CdSe Quantum Dots/g-C₃N₄ Heterostructure for Efficient H₂ Production under Visible Light Irradiation

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ABSTRACT: Novel photocatalysts - CdSe quantum dots (QDs)/g-C₃N₄ - were successfully constructed. The structure, chemical composition, and optical properties of the prepared samples were investigated via a series of characterization techniques. The results indicated that CdSe QDs/g-C₃N₄ photocatalysts exhibited remarkably enhanced photocatalytic activity for visible-light-induced H₂ evolution compared to pristine g-C₃N₄ and CdSe QDs and addition of 13.6 wt % CdSe QDs into the composite photocatalyst generated the highest H₂ production rate. The enhanced photocatalytic performance of CdSe QDs/g-C₃N₄ can be attributed to the synergistic effects of excellent visible absorption and high charge separation efficiency from the heterostructure. This work could not only provide a facile method to fabricate semiconductor QDs-modified g-C₃N₄ photocatalysts but also contribute to the design for heterostructures.

INTRODUCTION

The use of inexhaustible solar light to drive the decomposition of water to hydrogen has been perceived as one of the most promising solutions to alleviate the energy crisis and the pollution of fossil consumption. Because the pioneering work reported by Fujishima and Honda on photochemical splitting of water over TiO₂ electrodes,¹ the photocatalytic process has intrigued intensive research endeavor and appears to be more amenable to clean, low-cost, and environmentally friendly solar hydrogen production. Because of the fact that visible light takes up ∼43% of the solar spectrum, H₂ evolution under visible light irradiation should be particularly addressed if one thinks of the utilization of solar energy to the uttermost.² Recently, polymeric graphitic carbon nitride (g-C₃N₄) has shown good photocatalytic performance for hydrogen evolution from water splitting in the visible light region.³ Besides, g-C₃N₄ has presented a lot of advantages such as abundance of constituent elements, high stability, and comparatively simple synthesis, rendering it considerably applicable in the field of photocatalytic hydrogen generation.⁴−⁷ However, the high recombination rate of the photogenerated electron–hole pairs and deficient visible light absorption inhibited its photocatalytic performance.⁸,⁹ Tremendous efforts have thus been dedicated to improve the photocatalytic performance, such as construction of the mesoporous structure,¹⁰ doping of nonmetal¹¹−¹⁴ or metal,¹⁵,¹⁶ and coupling with other materials.¹⁷−²⁰ It is worth noting that a lot of semiconductors have been chosen to couple with g-C₃N₄ to form heterostructures with intimate conjunctions. Among them, traditional type-II heterojunctions have been mainly investigated. When the traditional type-II heterojunctions are irradiated, the photogenerated electrons in the conduction band (CB) of the semiconductor with more negative levels can migrate to the CB of another semiconductor, while the photogenerated holes in the valence band (VB) of the semiconductor with more positive levels can migrate to the VB of the other one, which implies more efficient charge separation. For example, Obregón and Colón developed Pt−TiO₂/g-C₃N₄−MnO₂ hybrid structures with enhanced photoactivities for H₂ evolution and ascribed it to the efficient separation of photogenerated charge carriers benefited from the type-II heterostructure.²¹ Chen et al. found that in the Cu₂O/g-C₃N₄ composites the efficient visible light absorption and type-II band alignment induced charge separation should be the key factor for the improved photocatalytic performance.²² Yu et al. established the g-C₃N₄/CdS composites with the type-II heterojunction, which presented significantly enhanced photocatalytic hydrogen production compared with pure g-C₃N₄ and CdS.²³ In addition, Z-scheme heterojunctions were reported as well. Different from the type-II heterojunction, the photo-
generated electrons in the CB of the semiconductor with more positive levels migrate to the VB of the other semiconductor, thus leaving holes and electrons in the VB and CB of the two semiconductors in Z-scheme heterojunctions, respectively. Chen et al. obtained Z-scheme WO3/g-C3N4 composite which exhibited the enhanced photocatalytic activity for degradation of methylene blue and fuchsin under visible light illumination.24 In the hybriding system of α-Fe2O3/g-C3N4 constructed by She et al., the remarkably efficient photocatalytic performance toward hydrogen production was resulted from effectively suppressing the recombination of electron–hole pairs with the Z-scheme junction.25 Wang et al. constructed the Z-scheme heterostructure of Bi1TaO2 quantum dots (QDs)/g-C3N4 with high-efficiency degradation of the antibiotic.26

