₂). In the experiment, the stability time of the sample's open-circuit potential is first investigated, and then, the impedance potential is measured after stabilization, with the initial and termination voltages of -1.0 and +1.0 V, respectively. The transient photocurrent is also tested with 0.1 M Na₂SO₄ solution as the electrolyte solution using the light irradiation with the wavelength >420 nm. The electrolyte used in the AC impedance spectrum test is a 0.1 M KCl solution containing a 5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] mixture (1:1), the scanning rate is 10 mV/s, the potential scanning range is -0.7-1 V, the scanning frequency range is 0.1 Hz–10 kHz, and the open-circuit potential 0.3487 V is taken as the initial potential for the test.

2.6. Band Energy Calculations. Based on Mott–Schottky analysis and UV–vis DRS data, the band edge potentials of the studied materials are estimated as follows. The flat band potential $(V_{\rm fb})$ is calculated by eq 2

$$V_0 = V_{\rm fb} + \frac{RT}{F} \tag{2}$$

where V_0 is the intercept of the tangent line of the Mott–Schottky curve and *x*-axis, *R* is the standard molar gas constant, *T* is the thermodynamic temperature, and *F* is the Faraday constant. The conduction band potential (E_{CR}) is calculated by eq 3

$$E_{\rm CB} = V_{\rm fb} - kT \ln \frac{N_{\rm c}}{N} \tag{3}$$

where k is the Boltzmann constant, N_c is the effective density of states of the conduction band, and N is the doping concentration. In the approximate calculation, the value of $kT \ln (N_c/N)$ is 0.1 eV. The valence band potential ($E_{\rm VB}$) is then calculated by eq 4, knowing the band gap energy (E_c)

$$E_{\rm VB} = E_{\rm CB} + E_{\rm g} \tag{4}$$

3. RESULTS AND DISCUSSION

3.1. Structure, Morphology, and Surface Chemistry. The composite nanomaterials are synthesized by the growth of AIS QDs in the presence of $g-C_3N_4$ (GCN) through a simple procedure in solution at low temperature, as illustrated in

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Figure 1. (a) XRD patterns and (b) FTIR spectra of GCN, AIS-QDs/GCN, and AIS QDs.

Scheme 1. The phase structures of bare GCN, AIS QDs, and AIS-QDs/GCN samples are investigated by XRD (Figure 1a). GCN has two characteristic diffraction peaks. The peak at 12.8° belongs to the in-plane accumulation characteristic of aromatic substances, which corresponds to the (100) crystal plane of GCN, and the peak at 27.4° belongs to the interlayer stacking of aromatic substances, which corresponds to the (002) crystal plane of GCN (JCPDS no. 87-1526).⁴⁰ These two peaks show that the synthesized GCN has a graphite-like layered carbon nitride structure. The diffraction pattern of AIS QDs contains two main broad peaks around 27 and 46°, which fairly correspond to the (112) and (204) crystal planes of tetragonal AgInS₂ (JCPDS no. 75-0117), respectively,⁴¹ but probably better match the (311) and (440) crystal planes of cubic phase $AgIn_5S_8$ (JCPDS no. 25-1329), respectively,³ which is closer to the nominal stoichiometry of the prepared QDs. The observed features are also comparable with the most intense peaks of the cubic structure of Ag-doped In₂S₃ nanoparticles.³⁰ The width of the AIS peaks suggests a small nanocrystal size. In the diffraction pattern of all AIS-QDs/ GCN samples, the peak at $2\theta = 27.5^{\circ}$ is the most obvious one because the main peak of GCN at 27.4° and that of AIS QDs at about 28° are too close to each other and become overlapping. With the increase of the proportion of AIS QDs in the system, this characteristic diffraction peak becomes slightly wider and weaker, while the peak of GCN at 12.8° gradually disappears, indicating that AIS QDs and GCN may form stable chemical bonds in the system, possibly mediated by the functional groups of glutathione (GSH) molecules retained on the surface of AIS after the synthesis, as evidenced by FTIR spectra (see below). Moreover, there is no obvious impurity peak in the composite, indicating that no other substances are produced.

