

Article

Non-Precious Co_{0.85}Se Cocatalyst Boosts Visible-Light-Driven Hydrogen Evolution on g-C₃N₄ by 53-Fold

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Abstract

The development of cost-effective, efficient, and visible-light-responsive photocatalysts for hydrogen evolution is pivotal for addressing global energy shortages and environmental degradation. In this context, non-precious metal cocatalysts have garnered significant attention for modifying semiconductor photocatalysts. Herein, a high-performance Co_{0.85}Se/g-C₃N₄ composite photocatalyst was successfully synthesized via a facile solvothermal method, where transition metal Co_{0.85}Se nanoparticles were grown on g-C₃N₄ nanosheets in situ. The optimized 6-Co_{0.85}Se/g-C₃N₄ composite exhibited a superior photocatalytic hydrogen evolution rate of 426 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under visible light irradiation, which is approximately 53 times higher than that of pristine g-C₃N₄. Experimental characterizations revealed that the Co_{0.85}Se nanoparticles were well dispersed on the g-C₃N₄ nanosheets without obvious agglomeration, which significantly broadened the visible-light absorption range of the composite. Furthermore, photoelectrochemical measurements confirmed that the Co_{0.85}Se cocatalyst effectively accelerated charge separation and migration kinetics. Consequently, the construction of this heterojunction endows the composite with excellent photocatalytic performance. This work offers new insights into the design of efficient, non-precious metal-based photocatalysts for sustainable hydrogen production.

Keywords: non-precious metal cocatalyst; Co_{0.85}Se/g-C₃N₄ heterojunction; visible-light photocatalysis; hydrogen production

1. Introduction

The rapid development of human society and the massive consumption of fossil energy have led to severe environmental pollution and an escalating energy crisis [1]. Consequently, there is an urgent need to develop clean, sustainable alternatives to fossil-based energy sources. Among various strategies, harnessing solar energy for hydrogen production via photocatalytic water splitting represents a highly promising approach. This process relies on efficient semiconductor photocatalysts capable of driving the H₂ evolution reaction under solar irradiation.

In recent years, extensive research efforts have been devoted to designing high-performance semiconductor photocatalysts. A key requirement for effective photocatalytic water splitting is the development of materials with strong reduction capability and an appropriate bandgap that enables visible-light absorption. However, many conventional semiconductor photocatalysts suffer from large band gaps, limiting their utilization of ultraviolet (UV) light, a spectral region that constitutes only ~4% of sunlight. For instance, titanium dioxide (TiO₂), despite its low cost, chemical stability, and widespread use [2],



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exhibits limited practical applicability due to its wide bandgap (~ 3.2 eV), which confines photoexcitation to UV wavelengths [3]. To overcome this limitation, visible-light-responsive photocatalysts are needed to maximize solar energy utilization. Graphitic carbon nitride (g-C₃N₄), a metal-free polymeric semiconductor, has emerged as a compelling candidate owing to its suitable bandgap (~ 2.7 eV), visible-light absorption capability, low cost, excellent thermal and chemical stability, non-toxicity, and earth-abundant constituents [4]. Nevertheless, pristine g-C₃N₄ suffers from rapid recombination of photogenerated electron-hole pairs, which severely limits its photocatalytic hydrogen evolution efficiency [5,6].

A widely adopted strategy to address these issues is the loading of cocatalysts onto g-C₃N₄. While noble metals such as Pt, Pd, and Au [7,8] exhibit exceptional catalytic activity for hydrogen evolution, their high cost and scarcity hinder large-scale applications. Therefore, considerable attention has shifted toward developing low-cost, earth-abundant, and efficient non-precious metal cocatalysts. Transition metal sulfides, including MoS₂ [9], NiS [10] and WS₂ [11], as well as phosphides such as Ni₂P [12], Co₂P [13] and MoP [14] have demonstrated significant enhancement of the photocatalytic H₂ production performance of g-C₃N₄. In contrast, transition metal selenides have received comparatively less attention, despite their promising catalytic properties. Notably, Zeng et al. [15] fabricated flower-like and mesh-like MoSe₂ nanostructures to modify g-C₃N₄, achieving H₂ evolution rates of $114.5 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and $136.8 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under visible light irradiation (>420 nm) at an optimal MoSe₂ loading of 5 wt%, highlighting MoSe₂ as a cost-effective and efficient cocatalyst. Similarly, Chen et al. [16] reported a NiSe/g-C₃N₄ composite synthesized via hydrothermal methods, which exhibited remarkable photocatalytic activity with a H₂ evolution rate of up to $1250 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. Furthermore, Co₃O₄ nanosheet/g-C₃N₄ hybrid photocatalysts reported by Chen et al. exhibited a visible-light-driven H₂ evolution rate of $134.6 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ in the presence of triethanolamine (TEOA) sacrificial reagent, indicating that the photocatalytic performance of noble-metal-free g-C₃N₄ systems still requires further improvement [17]. In a recent pioneering work, it was also reported that constructing a unique Co-Se-W configuration at the interfaces of phase-mixed cobalt selenides via a spontaneous phase transition can achieve extraordinary platinum-like hydrogen evolution activity [18]. These previous studies collectively demonstrate that rational morphology regulation and interface engineering can significantly promote the separation of photogenerated carriers and suppress charge recombination. In particular, cobalt-based selenides have demonstrated promising application potential owing to their earth abundance, relatively low cost, and suitable electronic structures for hydrogen evolution reactions. Therefore, the introduction of cobalt selenides into the g-C₃N₄ system is expected to further improve charge transfer efficiency and provide abundant catalytic active sites for photocatalytic hydrogen production.

Herein, we present a facile, one-step solvothermal strategy to construct a novel Co_{0.85}Se/g-C₃N₄ composite photocatalyst, in which non-stoichiometric Co_{0.85}Se nanoparticles are uniformly generated in situ and anchored onto the surfaces of g-C₃N₄ nanosheets. Benefiting from the tailored Co/Se molar ratio and optimized electronic coupling, the optimized sample yields an exceptional visible-light-driven H₂ evolution rate of $426 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which dramatically outstrips pristine g-C₃N₄ by a factor of 53. Comprehensive physicochemical and photoelectrochemical characterizations reveal that the in situ grown Co_{0.85}Se nanoparticles not only expose high-density catalytically active sites, but also establish an intimate micro-Schottky junction at the contact interface between the Co_{0.85}Se and g-C₃N₄ phases. This unique energy band alignment fundamentally constructs an efficient highway for the spatial directional migration of photogenerated electrons, thereby effectively suppressing catastrophic charge carrier recombination. The experimental insights demonstrate that Co_{0.85}Se acts as a robust, non-precious metal cocatalyst that

significantly enhances interfacial charge separation and surface reaction kinetics. Furthermore, the underlying mechanisms responsible for the improved photocatalytic activity of transition-metal-selenide-modified materials are systematically investigated, providing new insights into the rational design of cost-effective and highly efficient solar fuel production systems.