Despite enormous efforts that have been made in the design of g-C3N4-based heterojunctions, little consideration is given to the g-C3N4 photocatalysts modified with QDs. QDs often refer to semiconductor nanocrystals with their particle sizes less than twice the Bohr radius of exciton in the bulk materials. They present many unique properties such as quantum size effect and multiple exciton generation effect.7–31 Importantly, their band gaps could be modulated via the alteration of quantum size, which is beneficial for the design of heterojunction photocatalysts with matching band gap energy. In addition, the nanosized QDs present a sufficient contact with the substrate, which brings about efficient electronic mobile channel and shortens migration distance, and thus resulting in increased reactive sites. Particularly, CdSe QDs have gained special interest because of the suitable band gap and high efficiency in photocatalysis. For instance, previous study shows that the combination of TiO2 with CdSe QDs could effectively improve hydrogen evolution efficiency of the system.32 The combination of CdSe QDs and g-C3N4 will probably give rise to a suitable band alignment as well, which is important in separating electron–hole pairs in the system.33 Therefore, it is necessary to build heterostructure of CdSe and g-C3N4 for the enhanced photocatalytic performance.

In this study, we reported the facile synthesis of CdSe QDs/g-C3N4 composites with various loading contents for CdSe QDs. The microstructures, morphologies, chemical compositions, and optical properties of the samples were investigated via a series of characterization techniques. Photocatalytic hydrogen generation was used to evaluate the photoactivities of the as-prepared samples. The influence of sacrificial agent, pH value, and CdSe QDs contents on the photocatalytic performance of the CdSe QDs/g-C3N4 composite was systematically studied. Finally, the possible charge-transfer mechanisms of photoinduced charge carriers for the composite photocatalysts were depicted.

**RESULTS AND DISCUSSION**

**Structural Analysis.** CdSe QDs/g-C3N4 composites were fabricated by the mixing of g-C3N4 and CdSe QDs with addition of 3-mercaptopropionic acid (see Experimental section for detail). Figure 1 shows the X-ray diffraction (XRD) patterns of CdSe QDs/g-C3N4 samples with different CdSe QDs contents together with those of the pure CdSe QDs and g-C3N4. XRD profile of CdSe QDs indicates that the as-prepared CdSe QDs is crystallized in the zinc blende structure. Furthermore, the diffraction peaks at 26.6°, 42.6°, and 50.3° are ascribed to the diffraction of (111), (220) and (311) planes, respectively (PDF #19-0191). The grain size of CdSe QDs calculated from Scherrer’s formula is close to 2.1 nm. The XRD profile recorded for pure g-C3N4 features two distinct diffraction peaks at 27.6° and 13.1°. The high-intensity peak at 27.6° reflects the interlayer stacking of aromatic segments and can be indexed as the (002) peak of the graphitic phase. The peak at 13.1° indexed as the (100) peak should be associated with an interplanar separation. These diffraction patterns are consistent with the recent report on g-C3N4.34 For the CdSe QDs/g-C3N4 composites, the diffraction characters are similar with that of pure g-C3N4 indicating that the introduction of CdSe QDs does not impact the crystal structure of g-C3N4. It should be noted that when the loading amount of CdSe QDs is less than 13.6 wt %, no observable peak for CdSe QDs has been detected. However, exceeding the CdSe QDs content over 13.6% by weight gives rise to diffraction peaks corresponding to CdSe QDs and the intensity increases with further enhancement of the CdSe QDs content. This proves that CdSe QDs are indeed supported on g-C3N4.

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were taken to directly analyze the structure and morphology of the CdSe QDs/g-C3N4 composite. As reflected by Figure 2a, the CdSe QDs/g-

![Figure 1. XRD patterns of different photocatalysts. (a) g-C3N4, (b) 1.2 wt %, (c) 3.4 wt %, (d) 6.8 wt %, (e) 13.6 wt %, (f) 27.2 wt % CdSe QDs/g-C3N4, and (g) CdSe QDs.](image)

![Figure 2. TEM (a) and HRTEM (b) images of the CdSe QDs/g-C3N4 composite.](image)
16.4 nm which is bigger than individual g-C3N4 (13.5 nm). This may result from the formation of more pores because of aggregation of CdSe QDs on the surface of g-C3N4.