Figure 1b shows FTIR spectra of all the studied materials. It can be seen that the FTIR spectra of AIS-QDs/GCN and GCN are highly similar, indicating that the loading of AIS QDs has not damaged the original structure of GCN. The peak at about 810 cm⁻¹ is the stretching vibration band of the s-triazine ring structure, which is characteristic of GCN.⁴² The absorption peaks at 1200–1650 cm⁻¹ are attributed to the stretching vibrations of aromatic C–N heterocycles.⁴³ The broad absorption peak at 3000–3300 cm⁻¹ is assigned to the O–H stretching of water molecules adsorbed by GCN or the N–H stretching at the end of the defective position of the aromatic ring.⁴⁴ The main absorption peaks of AIS QDs appear at about 3300, 1605, and 1389 cm⁻¹ wavenumbers, which correspond to the stretching vibration of the O–H bond and C=O (amide bond I) and the symmetric stretching of COO

groups, respectively, indicating the presence of GSH ligands on the surface after the synthesis.⁴⁵ Finally, the peak at 2350 cm⁻¹ is due to the asymmetric stretching vibration of CO_2 in the air. To sum up, the FTIR spectra of the composites show that AIS QDs have been successfully in situ grown on the surface of GCN.

The sample with 10 wt % AIS QDs loading is chosen as a representative of the composites since it is found to be the best performing sample in photocatalytic experiments (see Section 3.2). TEM, high-resolution TEM, and energy-dispersive spectroscopy (EDS) are used to analyze the microstructure and elemental composition of the sample. Illustrative TEM images (Figures 2a and S1) show that AIS QDs are uniformly dispersed on the thin GCN nanosheets. From the high-resolution image (Figure 2b) it can be clearly seen that the AIS QD is firmly grown on the surface of GCN, the size of the nanocrystal being 8–10 nm across. The lattice fringe spacing is 0.17 nm, which may be ascribed to the AgInS₂ (116) facet.



Figure 2. (a) TEM, (b) high-resolution TEM, and (c) EDS elemental mapping images of 10%-AIS-QDs/GCN.

Figure 3. XPS spectra of 10%-AIS-QDs/GCN: (a) survey XPS spectrum; (b) Ag 3d; (c) In 3d; (d) S 2p; (e) C 1s; and (f) N 1s.

Figure 4. (a) Degradation efficiency of TC (40 mg/L) by different AIS QDs/GCN photocatalysts in 1 h under visible irradiation. (b) Photocatalytic activities for H_2 production from TEOA aqueous solution under UV-visible irradiation. The *x* % is the added percentage of AIS QDs.

Figure 2c displays the scanning electron microscopy/EDS surface elemental mappings of 10%-AIS-QDs/GCN. It can be observed that the five elements Ag, In, S, C, and N are uniformly distributed, indicating that the adopted synthesis strategy is effective in producing a material that can be

described as a uniform AIS-QDs/GCN composite with a 0D/ 2D nanostructure.

The chemical valence states of the elements constituting the 10%-AIS-QDs/GCN sample are studied through XPS. The survey spectrum of 10%-AIS-QDs/GCN (Figure 3a) mainly includes C, N, Ag, In, and S elements and some oxygen, which

Figure 5. Photoelectric properties of GCN and 10%-AIS-QDs/GCN: (a) UV-vis DRS spectra displayed as absorbance, (b) band gap diagram of GCN and AIS QDs, (c) steady-state PL spectra, (d) TRPL spectra, (e) photocurrent response, and (f) Nyquist curve: EIS spectrum.

may be originating prevalently from surface-adsorbed water molecules.⁴⁶ Figure 3b shows the XPS spectrum of atomic orbital Ag 3d, where Ag $3d_{3/2}$ and Ag $3d_{5/2}$ correspond to the binding energy peaks at 374.2 and 368.2 eV, respectively, and their spin separation energy of 6.0 eV indicates that silver in the sample exists in the form of Ag⁺.⁴⁷ The peaks at the binding energies of 452.6 and 445.1 eV (Figure 3c) correspond to In $3d_{3/2}$ and In $3d_{5/2}$, respectively, indicating that the valence state of indium is +3.³⁶ Figure 3d shows the binding energies of S 2p after peak separation. The fitted peaks at 161.6 and 163.0 eV correspond to S 2p_{3/2} and S 2p_{1/2}, respectively, showing that sulfur exists mainly in the form of S^{2-} .⁴⁸ Figure 3e shows the XPS high-resolution spectrum of C 1s. The peaks at 288.3 and 287.4 eV belong to the N-C=N bond, and the peak at 285.0 eV is related to indefinite carbon, such as the C-O/C-OH group,⁴⁹ possibly due to GSH. Figure 3f is the XPS diagram of N 1s. After fitting, the characteristic peaks appear at the binding energies of 401.2, 400.1, and 398.8 eV, which correspond to the N atom sp³ bonded amino functional group

(C–N–H), tertiary nitrogen $[N-(C)_3]$, and sp² bonded C-N-C group, respectively.⁵⁰