2. Results and Discussion

2.1. Crystalline Phase

The crystal structures of pure g-C₃N₄ and x-Co_{0.85}Se/g-C₃N₄ (x = 2, 6, 10, and 14 wt%) composites were analyzed using X-ray diffraction (XRD), as shown in Figure 1a. There are two characteristic diffraction peaks located at 13° and 27.4° in the spectrum of g-C₃N₄, which are assigned to the in-plane structural stacking and interfacial stacking of g-C₃N₄ [19,20]. The XRD pattern of the Co_{0.85}Se/g-C₃N₄ composite photocatalyst exhibits three additional diffraction peaks at 33.3°, 44.8°, and 50.8°. These peaks match well with the standard phase of Co_{0.85}Se (PDF#52-1008) and can be indexed to the (101), (102), and (110) crystal planes of Co_{0.85}Se, respectively. This distinct crystallization behavior confirms the successful preparation and anchoring of Co_{0.85}Se within the composite. When the loading of Co_{0.85}Se is as low as 2%, the characteristic diffraction peaks are so weak that no peaks can be observed because the loading is relatively low. However, when the loading is increased, the characteristic peaks in the XRD spectrum are enhanced. It is noteworthy that the diffraction intensity of Co_{0.85}Se does not increase monotonically with increasing loading amount. This behavior may be associated with the partial aggregation of Co_{0.85}Se nanoparticles at higher loadings, which influences their effective diffraction contribution in the composite.

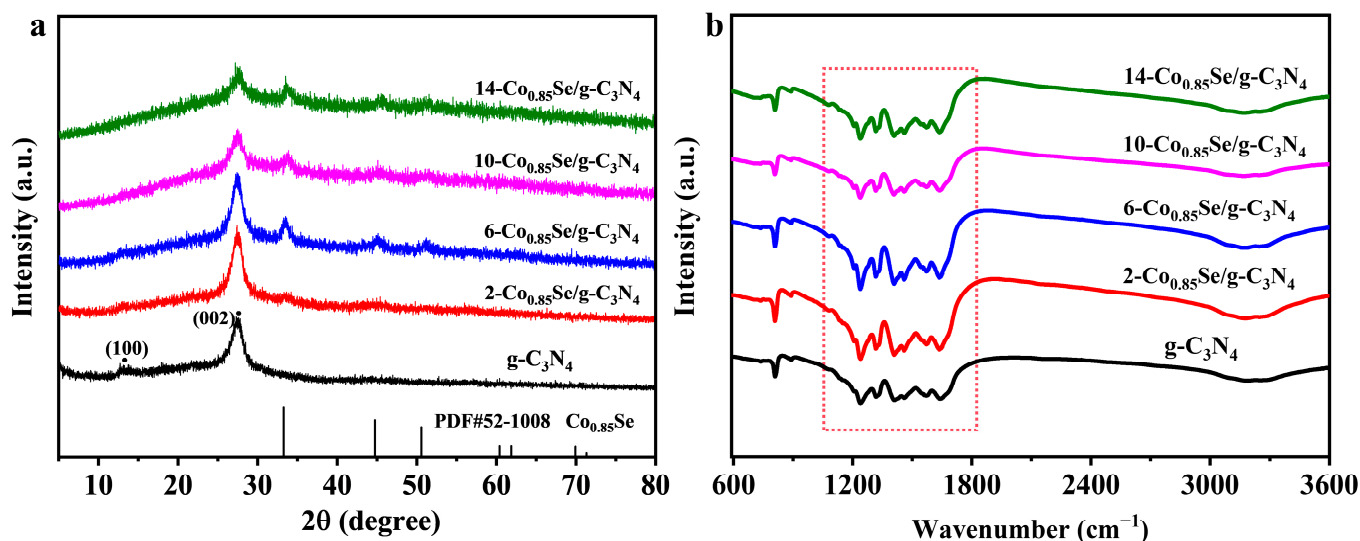


Figure 1. (a) XRD spectra and (b) Infrared spectra of g-C₃N₄ and x-Co_{0.85}Se/g-C₃N₄ samples (x = 2, 6, 10 and 14 wt%). The dashed box highlights the characteristic FTIR absorption region.

The molecular structures of pure g-C₃N₄ and composites modified with different loadings of Co_{0.85}Se were analyzed by Fourier transform infrared (FTIR) spectroscopy. As shown in Figure 1b, the characteristic absorption peak at about 810 cm⁻¹ is assigned to the stretching vibration of the triazine ring of g-C₃N₄ [21–23], the absorption peaks in the range of 1200–1700 cm⁻¹ belong to the stretching vibrations of aromatic C–N and C=N heterocyclic compounds of g-C₃N₄ [24–26], and the absorption peaks in the range of 3000–3500 cm⁻¹ are assigned to N–H bond stretching vibrations [27,28]. According to the

spectrum, $x\text{-Co}_{0.85}\text{Se/g-C}_3\text{N}_4$ and pure $\text{g-C}_3\text{N}_4$ have similar characteristics, indicating that the molecular structure of $\text{g-C}_3\text{N}_4$ is not destroyed after loading $\text{Co}_{0.85}\text{Se}$ on $\text{g-C}_3\text{N}_4$.

Since the $6\text{-Co}_{0.85}\text{Se/g-C}_3\text{N}_4$ sample exhibited the highest photocatalytic hydrogen evolution activity among all prepared composites, it was selected as the representative sample for subsequent detailed characterization to elucidate the origin of its superior photocatalytic performance.

2.2. Morphological and Structural Analysis

The scanning electron microscopy (SEM) images of pure $\text{g-C}_3\text{N}_4$ and the $6\text{-Co}_{0.85}\text{Se/g-C}_3\text{N}_4$ composite sample are presented in Figure 2. In Figure 2a, pure $\text{g-C}_3\text{N}_4$ exhibits a layered, stacked block-like structure. In Figure 2b, the SEM image of the $6\text{-Co}_{0.85}\text{Se/g-C}_3\text{N}_4$ composite sample is similar to that of the pure material, also showing sheet-like agglomerates forming a block-like structure. The SEM results indicate that the in situ loading of the $\text{Co}_{0.85}\text{Se}$ cocatalyst onto $\text{g-C}_3\text{N}_4$ via the one-step solvothermal method does not significantly alter the morphological structure of the $\text{g-C}_3\text{N}_4$ material.