**X-ray Photoelectron Spectroscopy Analysis.** The surface compositions and chemical states of the as-prepared samples were systematically investigated by X-ray photoelectron spectroscopy (XPS) measurement. The full XPS spectrum of the pure g-C3N4 shown in Figure S1 revealed the existence of chemical elements C and N. In comparison with g-C3N4, the CdSe QDs/g-C3N4 composite shows the evident Cd 3d and Se 3d peaks, which verifies the successful grafting of CdSe QDs on the g-C3N4. As shown in Figure 3a, the C 1s spectrum of pure g-C3N4 can be deconvoluted into two peaks at 284.9 and 288.4 eV, which are ascribed to sp²C–C bonds and the sp³-bonded carbon in N-containing aromatic rings (N–C=–N). The corresponding binding energies of the N 1s spectrum are determined to be 398.5, 399.7, and 401 eV (Figure 3b). The primary peak located at 398.5 eV is identified as the sp²-bonded N involved in the triazine rings (C–N=C). The two weak peaks at 399.6 and 401 eV can be indexed to the tertiary nitrogen N–(C)₃ groups and charging effects. Regarding to the CdSe QDs/g-C3N4 (Figure 3a,b), it can be detected that the C 1s peak at 284.9 eV became much more predominant compared with that of g-C3N4 which may be ascribed to the electron-withdrawing effect of CdSe QDs on g-C3N4. Similarly, this effect can also account for the descending binding energy of N 1s in CdSe QDs/g-C3N4. The fine XPS spectrum of Cd 3d can be devolved typically into two peaks at 405.4 and 412.2 eV (Figure 3c), which can be assigned to the binding energies of Cd 3d₅/₂ and Cd 3d₃/₂. Figure 3d shows the photoelectron peaks for Se 3d at 54.2 and 55.0 eV corresponding to Se 3d₃/₂ and Se 3d₅/₂. These results manifest a strong electronic interaction between CdSe QDs and g-C3N4.

**UV–Vis Absorption Properties.** The optical absorption behaviors of g-C3N4, CdSe QDs, and CdSe QDs/g-C3N4 composites were investigated by UV–vis diffuse and reflection spectroscopy. As depicted in Figure 4, the pristine g-C3N4 shows its fundamental absorption edge rising at about 450 nm, which can be assigned to its intrinsic band gap of 2.76 eV. The band gaps of the CdSe QDs/g-C3N4 composites were also estimated by Kubelka–Munk equation (Figure S2, Table S1), which nearly does not change when compared with that of pure g-C3N4. The absorption onset of CdSe QDs is 490 nm and the bandgap can be calculated to be 2.53 eV. It can thus be speculated that the excellent visible-region optical absorption of CdSe QDs makes it possible to sensitize g-C3N4 with extending optical response. On the other hand, in view of the fact that the VB maximum is fixed with the different sizes of CdSe QDs, namely 1.1 eV, the CB of CdSe QDs is therefore estimated as −1.43 eV. Compared to the pure g-C3N4, all CdSe QDs/g-C3N4 samples exhibited red-shift in the absorption edges, which enable them to utilize a higher fraction of the solar energy spectrum. Meanwhile, the spectral range is correlated to the content of CdSe QDs in the composite. The most exceptional absorption capability was achieved after g-C3N4 was hybridized with 13.6 wt % of CdSe QDs. This implies that the fabrication of the heterostructure can be regarded as a promising approach in tuning the desirable optical characters for photocatalysts.

**Photocatalytic Performance Study.** Photocatalytic H₂ evolution was employed to evaluate the photoactivity of CdSe QDs/g-C3N4 by monitoring the time-dependent production of H₂ gas under the visible light irradiation. First of all, species of sacrificial reagents for hole capture in the photocatalytic system...
were studied. As can be seen in Figure 5a, three different electron sacrificial agents including methanol, triethanolamine, and ascorbic acid (H2A) were chosen to investigate the photocatalytic hydrogen production of CdSe QDs/g-C3N4. It is interesting to find that the rate of hydrogen production for CdSe QDs/g-C3N4 in H2A is obviously advantageous over another two systems, but the further mechanism of the effect of the sacrificial reagent on the H2 production activity is still unclear at this stage. Furthermore, the effect of pH value on the photocatalytic efficiency of CdSe QDs/g-C3N4 was studied (Figure 5b). The hydrogen production ceased after 4 h irradiation either at the pH of 2.5, 7.1, or 9.2. On the contrary, the photocatalytic H2 evolution rate of 103.1 μmol·g−1·h−1 was retained with pH of 4.0. This is due to more efficient dissociation of H2A toward HA− considering the pKa of H2A as 4.0, which provides more HA− species acting as the sacrificial reductant to capture holes so that more photo-generated electrons can participate in proton reduction of hydrogen production.37

