Cadmium Sulfide and Nickel Synergetic Co-catalysts Supported on Graphitic Carbon Nitride for Visible-Light-Driven Photocatalytic Hydrogen Evolution

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Design and preparation of noble-metal-free photocatalysts is of great importance for photocatalytic water splitting harvesting solar energy. Here, we report the high visible-light-driven hydrogen evolution upon the hybrid photocatalyst system consisting of CdS nanocrystals and Ni@NiO nanoparticles grown on the surface of g-C₃N₄. The hybrid system shows a high H₂-production rate of 1258.7 μmol h⁻¹ g⁻¹ in the presence of triethanolamine as a sacrificial electron donor under visible light irradiation. The synergetic catalytic mechanism has been studied and the results of photovoltaic and photoluminescence properties show that efficient electron transfer could be achieved from g-C₃N₄ to CdS nanocrystals and subsequently to Ni@NiO hybrid.

Graphitic carbon nitride (g-C₃N₄), a stable polymer photocatalyst, was found to be an attractive candidate for direct production of hydrogen by using solar energy in water, due to its high stability, nontoxicity, abundance and excellent optical property. But the high photo-induced charge recombination rate and the lack of absorption above 460 nm of pristine g-C₃N₄ still make it unsatisfactory for practical applications. Then, it is necessary to load cocatalysts on pure g-C₃N₄ to achieve a high efficiency in spatial charge separation. As well known that, Pt has the largest work function and lowest overpotential, which is the best candidate cocatalyst for trapping electrons in H₂-production photocatalytic reactions. Taking into consideration of the cocatalysts on universality and low cost, the noble-metal based cocatalysts are too scarce and expensive to be used for large-scale energy production. The loading of cocatalyst not only can facilitate the charge separation but also can lower the activation energy or overpotential for the reactions. Therefore, pursuing a noble-metal free and highly active cocatalyst is highly desirable.

Cadmium sulfide (CdS), an attractive semiconductor sensitive to visible light, has been extensively studied for H₂ evolution due to its narrow band gap and favorable band structure. However, the sufficiently negative conduction band potential of CdS makes it photoinstable, which is usually due to photocorrosion. Generally, construct semiconductor heterojunctions with controllable interface electronic structure undoubtedly to be an effective strategy to promote the separation of photo-induced carriers. In that way, we employed CdS as H₂ evolution synergetic catalyst on g-C₃N₄ to execute high hydrogen evolution activity and photostability. Moreover, non-noble metal such as Co or Ni are also found to be efficient in photocatalytic H₂ production loading on various semiconductors photocatalyst. Agegnehu et al. found that ultrafine Ni nanoparticles loaded on graphene oxide (GO) sheets shows high photocatalytic properties for water splitting due to the easy transfer of photo-induced electrons from the GO photocatalyst to the Ni cocatalyst.

To the best of our knowledge, there are no existing reports on the investigation of such a promising Ni@NiO/CdS/g-C₃N₄ system. Consequently, inspired by such these factors, the central goal of our current work is to improve the photocatalytic H₂ evolution of g-C₃N₄ and explore the transfer of photo-induced charges in detail. Therefore, we report a Ni@NiO/CdS/g-C₃N₄ synergetic catalytic system, which investigated by presenting the excellent photocatalytic evolution properties and the enhanced photocatalytic activity mechanism. The broad

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range of light absorption character of CdS together with the efficient electron transfer from g-C3N4 to CdS nanoparticles and subsequently to Ni@NiO hybrid, attribute to the high photocatalytic H2 evolution activity of this composite photocatalytic system. The rate of H2 evolution of the optimized Ni@NiO/CdS/g-C3N4 is 486 times higher than that of pristine g-C3N4 and high stability can be achieved in these hybrid materials.

Results

Fig. 1 shows the XRD pattern of the obtained graphitic-like layer structures of g-C3N4 with two distinct diffraction peaks14: the weak diffraction peak (100) centered at 13.1° was attributed to in-planar structural packing motif with a separation of 0.675 nm, and the strong one located at 27.4° corresponds to the (002) peak of the interlayer d-spacing of 0.326 nm15,16. For N1, no difference was found compared with pure g-C3N4, because that (i) Ni is not in the form of Ni2+ but possibility the metal Ni; (ii) the low loading percentages and low crystallinity of Ni. The CdS sample has hexagonal wurtzite structure in accordance with JCPDS No. 65-3414. The composite sample of S40 exhibited diffraction peaks corresponding to both g-C3N4 and CdS, reflecting the presence of two phases, which could be distinctly observed in Fig. 1b.