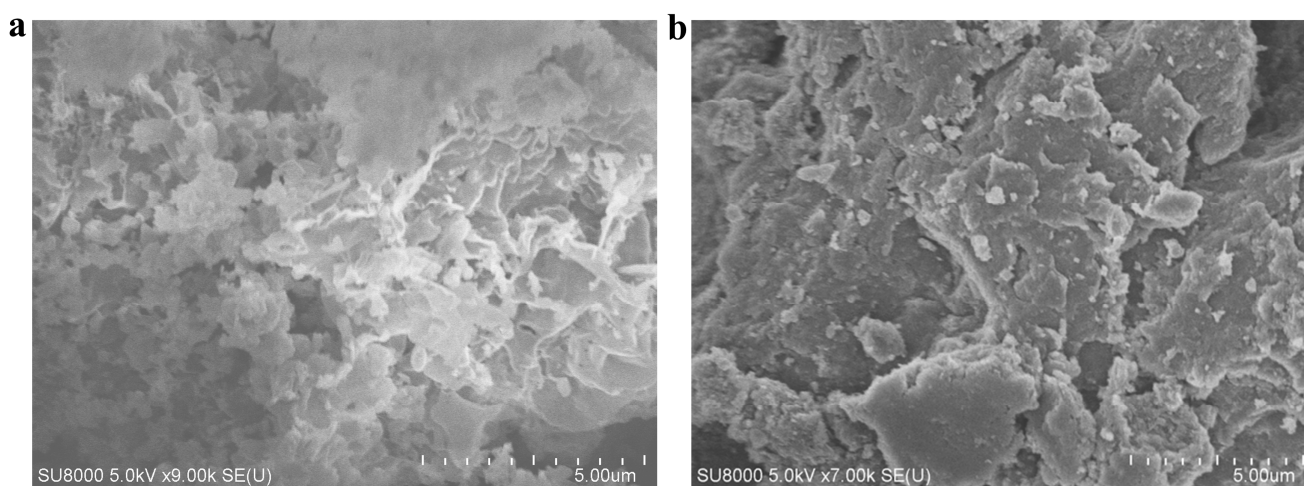


Figure 2. SEM images of (a) $\text{g-C}_3\text{N}_4$ and (b) $6\text{-Co}_{0.85}\text{Se/g-C}_3\text{N}_4$ samples.

The morphology and structure of the pure $\text{g-C}_3\text{N}_4$ and $6\text{-Co}_{0.85}\text{Se/g-C}_3\text{N}_4$ composite samples were further analyzed by transmission electron microscopy (TEM). As shown in Figure 3a,b, the prepared $\text{Co}_{0.85}\text{Se/g-C}_3\text{N}_4$ composite sample contains nanosheets and nanoparticles distributed on the nanosheets. The nanosheets observed in the TEM images are $\text{g-C}_3\text{N}_4$, exhibiting a typical graphitic sheet-like structure of carbon nitride, while the nanoparticles dispersed on the $\text{g-C}_3\text{N}_4$ nanosheets are $\text{Co}_{0.85}\text{Se}$. Some of these nanoparticles are relatively small, only about 5 nm in size, as can be seen from the high-resolution TEM (HRTEM) image in Figure 3b. The $\text{Co}_{0.85}\text{Se}$ nanoparticles are distributed over the $\text{g-C}_3\text{N}_4$ nanosheets without obvious agglomeration, although a perfectly uniform distribution is not observed. Figure 3b shows a high-resolution TEM image of a single $\text{Co}_{0.85}\text{Se}$ nanoparticle loaded on a $\text{g-C}_3\text{N}_4$ nanosheet, where the lattice fringes of $\text{Co}_{0.85}\text{Se}$ can be clearly observed, with a lattice spacing of 0.269 nm, corresponding to the (110) crystal plane of $\text{Co}_{0.85}\text{Se}$. Figure 3c–h show the elemental mapping images of a selected area, revealing the distribution of various elements in this region. These results demonstrate that $\text{Co}_{0.85}\text{Se}$ nanoparticles are distributed on the $\text{g-C}_3\text{N}_4$ nanosheets, indicating that $\text{Co}_{0.85}\text{Se}$ has been successfully loaded onto $\text{g-C}_3\text{N}_4$.

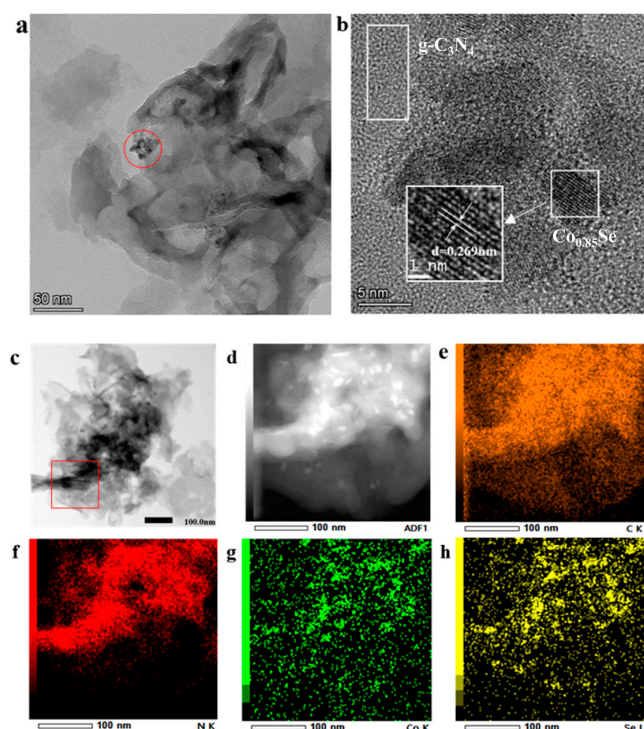


Figure 3. (a) TEM image, (b) HRTEM images, and (c–h) elemental distribution maps of the 6- $\text{Co}_{0.85}\text{Se}/\text{g-C}_3\text{N}_4$ sample. The red circle in (a) and the red box in (c) indicate the regions selected for the corresponding HRTEM and elemental mapping analyses, respectively.