We further explored the photocatalytic properties of CdSe QDs/g-C3N4 composites with various CdSe QDs loading amounts. A significant impact of the CdSe QD content is presented in Figure 6a. The hydrogen production of pristine g-C3N4 after exposure to visible light for 4 h was 0.14 μmol, which is probably caused by the high recombination efficiency of charge carriers and insufficient visible light absorption. Upon the introduction of CdSe QDs into g-C3N4, the rate of hydrogen evolution gradually elevates as the content of CdSe QDs in the composite increases. It reaches a maximum value of 615 μmol·g−1·h−1 for the composite loaded with 13.6 wt % CdSe QDs, which is approximately 76 times of that with bare g-C3N4 and twice with CdSe QDs. However, further augmentation of the amount of CdSe QDs from 13.6 to 27.2 wt % leads to reduced hydrogen production rate. This is within expectation because excessive CdSe QDs may aggregate to form the recombination center of electron−hole pairs. What is especially worth mentioning is that the amount of evolved hydrogen on 13.6 wt % CdSe QDs/g-C3N4 within 4 h has far exceeded that of g-C3N4 and CdSe QDs, indicating that the synergetic effects between CdSe QDs and g-C3N4 are key factors for the enhanced photoactivity of CdSe QDs/g-C3N4. Moreover, the stability of the 13.6 wt % CdSe QDs/g-C3N4 composite has been investigated. As reflected by Figure 6b, the composite has maintained a steady increase of photocatalytic hydrogen generation with slight fluctuations under continuous illumination for 12 h. Figure S3 shows that the H2 evolution rate was almost maintained after three cycles. Moreover, it is noted that the crystal structure of CdSe QDs/g-C3N4 after photocatalytic reaction is almost identical to that of original CdSe QDs/g-C3N4 (Figure S4). These results altogether verify the relatively good photostability of the CdSe QDs/g-C3N4 composite.

Possible Photocatalytic Mechanism Discussion. The low photocatalytic activity observed in the g-C3N4 sample is attributed to its limited visible light absorption as well as the high recombination efficiency of photogenerated charges. For the heterostructure, the significantly elevated photocatalytic activity could be rationalized from three factors: the optical absorption, separation of the charge carriers and surface reaction (often related with surface area), which are directly correlated with the photocatalytic performance. First, the visible light absorption of g-C3N4 has the maximum increase upon introduction of 13.6 wt % CdSe QDs, which is in line with the photocatalytic performance. In addition, the specific surface area obtained, respectively, for g-C3N4 and CdSe QDs/g-C3N4 is 8.0 and 9.2 m2/g, and such a small change implies that the effect of surface area on catalytic activity is not the most important factor.

Furthermore, charge separation efficiency of the composite was studied for better understanding of the system. The steady
state photoluminescence (PL) spectra of the samples excited at 390 nm were hence recorded (Figure 7). PL spectra of the g-C_3N_4 present a strong emission peak centered at around 450 nm, which could be associated with the intrinsic recombination of the photogenerated electron−hole pairs of g-C_3N_4. This was further confirmed by the negligible emission of CdSe QDs. For the CdSe QDs/g-C_3N_4 composites, emission peaks located at ca. 450 nm were maintained. It thus demonstrated that the PL property of the CdSe QDs/g-C_3N_4 composites should be mainly relevant with the recombination of the photogenerated charge carriers from g-C_3N_4 instead of CdSe QDs. Figure 7 further displays that all the CdSe QDs/g-C_3N_4 composites exhibit dramatically lower emission intensity than pure g-C_3N_4. This should not be caused by the light shielding of CdSe QDs because the absorption of CdSe QDs/g-C_3N_4 remained almost the same as that of pure g-C_3N_4 at the excitation wavelength. Therefore, PL quenching of g-C_3N_4 by CdSe QDs demonstrates the improved charge separation process in the composite.

To further elucidate the efficient charge transportation, the photoelectrochemical properties of pure g-C_3N_4 and 13.6 wt % CdSe QDs/g-C_3N_4 composite electrodes were investigated for several on−off cycles of irradiation. As can be seen from Figure 8a, the photocurrent value rapidly decreases to zero as soon as the irradiation of light turns off but rises to a constant value once the light is on, verifying the photoactivated nature of the process. Notably, the photocurrent intensity of the CdSe QDs/g-C_3N_4 composite is much higher than that of pure g-C_3N_4 sample, which corroborates the accelerated electron transfer on the interface of the composite thus decreasing the back recombination of charge carriers. Electrochemical impedance spectroscopy (EIS) of the samples have also been portrayed (Figure 8b). In contrast to bare g-C_3N_4, CdSe QDs/g-C_3N_4 shows a much smaller semicircle, indicating the smaller impedance of the composite, which further confirms more efficient charge separation in the composite.