To precisely confirm the chemical composition and structure of the photocatalysts, X-ray photoelectron spectroscopy (XPS) was further undertaken in our work. In sample of N1S40, the typical C, N, Cd, S and O were observed, as in previous studies15. O is presumably originated from the surface absorbed H2O or CO2 molecules when urea under the high temperature pyrolysis in air17–19. The high resolution C 1s XPS spectra of pure g-C3N4 (Fig. 2b) show C-C, C-NH2, and N-C= N bonding at 284.6, 286.1 and 288.3 eV, respectively. Curiously, a slight C-C XPS peak shifts to higher binding energy, which can be ascribed to the chemical bonding between g-C3N4 and Ni/CdS. In Fig. 2c, the N 1s spectra can be fitted to four separate peaks at banding energy of 398.8, 399.7, 401.0 and 405.2 eV, respectively. The strong peak centering at 398.8 eV is identified as the sp2-hybridized N involved in triazine rings (C-N=C) and the peak at 399.7 eV regarded as the tertiary nitrogen N-(C)3 groups14,19. The weak peak at 401.0 eV indicates the presence of amino functional groups (C-N-H). Moreover, the last peak at 405.2 eV is attributed to terminal nitrate groups, charging effects, or π excitations14,17. Typically, metallic Ni nanoparticles are prepared by chemical reduction nickel precursor using NaBH4, but the XPS spectra peak to Ni0 is not found for the exposure of the sample to air to form a thin layer of NiO12,20. And the results indicate that the peak of Ni 2p3/2 at 874.2 eV are the divalent Ni2+ in NiO. Also, the peak of Ni 2p3/2 at 856.3 and 861.7 eV are the Ni2+ in Ni species21, which due to the fact that the Ni element can be easily oxidized by O2 in air. These phenomena imply that a thin NiO layer exists on the surface of Ni, the same as that in metallic Ni22. The high resolution Cd 3d XPS spectra of N1S40 (Fig. 2e) reveals the peaks of Cd 3d3/2 and Cd 3d5/2 located at 405.2 and 412.0 eV, which corresponded to the Cd2+ state23. Figure 2f shows the XPS signals of S 2p observed at 161.6 and 162.8 eV, as expected for the S2− in CdS nanoparticles. It is worth noting that the peak around 168.2 eV can be assigned to the band between S and carbon substrate (S–C), suggesting the important interaction between g-C3N4 and CdS.

The more detailed characterization of the morphologies and microstructures of the samples were based on SEM and TEM. Fig. 3 shows SEM images of (a) pure g-C3N4 and (b) N1S40 samples and the results present that both pristine g-C3N4 and N1S40 have a sheet structure with thin thickness. As illustrated in Fig. 4(a,b), the pristine g-C3N4 exhibits the morphology of stacking flat sheets with wrinkles and irregular shape, a two-dimensional structure with typical irregular porous. Fig. 4c gives direct evidence that CdS nanoparticles are firmly loaded on the surface of g-C3N4. The HRTEM image of N1S40 in Fig. 4d shows the crystallinity of CdS and g-C3N4, with an interplanar spacing of 0.336 nm and 0.326 nm, which are assigned to the (002) and (002) planes of the corrodible phase, respectively.

Optical absorption properties. Fig. 5 shows the UV-vis DRS obtained to evaluate the optical absorption properties of the as-prepared products. The absorption edges of pure g-C3N4 and CdS are estimated to be 460 and 575 nm, which are correspond to the band gaps of 2.7 and 2.2 eV, respectively. After coupling with one species of Ni or CdS to g-C3N4, the composites of N1 or S40 shows the absorption edge at a higher wavelength with
the absorbance intensity of them increased (Fig. S3). Meanwhile, with the CdS content increasing, remarkably enhanced absorbance in the visible region ranging from 450 to 700 nm was apparently observed in system of Ni/CdS/g-C$_3$N$_4$, which is because of their narrow band gap and deep color (Fig. 5)\textsuperscript{24}. Moreover, this phenomenon gives a fact of intimate contact between light and the photocatalysts, which will facilitate the separation and transfer of photo-induced charge carriers in the hybrid structure\textsuperscript{25}.