Figure 4 shows the N_2 adsorption–desorption isotherms of $\text{g-C}_3\text{N}_4$ and 6- $\text{Co}_{0.85}\text{Se}/\text{g-C}_3\text{N}_4$. Both curve shapes belong to type IV isotherms, indicating that both materials belong to mesoporous structures. The specific surface area of $\text{g-C}_3\text{N}_4$ was determined to be $39.9 \text{ m}^2/\text{g}$, and the specific surface area of 6- $\text{Co}_{0.85}\text{Se}/\text{g-C}_3\text{N}_4$ composite was $54.0 \text{ m}^2/\text{g}$, indicating that the generation of $\text{Co}_{0.85}\text{Se}$ on $\text{g-C}_3\text{N}_4$ by the solvothermal method can effectively enlarge the specific surface area. The larger specific surface area of 6- $\text{Co}_{0.85}\text{Se}/\text{g-C}_3\text{N}_4$ provides more active sites for photocatalytic reactions and improves the photocatalytic performance of the sample.

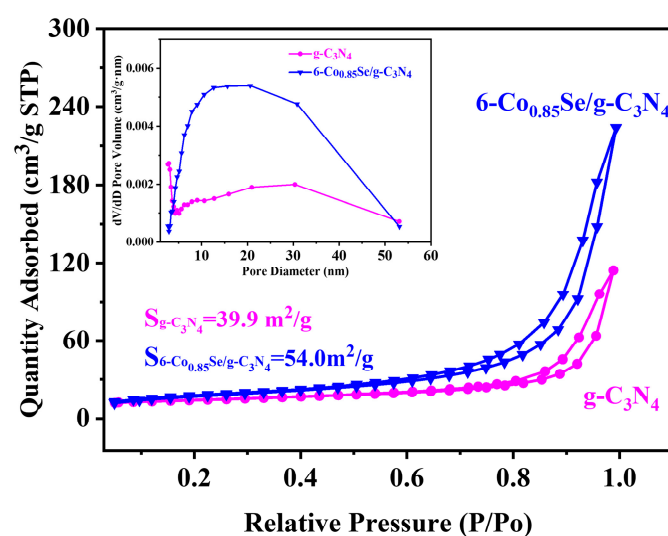


Figure 4. Low-temperature N_2 adsorption–desorption isotherms of $\text{g-C}_3\text{N}_4$ and 6- $\text{Co}_{0.85}\text{Se}/\text{g-C}_3\text{N}_4$ samples.

2.3. Optical Properties

The optical properties of pure g-C₃N₄ and x-Co_{0.85}Se/g-C₃N₄ composites were analyzed by UV-vis diffuse reflectance spectrometry (UV-vis DRS). As shown in Figure 5a, both pure g-C₃N₄ and all composite samples can absorb a portion of visible light. Compared with pure g-C₃N₄, the Co_{0.85}Se/g-C₃N₄ composites exhibit significantly enhanced light absorption capacity in the visible region. With increasing Co_{0.85}Se loading, the absorption intensity of the composites continuously increases, and their absorption edge shows an obvious red shift, indicating an expanded visible-light response range. This enhanced light absorption can be attributed to the loading of the black Co_{0.85}Se cocatalyst, suggesting that the formation of Co_{0.85}Se nanoparticles on g-C₃N₄ nanosheets can effectively improve the light utilization efficiency of the material, which is beneficial for the photocatalytic reaction. Further optical and electrochemical analyses were carried out on the 6-Co_{0.85}Se/g-C₃N₄ sample. Based on the Tauc plots shown in Figure 5b, the optical bandgap of pristine g-C₃N₄ was determined to be 2.90 eV. Upon the in situ loading of Co_{0.85}Se, the bandgap of the 6-Co_{0.85}Se/g-C₃N₄ composite slightly decreases to 2.83 eV, which is consistent with the red shift observed in the DRS spectra. Combined with the Mott-Schottky measurement results shown in Figure 5c, the flat-band potential of 6-Co_{0.85}Se/g-C₃N₄ was determined to be −0.70 V (vs. NHE) by extrapolating the linear portions of the curves to the potential axis. The positive slope of the M-S curves indicates that the catalyst is a typical n-type semiconductor, whose flat-band potential is very close to the conduction band minimum (CBM) position. Therefore, the conduction band potential of this composite material was determined to be approximately −0.70 V (vs. NHE), and the valence band potential was calculated to be approximately +2.13 V (vs. NHE). The above band structure indicates that the 6-Co_{0.85}Se/g-C₃N₄ composite satisfies the thermodynamic requirements for photocatalytic hydrogen evolution.

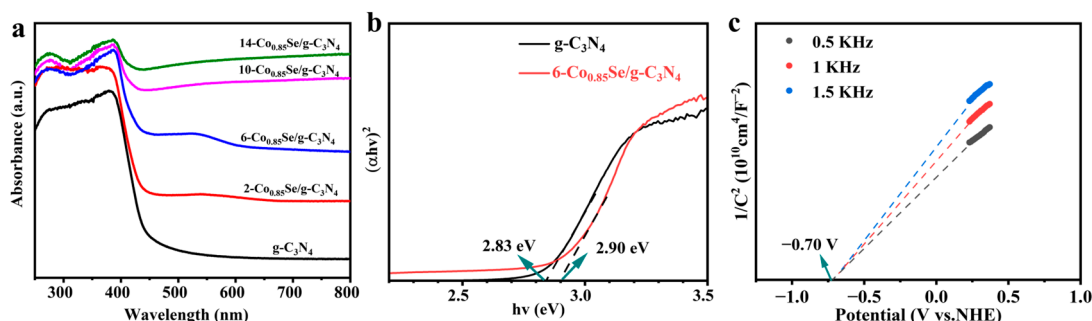


Figure 5. (a) UV-Vis DRS of g-C₃N₄ and x-Co_{0.85}Se/g-C₃N₄, (b) Tauc curves of g-C₃N₄ and 6-Co_{0.85}Se/g-C₃N₄, (c) Mott-Schottky plots of 6-Co_{0.85}Se/g-C₃N₄ at different frequencies. The dashed lines represent the linear extrapolation.

Photocurrent measurements were carried out on the as-prepared g-C₃N₄ and Co_{0.85}Se/g-C₃N₄. As shown in Figure 6a that the photocurrent density of 6-Co_{0.85}Se/g-C₃N₄ is 4 times higher than that of pure g-C₃N₄. It is shown that the loading of Co_{0.85}Se particles on g-C₃N₄ nanosheets can effectively improve the separation efficiency of photogenerated electrons and holes. Figure 6b presents the electrochemical impedance spectroscopy (EIS) of the samples. It can be clearly observed that the 6-Co_{0.85}Se/g-C₃N₄ composite exhibits a significantly smaller arc radius compared to pure g-C₃N₄. This result indicates a decreased charge transfer resistance and a higher separation efficiency of photogenerated carriers. These results indicate that loading Co_{0.85}Se nanoparticles on g-C₃N₄ can effectively improve the separation and migration efficiency of photogenerated electrons and holes, which is of great significance for improving the photocatalytic performance of photocatalysts.