According to the abovementioned analysis, we further studied the photocatalytic mechanism of the system. First, the band levels of CdSe QDs and g-C_3N_4 were compared with each other. The VB of g-C_3N_4 (2.41 V) is more positive than that of CdSe QDs (1.1 V), whereas the CB of CdSe QDs (−1.43 V) is more negative than that of g-C_3N_4 (−0.35 V), obtained from Mott−Schottky (MS) plots, Figure S5). Moreover, work function of CdSe QDs and g-C_3N_4 was determined by the density functional theory (DFT) calculation, which was determined to be 4.76 and 3.99 eV, respectively. This implies that g-C_3N_4 has a higher Fermi level than CdSe QDs. Accordingly, when the two semiconductors are in direct contact, the free electrons will flow from g-C_3N_4 to CdSe QDs until their E_f are aligned at the same level, which results in a built-in electric field at the interface. The interfacial electric field then causes the depletion or accumulation of free-charge carriers near the semiconductor surface compared with the bulk (Figure 9). Ultimately, the energy band edges in g-C_3N_4 are bended upward continuously toward the interface, and those in CdSe QDs are bended downward toward the interface. The downward band bending allows the electrons to flow out freely while holes are inhibited. Therefore, the type-II heterojunction is formed for the CdSe QDs/g-C_3N_4 composite.

Schematic demonstration on the photocatalytic mechanism is then presented in Figure 10. When the CdSe QDs/g-C_3N_4 composite is illuminated, both CdSe QDs and g-C_3N_4 are excited to generate electrons. The electrons on the CB of CdSe QDs are inclined to flow toward the interface of the composite, and those in CdSe QDs are inclined to flow toward the CB of g-C_3N_4 which further reduce protons into H_2. At the same time, the holes left on VB of g-C_3N_4 will move to the valence band of CdSe QDs and are subsequently consumed by sacrificial reagents. In the
system, both the visible light response and charge separation efficiency were promoted, which improves the photocatalytic efficiency in the end.

**CONCLUSIONS**

In summary, an efficient visible-light-driven CdSe QDs/g-C₃N₄ composite was achieved by simply hybriding of individual components. The highest photocatalytic hydrogen production rate was obtained at 615 μmol·g⁻¹·h⁻¹ for the 13.6 wt % CdSe QDs/g-C₃N₄ composite, which was almost 76 times over that of pristine g-C₃N₄. Furthermore, the composite showed a good photostability under visible light irradiation. The enhanced photocatalytic capability was ascribed to the formation of the type-II heterojunction between g-C₃N₄ and CdSe QDs, which not only promoted the visible light absorption but also resulted in an efficient charge separation of the photoexcited electron–hole pairs. The current work would offer new insights into architecture of visible-light-driven photocatalysts from viewpoint of QDs-based heterojunctions.

**EXPERIMENTAL SECTION**

**Synthesis of CdSe QDs.** CdSe QDs were synthesized according to the previous literature with modifications. In a typical process, 46 mg of CdCl₂·2.5H₂O and 26 μL of 3-mercaptopropionic acid were sequentially added to a flask containing 190 mL of deionized water, and the pH value of the solution was adjusted to 11 with a NaOH aqueous solution (10 mol·L⁻¹). After adding polyethylene glycol (20 mg, molecular weight 20,000), Ar gas was passed for 30 min to provide an oxygen-free atmosphere. Then 10 mL of Na₂SeSO₃ solution (5 mmol·L⁻¹) was added in two portions, the resulting mixture was refluxed at 130 °C for 4 h to obtain a yellow-green CdSe QDs solution. The CdSe QDs were precipitated by adding isopropanol into the transparent solution and separated by centrifugation at 10,000 rpm. After drying at 60 °C for 6 h, they can be redispersed into water.

**Preparation of g-C₃N₄.** The g-C₃N₄ nanosheets were synthesized by thermal polymerization. Melamine powder (15 g) was heated in an alumina crucible with a cover in a muffle furnace to 550 °C at a heating rate of 4.6 °C/min and maintained for 2 h. After the crucible was cooled to room temperature, the reacted bulk sample was ground into powder and placed in a crucible, annealed at 550 °C for another 2 h. After naturally cooling to room temperature, a pale yellow solid powder was obtained.