**Photocatalytic H$_2$-production activity.** Fig. 6 shows the photocatalytic hydrogen evolution activities of the aforementioned samples. From Fig. 6a,b, it can be seen that after loading slight Ni on the surface of g-C$_3$N$_4$, all Ni/g-C$_3$N$_4$ products show much higher photocatalytic activities than that of pure g-C$_3$N$_4$. Especially, the N1 sample shows the highest hydrogen evolution rate of 124.5 μmol h$^{-1}$ g$^{-1}$ for the recombination delay of electron-hole pairs in g-C$_3$N$_4$. Fig. 6b shows the H$_2$-production performance of the CdS, S40, N1, N1S, N1S10, N1S20, N1S40 and N1S60 samples. It can be seen that pure CdS shows negligible activity because of recombination of electron-hole pairs. S40 (40% CdS/g-C$_3$N$_4$) also exhibits slight photocatalytic hydrogen production activities. That is to say, after loading either Ni or CdS, the photocatalytic hydrogen production activities of g-C$_3$N$_4$ are not significant enhanced. However, after addition two species of Ni and CdS into this system, the H$_2$ evolution rate is improved remarkably, which may be credited to the existence of the synergetic effect between Ni and CdS. The optimal photocatalytic activity was achieved at 1% Ni and 40% CdS contents, whose high hydrogen-production rate reached to 1258.7 μmol h$^{-1}$ g$^{-1}$. Table S1 shows comparison of photocatalytic

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**Figure 2.** The XPS profiles of the obtained samples for (a) Survey, (b) C 1s, (c) N 1s, (d) Ni 2p, (e) Cd 3d, and (f) S 2p, respectively.
hydrogen evolution performance for Ni@NiO/CdS/g-C₃N₄ system with other photocatalysts. As shown in Fig. 6c, though 1% of Pt loading on g-C₃N₄ exhibited the higher photocatalytic activity toward H₂ evolution than that of N1S40, we can say that the Ni/CdS also has superior cocatalytic activity on H₂ evolution. Fig. 6d presents the hydrogen evolution rates of N1S40 under both UV and visible-light irradiation, and the results shows that the rate of H₂ evolution over N1S40 reaches to a great value of 7.3 mmol h⁻¹ g⁻¹ under UV light irradiation.

To demonstrate the stability of Ni/CdS/g-C₃N₄ hybrid photocatalysts, recycling rest was performed and the results are shown in Fig. 6e. Almost no decrease H₂-production rate is observed after six cycling irradiation of 24 h, indicating sufficient stability of this material for hydrogen generation. XRD and XPS analysis of the samples before and after the recycling experiment (Fig. S5 and S6) also illustrates the exceeding stability of our photocatalysts.

**Photovoltaic and photoluminescence properties.** To explore the separation and transfer process of the photo-induced charge carriers of the samples, the lock-in-based SPV measurements were carried out. Figure 7 shows the SPV spectra of g-C₃N₄ and N1S40. The pure g-C₃N₄ shows a weak signal while N1S40 presents much obvious response signal, which means that much more charge carriers were separated on N1S40 in spatially²⁶,²⁷.

In addition, an interesting observation is that a negative response of N1S40 in the response region of 500–700 nm...
was found, which indicates that the electrons accumulate at the surface of the samples. From the phase spectra in Fig. 7a, a less phase retardation with respect to $-90^\circ$ can be observed in comparing g-C$_3$N$_4$ with N1S40, and this phenomenon shows that the trend of photo-induced electrons moving to the outer surface of N1S40 sample. That means much more photo-induced electrons have chances to take part in the photocatalytic H$_2$ generation which results in increasing the photocatalytic H$_2$ evolution rate of Ni@NiO/CdS/g-C$_3$N$_4$ system.

Fig. 7b shows the PL spectra of N1S40 and g-C$_3$N$_4$ excited at 325 nm. A strong PL emission peak is observed for g-C$_3$N$_4$, which can be attributed to the recombination of photo-induced electrons and holes. As a contrast,
the PL emission peak intensity of N1S40 is much weaker than the g-C3N4, which confirms the high separation efficiency of the photo-induced charge carriers in composite of N1S40 and makes for the photocatalytic process.

In Fig. S7, a marked increase transient photocurrent response for N1S40 is observed as compared to pure g-C3N4 sample, which suggests that the mobility and separation of the photo-induced charge carriers is promoted by the synergetic cocatalysts of Ni/NiO/CdS supported on g-C3N4. In addition, after five light-on and -off cycles, the transient photocurrents of the two samples have no obvious decay, strongly once again indicating good stability of our photocatalysts.