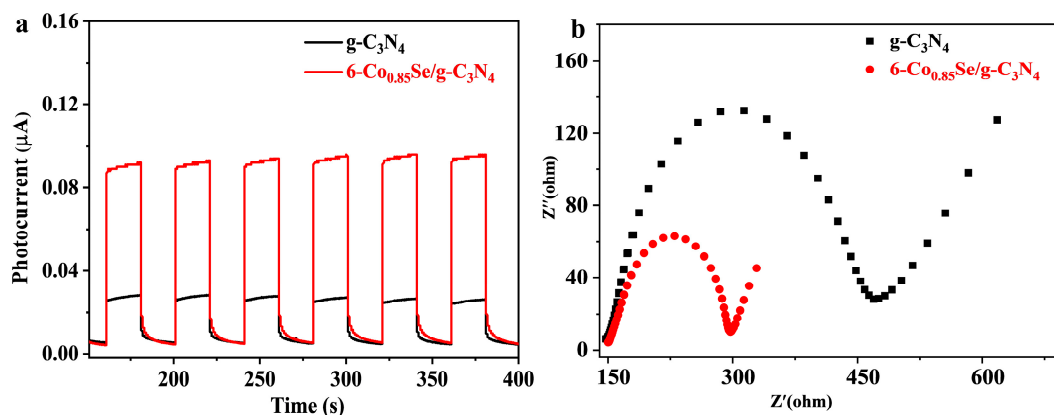


Figure 6. (a) Transient photocurrent responses, (b) EIS Nyquist plots of $g-C_3N_4$ and $6-Co_{0.85}Se/g-C_3N_4$.

Figure 7 shows the photoluminescence (PL) spectra of the pure $g-C_3N_4$ and $6-Co_{0.85}Se/g-C_3N_4$ composite samples. It can be seen that pure $g-C_3N_4$ exhibits a broad and strong peak at 464 nm. After loading the $Co_{0.85}Se$ cocatalyst onto it, the main emission peak of $g-C_3N_4$ splits into two peaks at 464 nm and 445 nm, corresponding to the intrinsic peak and the defect peak, respectively. It can be observed that the presence of the $Co_{0.85}Se$ cocatalyst significantly reduces the PL intensity of $g-C_3N_4$. The PL intensity reflects the recombination situation of photogenerated charge carriers in the photocatalyst, with a higher PL intensity indicating that photogenerated electrons and holes recombine more easily. Therefore, the PL results show that the PL intensity of the $6-Co_{0.85}Se/g-C_3N_4$ composite sample is significantly weaker than that of pure $g-C_3N_4$, indicating that the loading of the $Co_{0.85}Se$ cocatalyst can effectively suppress the recombination of electrons and holes. Thus, for the $Co_{0.85}Se/g-C_3N_4$ composite photocatalyst, when $g-C_3N_4$ is photoexcited to generate photogenerated electrons and holes, the electrons migrate to the $Co_{0.85}Se$ cocatalyst, thereby achieving effective separation of electrons and holes.

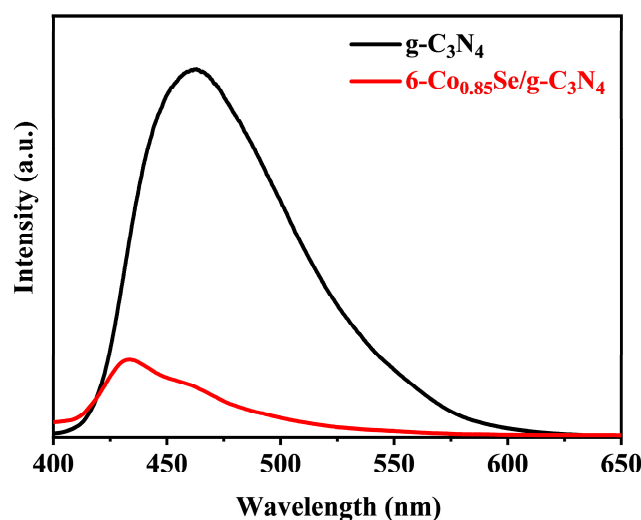


Figure 7. Fluorescence spectra of $g-C_3N_4$ and $6-Co_{0.85}Se/g-C_3N_4$ samples.

2.4. Photocatalytic Behaviors of Samples for H_2 Production

The photocatalytic hydrogen evolution activity of the samples was evaluated under visible-light irradiation. Typically, 20 mg of the catalyst was dispersed in 90 mL of deionized water, followed by the addition of 10 mL of TEOA as a sacrificial hole scavenger. The photocatalytic hydrogen production activities of $g-C_3N_4$ and $x-Co_{0.85}Se/g-C_3N_4$ were tested under visible light irradiation at >420 nm. As shown in Figure 8a, the hydrogen

evolution activity of pure g-C₃N₄ is low (only 8 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), while the hydrogen evolution activity of the composites is significantly increased after modification of g-C₃N₄ with different Co_{0.85}Se contents, among which 6-Co_{0.85}Se/g-C₃N₄ has the highest hydrogen evolution activity, reaching 426 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is 53 times higher than that of pure g-C₃N₄. However, when the Co_{0.85}Se loading exceeds the optimal value, the photocatalytic hydrogen evolution activity decreases. Excessive Co_{0.85}Se nanoparticles partially cover the surface of g-C₃N₄, reduce the exposed photocatalytic active sites, and simultaneously introduce additional recombination centers, thereby decreasing the overall photocatalytic hydrogen evolution activity despite enhanced visible-light absorption. The above results show that the presence of Co_{0.85}Se can effectively improve the photocatalytic performance of g-C₃N₄. At the same time, 6-Co_{0.85}Se/g-C₃N₄ also has good photocatalytic hydrogen evolution stability (Figure 8b), and the hydrogen evolution activity of the sample did not decrease significantly in the four-cycle hydrogen production test. To further evaluate the effectiveness of the present catalyst, its photocatalytic hydrogen evolution performance was compared with several recently reported Co-based or transition-metal-selenide-modified g-C₃N₄ photocatalysts. As summarized in previous studies, Co₃O₄/g-C₃N₄ exhibits a H₂ evolution rate of 134.6 $\mu\text{mol g}^{-1} \text{h}^{-1}$ under visible-light irradiation, while MoSe₂/g-C₃N₄ and NiSe/g-C₃N₄ composites achieve H₂ evolution rates of 136.8 and 1250 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively [15–17]. Although the hydrogen evolution rate of the present catalyst is not the highest among all reported systems, the combination of a facile one-step synthesis and noble-metal-free composition enhances the practical potential of Co_{0.85}Se/g-C₃N₄ in sustainable photocatalytic hydrogen evolution.