3.2. Photocatalytic Activity. A preliminary assessment of the photocatalytic properties of the synthesized nanocomposites is carried out in two different processes, namely, the degradation of a water pollutant and hydrogen production. The photocatalytic degradation activity is tested under visible light irradiation, taking TC as a model pollutant. Figure 4a shows the TC degradation efficiency of all the studied samples. The photocatalytic degradation of TC by GCN is limited, and only 15.4% of TC is removed within 1 h. This results from its fast charge recombination rate due to its poor charge separation ability and from its limited visible light absorption. As expected, the addition of AIS QDs improves the photocatalytic activity of GCN. A trend is observed, with an efficiency increasing up to 10 wt % loading of AIS QDs and then decreasing. The fraction of TC degraded in 1 h by 10%-AIS-QDs/GCN is 48.5%, 3.2 times higher than that by GCN.

In order to further understand the photocatalytic performance of the composites and check their potential application in different industrially important processes, the photocatalytic hydrogen generation by water splitting is also tested. The hydrogen generation rates under UV-visible light irradiation are shown in Figure 4b. When GCN is used as the photocatalyst, the hydrogen yield is very low, almost negligible. After loading AIS QDs, the hydrogen production efficiency of GCN is obviously enhanced, with a trend similar to that observed for TC degradation. Also, in this case, the efficiency of 10%-AIS-QDs/GCN is the highest, and the hydrogen production rate reaches 62.3 μ mol g⁻¹ h⁻¹. When the loading amount of AIS QDs is increased up to 15%, the hydrogen production rate decreases, reaching 48.5 μ mol g⁻¹ h⁻¹. This may be due to the excessive density of AIS, which covers the active sites on the GCN surface and hinders the light absorption by GCN. It can be seen that loading an appropriate amount of AIS QDs can effectively improve the ability of GCN in both photodegradation of an organic contaminant and water photolysis for hydrogen production. The structural stability of the sample with the optimal composition (10%-AIS-QDs/ GCN) was evaluated by repeating the XRD analysis after the photocatalytic degradation of TC and H₂ production reactions. As shown in Figures S2a,b, the XRD pattern of 10%-AIS-QDs/ GCN does not change after the reaction compared to that of the fresh sample, which verifies an excellent stability of the 10%-AIS-QDs/GCN photocatalyst in the operating conditions. With the aim to shed light on the relationships between the electronic structure of the nanocomposites and their photoactivity, optical and electrochemical measurements were carried out.

3.3. Photoelectrochemical Properties. The light absorption properties of the nanomaterials are determined by UV–vis DRS. Figure 5a shows the UV–vis DRS spectra of all the prepared samples. The absorption of light by GCN extends from the ultraviolet to the visible light region, with a sideband at 440 nm,⁵¹ while AIS QDs have obvious light absorption in the range of 300–700 nm. Compared with that of GCN, the absorption capacity of AIS-QDs/GCN composites in the ultraviolet region appears enhanced, and the absorption of visible light extends to the 550 nm wavelength. Thus, the modification of AIS QDs effectively improves the light absorption performance of GCN, which is conducive to further enhancing its photocatalytic activity. Based on the absorption spectra, the band gaps (E_g) are calculated using eq S

$$\alpha h\nu = A(h\nu - E_{\rm g})^{n/2} \tag{5}$$

In the above formula, α , h, ν , and A, respectively, signify the light absorption factor, Planck constant, frequency of light, and a constant; according to the type of the semiconductor band structure, n is taken as 1 or 4 (n = 1 for direct semiconductor and n = 4 for indirect semiconductor).⁵² According to the reported literature, In₂S₃ and Ag–In sulfides are direct gap semiconductors, while GCN has an indirect band gap.²⁶ As shown in Figure 5b, the estimated band gaps of GCN and AIS QDs are about 2.83 and 2.40 eV, respectively. The band gap found for AIS QDs is somewhat larger than the values reported for AgIn₅S₈³¹ or other AIS materials, which can be ascribed to the quantum confinement effect in the prepared nanocrystals.