Discussion

It is well known that, to a great extent, the activity of a photocatalyst mostly depends on the separation and transfer of photo-induced electron-hole pairs. Then the band structures of CdS and g-C3N4 were revealed according to the previously reported works\(^5\text{,}^6\). For CdS, the CB and VB positions are valued theoretically by the following empirical equations\(^5\text{,}^6\): 

\[
E_{\text{CB}} = X - E_c - 1/2E_g \quad \text{and} \quad E_{\text{VB}} = E_{\text{CB}} + E_g,
\]

where \(X\) is the electronegativity for semiconductor; \(E_{\text{CB}}\) is the CB potential, \(E_{\text{VB}}\) is the VB potential; \(E_c\) is the energy of free electrons on the hydrogen scale (ca. 4.5 eV); and \(E_g\) is the band gap of the semiconductor. The \(X\) value of CdS is 5.18 eV\(^3\text{0}\). So, the \(E_{\text{VB}}\) and \(E_{\text{CB}}\) edge positions are 1.78 and \(-0.42\) eV, respectively. For g-C3N4, the \(E_{\text{VB}}\) and \(E_{\text{CB}}\) edge positions are 1.57 and \(-1.13\) eV, respectively\(^3\text{1}\).

Based on the above analyses, a postulated synergetic photocatalytic mechanism is proposed and depicted in Fig. 8. Under the visible light irradiation, the photo-induced charge transfer process would occur between CdS and g-C3N4 because of the inner electric field. More specifically, both CdS and g-C3N4 can be easily activated and generate electrons and holes under the irradiation of visible light. CB-electrons of g-C3N4 transfer to the CB of CdS and simultaneous VB-holes of CdS inject into the VB of g-C3N4. Besides, similar to the noble metal of Pt, Ni/NiO cocatalyst also has the ability of trapping electrons\(^1\text{2}\). So the electrons will accumulate on the Ni/NiO reduction active sites for participating H\(_2\) evolution reaction, while holes to react with the TEOA in the aqueous solution. In this way, the efficient photo-induced electron-hole pairs lead to a significant enhancement of photocatalytic H\(_2\) production in the Ni/CdS/g-C3N4 composite system.

In summary, a hybrid nanophotocatalyst system with a 1258.7 μmol h\(^-1\) g\(^-1\) H\(_2\) evolution rate in triethanolamine solution has been achieved under visible light irradiation. It is believed that the wide range of light absorption of CdS together with the efficient electron transfer from g-C3N4 to CdS nanoparticles and subsequently to Ni@NiO hybrid, attribute to the high photocatalytic H\(_2\) evolution activity of this composite photocatalytic system. This work not only shows a good strategy to enhance the photocatalytic H\(_2\)-production activity of g-C3N4 by loading noble-metal-free cocatalysts of Ni@NiO/CdS, but also provides a new insight into the design and fabrication of other hybrid composite photocatalysts with high photocatalytic H\(_2\) evolution activity.

Method

**Fabrication of Graphitic carbon nitride (g-C\(_3\)N\(_4\)).** g-C\(_3\)N\(_4\) was synthesized thermally by heating urea (10 g) at 550 °C for 3 h with a heating rate of 4.6 °C min\(^{-1}\) under ambient pressure in air. Then, the as-obtained yellowish powder solid were collected and grinded to get the final sample.

**Fabrication of CdS/g-C\(_3\)N\(_4\).** A mixture of certain amount of Cd(NO\(_3\))\(_2\)-4H\(_2\)O, 0.083 g of thiourea and 0.5 g of g-C3N4 was dissolved in 25 mL of deionized water and ultrasonicated for 30 min. Then, the resulting solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed tightly, and heated at 180 °C for 12 h. Afterward the precipitates were washed several times with deionized water and ethanol, and then dried at 80 °C overnight. The molar ratios of CdS to g-C3N4 were 10%, 20%, 40%, and 60%, and the resulting samples were labeled as S10, S20, S40, and S60, respectively. Single phase CdS was also prepared using an identical procedure for comparison.

**Fabrication of Ni/g-C\(_3\)N\(_4\), Ni/CdS, and Ni/CdS/g-C\(_3\)N\(_4\).** The Ni/g-C\(_3\)N\(_4\), Ni/CdS, and Ni/CdS/g-C3N4 were prepared by a NaBH\(_4\) reduction method. Typically, g-C3N4 powder (0.5 g) and Ni(NO\(_3\))\(_2\)-6H\(_2\)O (0.027 mM)
were first ultrasonicated in deionized water (25 mL) for 5 min and subsequently stirred for 30 min. Then, NaBH₄ solution (5 mL, 0.08 M) was gradually added to the above liquid, and the mixture was stirred for 5 min. After that, the obtained precipitates were washed and dried to get 0.5% Ni/g-C₃N₄. The deposition content of metal Ni can be varied by changing the amount of Ni(NO₃)₂·6H₂O, and the final composites were marked as N0.5, N1, N1.5, correspondently. With the same method as above, we got the 1% Ni/CdS(10%)/g-C₃N₄, 1% Ni/CdS(20%)/g-C₃N₄, 1% Ni/CdS(40%)/g-C₃N₄, 1% Ni/CdS(60%)/g-C₃N₄, and 1% Ni/CdS, which were labeled as N1S10, N1S20, N1S40, N1S60, and N1S, respectively.