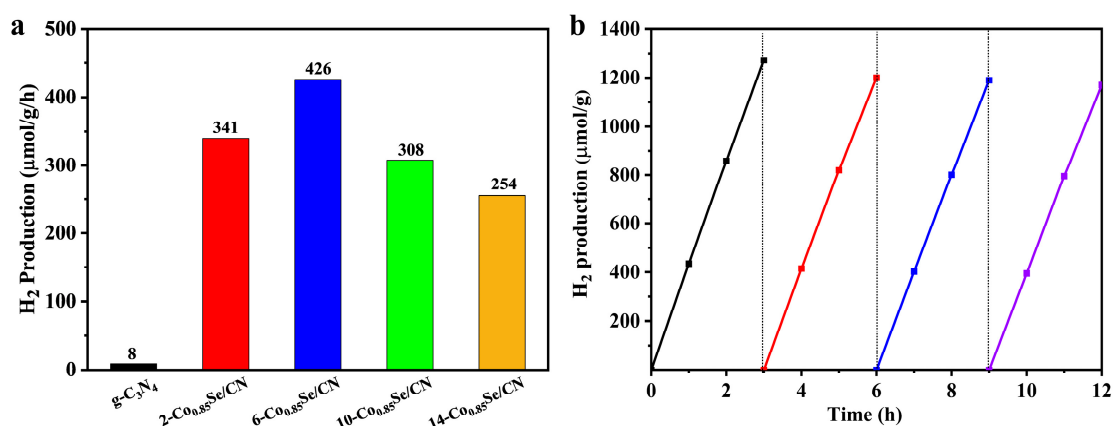


Figure 8. (a) H₂ production rate of g-C₃N₄ and x-Co_{0.85}Se/g-C₃N₄ with different Co_{0.85}Se loadings, (b) Cyclic hydrogen production test of 6-Co_{0.85}Se/g-C₃N₄. The different colored lines in (b) represent the four consecutive reaction cycles.

2.5. Surface Composition and Photoelectrochemical Properties

The surface elements and chemical states of the g-C₃N₄ and 6-Co_{0.85}Se/g-C₃N₄ composite samples were analyzed by X-ray photoelectron spectroscopy (XPS). Figure 9a shows the high-resolution C 1s spectrum. The peak at 286.2 eV is assigned to C-NH₂ in the aromatic ring; the peak at 288.1 eV is assigned to the sp² hybrid carbon of g-C₃N₄, [29]; and the 6-Co_{0.85}Se/g-C₃N₄ sample shifted to a 0.3 eV higher binding energy (located at 288.4 eV). The peaks at 398.5, 400.2, 401.0 and 404.1 eV of g-C₃N₄ in the N 1s XPS spectrum in Figure 9b correspond to the C=N-C group, N-(C)₃, surface amino group (-NH₂) and C-N heterocycle, respectively, along with π excitation [29–32]. Compared with g-C₃N₄, the peaks of 6-Co_{0.85}Se/g-C₃N₄ were all shifted to higher binding energies, indicating a strong interaction between Co_{0.85}Se and g-C₃N₄. The Co 2p and Se 3d XPS spectra are shown in Figure 9c,d. In Figure 9c, for Co_{0.85}Se, the two peaks with binding energies at

781.6 and 797.3 eV are assigned to Co 2p_{3/2} and Co 2p_{1/2} of Co²⁺, the peaks at 786.7 and 802.5 eV belong to the satellite peaks of Co²⁺ [33–35], and the Co²⁺ peaks of 6-Co_{0.85}Se/g-C₃N₄ are shifted to 781.5 and 797.0 eV towards low binding energies. Figure 9d shows the high-resolution XPS spectrum of Se 3d. The peaks of Co_{0.85}Se's binding energy at 54.28 eV and 55.03 eV are assigned to Se 3d_{5/2} and Se 3d_{3/2}, respectively [36,37]. The binding energies of the Se 3d_{5/2} and Se 3d_{3/2} peaks of 6-Co_{0.85}Se/g-C₃N₄ are both shifted to lower binding energies than those of Co_{0.85}Se. It can be seen from the above XPS results that Co_{0.85}Se and g-C₃N₄ are in close contact, forming a strong interaction interface, and electrons are transferred from g-C₃N₄ to Co_{0.85}Se during the photocatalytic process. These results indicate that Co_{0.85}Se can accelerate the separation and transfer of electrons and promote the photocatalytic reaction.

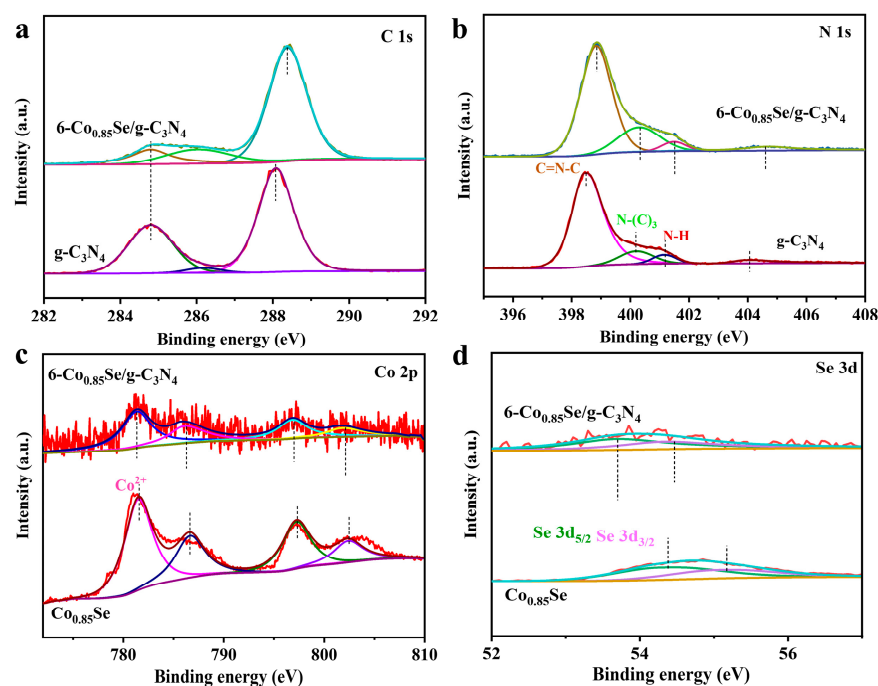


Figure 9. High-resolution XPS spectra of (a) C 1s, (b) N 1s, (c) Co 2p and (d) Se 3d for g-C₃N₄, Co_{0.85}Se and 6-Co_{0.85}Se/g-C₃N₄ samples. Colored lines denote deconvoluted peaks and baselines, while black dashed lines indicate binding energy shifts.