The recombination of photogenerated charge carrier pairs is one of the key factors affecting the activity of photocatalysts. The recombination of photogenerated electron-hole pairs in the samples after excitation is analyzed by PL spectroscopy

(Figure 5c). When AIS QDs are compounded with GCN, the shape of the emission spectrum does not substantially change, with the strongest emission peak concentrated at 435 nm, while the PL intensity decreases significantly with the increase of AIS content up to 10 wt % and then gradually increased again. Therefore, the recombination of charge carrier pairs in GCN is reduced. The AIS QDs could either donate photoexcited electrons to GCN or capture electrons acting as an acceptor, depending on the band energy alignment. In both cases, their introduction promotes the separation efficiency of photogenerated electrons and holes in GCN, thereby contributing to the improvement of the photocatalytic activity. It is worth noting that the trend of PL intensity decrease with the AIS QDs content reflects the trend observed in the photocatalytic activity (Figure 4), confirming the relationship between the suppression of recombination and the photocatalytic efficiency. The enhanced charge separation rate through the formation of the heterojunction is also supported by the TRPL spectra (Figure 5d). The PL intensity decay curves of 10%-AIS-QDs/GCN and GCN were fitted using a double-exponential function (eq 6)

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$
(6)

where τ_1 and τ_2 are PL lifetimes, while A_1 and A_2 represent the corresponding amplitudes. The results are reported in the inset of Figure 5d and include the average PL lifetime (τ_{ave}), calculated by eq 7

$$\tau_{\text{ave}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2_1} \tag{7}$$

Both the short lifetime component (τ_1), associated to nonradiative recombination in defects states of carbon nitride, and the longer lifetime component (τ_2), attributed to band-toband recombination,⁵³ are slightly shorter in the composite, as well as τ_{ave} , which decreases from 4.91 to 4.26 ns. This phenomenon points at a more effective separation and transfer of photogenerated electron—hole pairs in the AIS-QDs/GCN composites owing to the fast charge migration at the interface between the two materials. A similar effect of simultaneous reduction of PL intensity and average lifetime was observed in other literature reports on GCN-based heterostructures as a confirmation of effective charge transfer.^{54,55}

In order to further investigate the separation and transmission characteristics of photogenerated carriers in AIS-QDs/ GCN composites, photoelectrochemical tests were carried out on samples of GCN and 10%-AIS-QDs/GCN. Figure 5e shows the photocurrent response data in 10 optical switching cycles. The photocurrent response of GCN and 10%-AIS-QDs/GCN tends to slowly decrease in the first switching cycles, and then, it remains relatively stable and repeatable. The photocurrent density of 10%-AIS-QDs/GCN (0.242 μ A/cm² in the first cycle) is obviously higher than that of pure GCN (0.123 μ A/ cm²). In general, a higher photocurrent value implies a higher separation efficiency of e⁻ and h⁺ and consequently a stronger photoactivity. This is also consistent with the experimental results of TC photodegradation and hydrogen production (see Section 3.2).

EIS is a test method to characterize the charge transfer capability of samples, as shown in Figure 5f. Compared with that of GCN, the semi-circular arc radius of the EIS Nyquist curve of 10%-AIS-QDs/GCN is reduced, indicating that the composite has lower electron transfer resistance and higher

Figure 6. (a) Mott–Schottky plot: flat band potential spectrum of GCN and AIS QDs, (b) radical capture experiment of 10%-AIS-QDs/GCN, and (c) photocatalytic mechanism for AIS-QDs/GCN.

conductivity. The loading of AIS QDs effectively reduces the interface charge transfer impedance of GCN, and the transport rate of photogenerated carriers is accelerated. In response to PL results, the low recombination rate and high separation and transmission rate of photogenerated electron-hole pairs are among the key factors conferring AIS-QDs/GCN higher photocatalytic activity than that of GCN.

3.4. Photocatalytic Mechanism. To get deeper insights into the redox mechanism and charge transfer scheme in the composites, their electronic structure is further investigated. The impedance potential method is used to evaluate the flat band potential of semiconductors. The capacitance data of samples GCN and AIS QDs are converted to the corresponding Mott-Schottky curves, as shown in Figure 6a. The slopes of both curves are greater than 0, indicating that the prepared materials are n-type semiconductors. The linear intercepts of GCN and AIS QDs on the x-axis are -0.47 and -0.73 V (vs SCE), respectively. Starting from these data and from the UV-vis DRS results, the band potentials are calculated following the procedure described in the Experimental Section (Section 2.6). According to eq 2, the corresponding flat band potential $(V_{\rm fb})$ values are -0.50 V (GCN) and -0.76 V (AIS QDs). According to the approximate calculation by eq 3, the conduction band potential (E_{CB}) values of GCN and AIS QDs are -0.60 and -0.86 V (vs SCE), respectively. Then, the valence band potential (E_{VB}) can be calculated by eq 4, knowing the band gap energy (E_g) derived from the elaboration of UV-vis DRS spectra (Figure 4b). As E_{σ} values of GCN and AIS QDs are 2.83 and 2.40 eV,

respectively, the corresponding $E_{\rm VB}$ results equal 2.23 and 1.54 V, respectively.