**Fabrication of Pt/g-C₃N₄.** Typically, 0.5 g of g-C₃N₄ power was dispersed into 25 mL of deionized water containing 2.8 mL of H₂PtCl₆ aqueous solution (10 g/L), ultrasonicated for 5 min and subsequently stirred for 30 min. After that, NaBH₄ solution (10 mL, 0.08 M) was quickly added to the above liquid, and the mixture was stirred for 30 min. After that, the obtained precipitates were washed and dried to get 1% Pt/g-C₃N₄.

**Characterization.** The crystalline structure of the as-prepared sample was characterized by powder X-ray diffraction (XRD) with a Rigaku D/Max-2550 diffractometer using Cu Kα radiation (λ = 1.54056 Å) at 50 kV and 200 mA in the 2θ range of 10–80° at a scanning rate of 10° min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG Scientific ESCALAB 250 spectrometer using monochromatized Al Kα excitation. The optical absorption spectra of the samples were measured on a UV-Vis-NIR spectrophotometer (Shimadzu UV-3600) detecting absorption over the range of 300–650 nm. SEM images were obtained on a field emission scanning electron microscope (JSM-6700F, Japan). The transmission electron microscopy (TEM) was conducted on a Tecnai G2 S-Twin F20 TEM microscope (FEI Company). The element mappings were applied on a HITACHI SU-8020 transmission electron microscopy. N₂ adsorption and desorption isotherms were carried out at 77 K using a Micrometrics ASAP 2020. The Brunauer-Emmett-Teller (BET) surface area was analyzed by a multipoint BET method using adsorption data in the relative pressure (P/P₀) range of 0.05–0.25. Room temperature photoluminescence (PL) spectra with an excitation wavelength of 325 nm were measured on a FLUOROMAX-4.

The lock-in-based SPV spectroscopic measurement system consists of a source of monochromatic light, a sample cell, a computer, and a lock-in amplifier (SR830-D SP) with an alight chopper (SR540). A low chopping frequency of 24 Hz was used. A 500 W xenon lamp (CHF-XM-500 W, Global Xenon Lamp Power) and a grating monochromator (Omni-5007, Zolix) provide monochromatic light. The samples were studied without further treatment during the SPV measurements, and the photovoltaic cell was a structure of fluorine tin oxide (FTO)-mica-sample-FTO. The system was calibrated by a DSI200 UV enhanced silicon detector to eliminate the possible phase shift which was not correlated to the SPV response, so that anyphase retardation reflected the kinetics of SPV response.

![Figure 8. Schematic illustration of the mechanism for photocatalytic activity of Ni/CdS/g-C₃N₄.](image-url)
Photoelectrochemical measurements were performed with an electrochemical analyzer (CHI760E, Shanghai) in a three-electrode cell. The corresponding sample films on FTO used as the working electrode, Pt plate served as the counter electrode, and an Ag/AgCl (sat. KCl) acted as reference electrode. An aqueous solution of 0.5 M Na₂SO₄ was used as the electrolyte (pH = 7) and the voltage is 0.5 V versus Ag/AgCl. A 300 W xenon lamp was utilized as the simulated sunlight source.

**Photocatalytic H₂-production.** The photocatalytic hydrogen evolution experiments were performed with 0.1 g of photocatalyst suspended in a 100 mL solution containing 90 mL H₂O and 10 mL triethanolamine, in a Pyrex glass reaction cell at ambient temperature and atmospheric pressure. A 300 W Xe lamp with cooling water (stabilize the temperature at 298 K) and a UV cutoff filter (≥ center wavelength 420 nm) was served as the visible-light source to trigger the photocatalytic reaction. Hydrogen gas evolution was analyzed using an online gas chromatograph (GC-8A, Shimadzu Co., Japan) equipped with an MS-5A column and a thermal conductivity detector (TCD). (see in Fig. S1)

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Author Contributions
X.Y. and S.Y. performed the experiments and wrote the main manuscript text. X.Y. drew all the figures. Z.Z. guided the whole work and made critical revision of the manuscript. R.W. and S.Q. privided all the characterization equipments. All authors reviewed the manuscript.

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