2.6. Photocatalytic Mechanism Research

The contact potential difference (CPD) of the samples was measured using a Kelvin probe system, as shown in Figure 10, which can be converted into the work function (WF) of the materials. The calculation formula is as follows:

$$WF_{sample} = WF_{Au} + CPD$$

where WF_{Au} represents the standard work function of Au (5.1 eV). The measured CPD values of g-C₃N₄ and Co_{0.85}Se were 350 mV and 570 mV, respectively, corresponding to calculated work functions of 5.45 eV and 5.67 eV. Therefore, the Fermi level of Co_{0.85}Se is lower than that of g-C₃N₄. When Co_{0.85}Se is in intimate contact with g-C₃N₄, the photogenerated electrons excited under light irradiation can rapidly migrate from g-C₃N₄ to Co_{0.85}Se until the Fermi levels reach equilibrium. At the same time, a Schottky junction forms within the g-C₃N₄/Co_{0.85}Se interface.

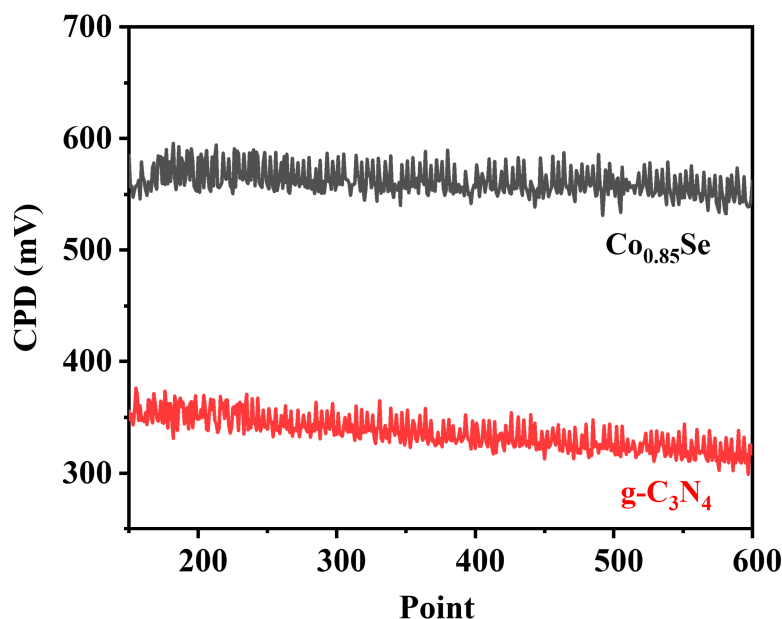


Figure 10. CPD of g-C₃N₄ and Co_{0.85}Se measured via Kelvin probe.

As shown in Figure 11, under the irradiation of visible light (>420 nm), the CB electrons of g-C₃N₄ are easily transferred to the Co_{0.85}Se particles through the Schottky junction to react with H⁺ to generate H₂, and Co_{0.85}Se also acts as the reactive site. The holes remain on the VB of g-C₃N₄ to undergo oxidation reaction with TEOA. The existence of Co_{0.85}Se cocatalyst enhances the capture of photogenerated electrons, thus effectively preventing the recombination of photogenerated electrons and holes, which significantly improves the photocatalytic hydrogen production activity of Co_{0.85}Se/g-C₃N₄ composites.

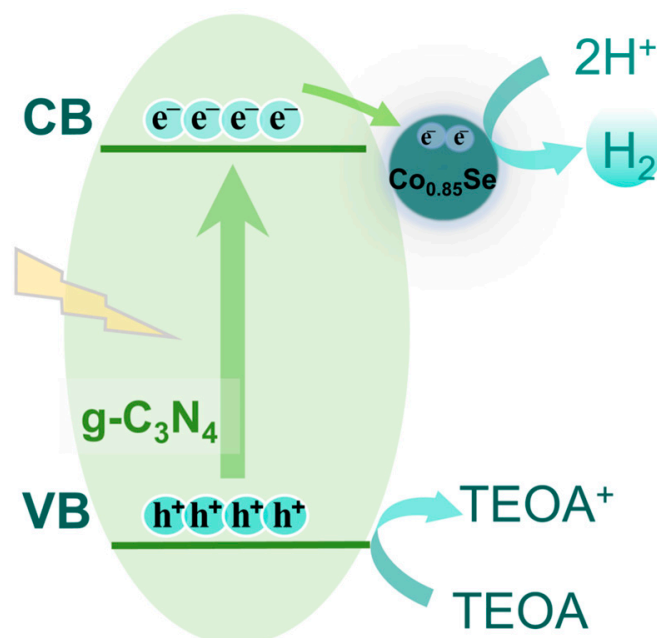


Figure 11. Hydrogen production mechanism of Co_{0.85}Se/g-C₃N₄ composite photocatalyst.

3. Experimental Section

3.1. Materials and Reagents

Urea (CH₄N₂O, AR), cobalt acetate tetrahydrate (Co(CH₃COO)₂·4H₂O, AR), sodium selenite (Na₂SeO₃, AR), triethanolamine (C₆H₁₅NO₃, AR), ethylene glycol (AR), and

ethanol (AR) were all purchased from Sinopharm Chemical Reagents Co., Ltd. All chemical reagents were used as received without further purification. Deionized water was used throughout the experiments.

3.2. Synthesis of Photocatalysts

Preparation of pure g-C₃N₄. Graphitic carbon nitride (g-C₃N₄) nanosheets were synthesized via thermal polycondensation of urea. Typically, 10 g of urea was placed in a 30 mL ceramic crucible with a lid and calcined in a muffle furnace at 550 °C for 4 h in air, at a heating rate of 5 °C·min^{−1}. After naturally cooling to room temperature, the resulting light yellow product was collected and ground into a fine powder for further use.