In order to clarify the photocatalytic mechanism, active species capture experiments are conducted on 10%-AIS-QDs/ GCN. The experimental process is the same as the photocatalytic degradation experiment. The difference is that 1 mL of 0.01 mol/L benzoquinone solution (BQ), disodium ethylenediaminetetraacetate solution (EDTA-2Na), potassium persulfate (KPS), or 1 mL of n-butanol solution (n-BA) are added as the capture agents (scavengers) of the superoxide radical ($^{\bullet}O_2^{-}$), hole (h⁺), electron (e⁻), and hydroxyl radical (•OH), respectively, so as to determine the main active species involved in the degradation process. After adding each capture reagent, the degradation efficiency of TC decreased, indicating that all active substances (${}^{\bullet}O_{2}^{-}$, ${}^{\bullet}OH$, h^{+} , and e^{-}) participated in the photodegradation process, as shown in Figure 6b. Among these scavengers, the addition of BQ and EDTA-2Na reduced the degradation efficiency to the largest extent, indicating that the dominant active species during the degradation of TC are ${}^{\bullet}O_2^{-}$ and h⁺.

The photocatalytic mechanism of AIS-QDs/GCN for degradation of TC is proposed, as shown in Figure 6c. The excited electrons from the CB of AIS are easily transferred to the CB of GCN, whereas the holes in the VB of GCN tend to be transferred to the VB of AIS. Therefore, the nanocomposite can be described as a type-II heterojunction semiconductor with improved charge carrier pair separation. The excited electrons will react with O_2 to generate O_2^- , while the holes collected by the QDs, whose potential is not large enough to

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oxidize H_2O to generate [•]OH, will directly degrade TC. The type-II charge transfer pathway seems the most probable also in relation to the above free radical capture experiment, which reveals a very low hydroxyl radical-mediated oxidation compared to the contributions of direct hole oxidation and superoxide radicals, consistent with this interpretation.

A similar heterojunction scheme was proposed in other reports on GCN heterostructures with indium-based sulfides finding quite low separation energies between the CB band edges.^{29,56} However, it is interesting to note that in most cases, the CB energy of In_2S_3 is found to be lower than that of GCN, while AIS QDs, having a higher CB potential, can transfer photogenerated electrons to GCN.

Furthermore, the proposed mechanism could also be effective in the oxidation of TEOA, the sacrificial agent in the hydrogen generation experiments, which, coupled with the electron supply coming from AIS QDs, supports a significant increase of the hydrogen yield in comparison with that of bare GCN. In summary, the enhanced photocatalytic efficiency of the AIS-QDs/GCN composite is principally credited to the enhanced separation of charge carrier pairs owing to the formation of a type-II heterojunction.

4. CONCLUSIONS

This work proves that indium-rich AIS QDs can form a heterojunction composite with g-C₃N₄, remarkably improving its photocatalytic activity. AIS QDs are successfully grown on the surface of GCN, originating uniform 0D/2D nanocomposites, whose photocatalytic performances are assessed in the degradation of TC and production of hydrogen. The sample with the optimized composition, 10%-AIS-QDs/GCN, can reach a visible light-driven photodegradation efficiency of 48.5% in 1 h, 3.2 times that of GCN. The rate of hydrogen evolution from water splitting photocatalyzed by 10%-AIS-QDs/GCN is 62.3 μ mol·g⁻¹·h⁻¹. This sample also showed the lowest PL emission and a doubled photocurrent response compared to GCN. The valuable photocatalytic activity of AIS-QDs/GCN is mainly attributed to the enhanced visible light utilization and to the close contact between AIS QDs and GCN. The two nanomaterials form a type-II heterojunction, which accelerates the charge transfer at the interface and reduces the carrier pair recombination. Therefore, electrons and holes can quickly participate in the photocatalytic degradation of organic pollutants and hydrogen production; in other words, the photocatalytic efficiency in both oxidative and reductive reactions can be greatly improved. The results suggest that the studied nanocomposite is potentially useful also for photoelectrocatalytic processes. Hopefully, the attempt to modify GCN with polysulfide QDs to enhance the photoactivity presented in this work will provide a starting point for optimizing the optical and electronic properties of GCN toward further applications of such nanostructured composite semiconductors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.3c00404.

TEM image of 10%-AIS-QDs/GCN and XRD patterns of the 10%-AIS QDs/GCN composite before and after degradation of TC (PDF)

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Author Contributions

J.S. conducted the catalyst synthesis and activity test. J.Z. carried out the characterization. S.-y.L. contributed to the data analysis and discussed the photocatalytic mechanism. K.Q. and C.I. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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