**Preparation of CdSe QDs/g-C₃N₄ Composites.** 50 mg of g-C₃N₄ solid powder was dispersed in 10 mL of ethanol and subjected to sonication for 30 min. After this, 40 mL of CdSe QDs solution (0.17 mg·mL⁻¹) and 100 μL of 3-mercaptopropionic acid were added and the mixture solution was vigorously stirred for 2 h. The suspension was then centrifuged at 5000 rpm for 8 min and the supernatant was removed. The resulting solid was dried at 60 °C for 12 h to give a 13.6 wt % CdSe QDs/g-C₃N₄ composite. CdSe QDs/g-C₃N₄ nanocomposites with other CdSe loading amounts were synthesized using the similar route by adjusting the dosage of CdSe QDs solution. Unless otherwise stated, the CdSe QDs/g-C₃N₄ mentioned in this work all refers to 13.6 wt % CdSe QDs in the CdSe QDs/g-C₃N₄ composite.

**Characterization.** A PANalytical X’Pert X-ray diffractometer (Cu Kα radiation source, operating voltage: 40 kV, operating current: 40 mA, scanning range: 10°–70°) was used to characterize the crystal structure of the sample. TEM images were obtained from an FEI Tecnai G2 F30 transmission electron microscope at an accelerating voltage of 200 kV. Brunauer–Emmet–Teller measurements were conducted using ASAP 2020 V4.02 with N₂ as the adsorbate at liquid nitrogen temperature. The surface chemical composition of the CdSe QDs/g-C₃N₄ composites were further analyzed by the X-ray photoelectron spectrometer (ESCALAB 250XI, Thermo-Fisher Scientific USA), where the binding energy shifts were corrected using the C 1s level at 284.6 eV as the benchmark. UV–vis diffuse reflectance spectra were taken with a Shimadzu 2600 UV–vis spectrophotometer. The PL spectra of the samples were obtained by a HITACHI F-7000 fluorescence spectrophotometer. The photoelectrochemical properties of g-C₃N₄ and CdSe QDs/g-C₃N₄ were evaluated using a CHI660E electrochemical workstation with a standard three-electrode system using the fluoroine-doped tin oxide conductive glass coated with prepared samples as the working electrodes, a Pt wire as the counter electrode, and a saturated calomel as a reference electrode. A 0.5 M Na₂SO₄ aqueous solution was used as the electrolyte. Working electrodes were prepared according to our previous work.²⁷

**DFT Calculations.** All DFT calculations were performed by the plane-wave pseudopotential approach implemented in the Cambridge Sequential Total Energy Package (CASTEP) code with the cutoff energy of 380 eV. The valence electron configurations were 4d¹⁰5s² for Cd, 4s⁴4p⁴ for Se, 2s²2p² for C, and 2s²2p⁴ for N, respectively. The electron-ion interactions were represented by the Vanderbilt ultrasoft pseudopotential. The 2 × 2 × 1 Monkhorst–Pack k-points were used for the monolayer sheets. All atoms were relaxed and the geometry optimization stopped until the residual force was below 0.01 eV/Å. Spin polarization and dipole correction were applied for all calculations. The van der Waals interactions in the CdSe QDs/g-C₃N₄ system were properly described by the Grimme dispersion corrected method.

**Photocatalytic Activity Evaluation.** The photocatalytic reaction was carried out in an outer-irradiation-type Pyrex glass reactor. A 500 W high-pressure Hg lamp equipped with a cutoff filter (λ ≥ 420 nm) was used as the light source, which was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket to cool the lamp. The Pyrex glass reactor was located parallel to the Hg lamp to which 10 mL of the water suspension containing 5 mg of the prepared photocatalysts and 0.1 M L-ascorbic acid was added. The pH value of the system was adjusted with 1 M NaOH aqueous solution.
solution. The suspension was thoroughly deoxygenated before the photocatalytic reaction took place. The amount of evolved H₂ when exposing the system to visible light irradiation was determined by analyzing the gas compositions through Shimadzu GC-2010 Plus gas chromatograph with the TCD detector.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02585.

Full XPS spectra of the pure g-C₃N₄ and CdSe QDs/g-C₃N₄ before and after irradiation, and MS plots of g-C₃N₄ (PDF)

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Notes

The authors declare no competing financial interest.

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