Preparation of Co_{0.85}Se/g-C₃N₄ composite photocatalysts. The Co_{0.85}Se/g-C₃N₄ nanocomposites were synthesized via a one-step solvothermal method with in situ growth of Co_{0.85}Se on g-C₃N₄. In a typical synthesis reaction, 30 mL of ethylene glycol was transferred into a 50 mL Teflon-lined stainless-steel autoclave. Subsequently, stoichiometric amounts of Co(CH₃COO)₂·4H₂O and Na₂SeO₃ (maintaining a Co/Se molar ratio of 0.85:1) and 200 mg of g-C₃N₄ were added to the solvent. The mixture was stirred at 500 rpm for 20 min to ensure uniform dispersion. The autoclave was then sealed and heated in an oven at 180 °C for 10 h. After cooling to room temperature, the resulting black colloidal precipitate was collected by centrifugation and washed repeatedly with deionized water and ethanol. Finally, the product was freeze-dried for 12 h and ground into a powder for further application.

To optimize the cocatalyst loading, a series of x-Co_{0.85}Se/g-C₃N₄ composites (where x = 2, 6, 10, and 14 wt%) was synthesized by adjusting the dosages of cobalt acetate tetrahydrate and sodium selenite while keeping the Co/Se molar ratio constant at 0.85:1. Additionally, pure Co_{0.85}Se was synthesized under identical experimental conditions without the addition of g-C₃N₄.

3.3. Photocatalytic H₂ Production Experiment

The photocatalytic H₂ evolution performance of the samples was evaluated using a photocatalytic activity evaluation online analysis system (China Education Au-light Co., Ltd., Tengzhou, China). In a typical experiment, a certain amount of the photocatalyst powder was dispersed in an aqueous solution containing 90 mL of deionized water and 10 mL of TEOA, which served as the sacrificial reagent. The suspension was then transferred into the reactor and evacuated to remove air. During the reaction, the temperature of the reactor was maintained at 5 °C using an external circulating cooling water system. The suspension was irradiated by a 300 W xenon lamp (PLS-SXE 300C, Beijing Perfect Light Technology Co., Ltd., Beijing, China) equipped with a 420 nm cutoff filter to ensure visible-light irradiation. The evolved H₂ gas was continuously carried by high-purity Ar gas and quantified using an online gas chromatograph (GC-2014C, Shimadzu, Kyoto, Japan) equipped with a thermal conductivity detector (TCD).

3.4. Physicochemical Characterizations

The crystalline structure of the synthesized photocatalysts was characterized by XRD using Cu K α radiation (λ = 0.15406 nm). The measurements were performed at an operating current of 40 mA over a 2 θ range of 5–80° with a step size of 0.05°. FTIR spectroscopy was employed to analyze the molecular structure of the photocatalysts. Samples were mixed with excess KBr, ground, and pressed into pellets. Measurements were conducted over a wavenumber range of 400–4000 cm^{−1} with a resolution of 4 cm^{−1} using 64 scans. The microscopic morphology of the samples was observed using SEM at room temperature. The samples were mounted on a circular sample stage using conductive tape, and the observations were conducted at an accelerating voltage of 5–10 kV under a chamber

vacuum below 2.7×10^{-5} Pa. To further examine the morphology, particle size, and elemental distribution, TEM was utilized. For TEM analysis, the samples were dispersed in anhydrous ethanol via ultrasonication for 6 min, dropped onto a carbon-coated copper grid, and dried prior to measurement. The optical absorption properties were characterized using UV-vis DRS with BaSO_4 as the reference standard, scanning over a wavelength range of 200–800 nm. The specific surface area of the samples was determined using N_2 adsorption-desorption isotherms at -196°C , measured using a fully automated physical/chemical adsorption instrument. Prior to testing, 0.2 g of sample was degassed at 150°C for 6 h. The specific surface area was subsequently calculated using the Brunauer–Emmett–Teller (BET) method. The surface elemental composition and chemical states were analyzed by XPS and the binding energies were calibrated against the adventitious C 1s peak at 284.8 eV.

Photoelectrochemical (PEC) measurements, including transient photocurrent and EIS, were performed on an electrochemical workstation using a standard three-electrode system. The working electrode was prepared by drop-casting a catalyst ink (5 mg catalyst dispersed in 0.4 mL ethanol, 0.1 mL water, and 20 μL Nafion) onto an FTO glass substrate (radius = 0.5 cm). A Pt electrode and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The photocurrent was measured in a 0.5 M Na_2SO_4 electrolyte under intermittent visible-light illumination ($\lambda > 420$ nm, 20 s on/off cycles for 6 min), while the EIS was conducted in a 10 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ solution with 0.5 M KCl. The recombination and migration behavior of photogenerated charge carriers was investigated via PL spectroscopy at room temperature using an excitation wavelength of 367 nm. Finally, the work function of the photocatalysts was determined using a Scanning Kelvin Probe System (SKP5050, KP Technology Ltd., Wick, Scotland, UK). The sample powder was pressed into a pellet and measured under dark conditions. The work function of the tip was initially calibrated using a gold disk.

4. Conclusions

In conclusion, $\text{Co}_{0.85}\text{Se}$ was successfully generated in situ on $\text{g-C}_3\text{N}_4$ via a simple solvothermal method, yielding a novel visible-light-responsive composite photocatalyst. $\text{Co}_{0.85}\text{Se}$ nanoparticles with a smaller particle size were dispersed on $\text{g-C}_3\text{N}_4$ nanosheets. Compared with pristine $\text{g-C}_3\text{N}_4$, the $\text{Co}_{0.85}\text{Se}/\text{g-C}_3\text{N}_4$ composite, in which $\text{Co}_{0.85}\text{Se}$ serves as a hydrogen evolution cocatalyst, exhibits significantly enhanced visible-light-driven photocatalytic hydrogen evolution activity. The optimized 6- $\text{Co}_{0.85}\text{Se}/\text{g-C}_3\text{N}_4$ achieves a hydrogen evolution rate of $426 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is approximately 53 times higher than that of pristine $\text{g-C}_3\text{N}_4$ ($8 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). The experimental results show that the modification of $\text{Co}_{0.85}\text{Se}$ significantly enhances the visible-light absorption of $\text{g-C}_3\text{N}_4$, broadens the photo-response range, promotes the separation and migration of photogenerated carriers, and provides active sites for photocatalytic reactions. $\text{Co}_{0.85}\text{Se}$ is an excellent hydrogen evolution cocatalyst that can effectively address the poor photocatalytic performance of $\text{g-C}_3\text{N}_4$. This work explored a facile synthetic approach that combines $\text{g-C}_3\text{N}_4$ and transition-metal selenide materials for photocatalytic hydrogen production under visible light. It provides a basis for the development and research of low-cost, high-performance, novel visible-light-responsive photocatalytic materials.

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