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Controlled synthesis of 2D–2D conductive metal–organic framework/g-C₃N₄ heterojunctions for efficient photocatalytic hydrogen evolution†

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Designing photocatalysts with efficient charge separation and electron transport capabilities to achieve efficient visible-driven hydrogen production remains a challenge. Herein, 2D–2D conductive metal–organic framework/g-C₃N₄ heterojunctions were successfully prepared by an *in situ* assembly. Compared to pristine g-C₃N₄, the ratio-optimized Ni-CAT-1/g-C₃N₄ exhibits approximately 3.6 times higher visible-light H₂ production activity, reaching 14 mmol g^{−1}. Through investigations using time-resolved photoluminescence, surface photovoltage, and wavelength-dependent photocurrent action spectroscopies, it is determined that the improved photocatalytic performance is attributed to enhanced charge transfer and separation, specifically the efficient transfer of excited high-energy-level electrons from g-C₃N₄ to Ni-CAT in the heterojunctions. Furthermore, the high electrical conductivity of Ni-CAT enables rapid electron transport, contributing to the overall enhanced performance. This work provides a feasible strategy to construct efficient dimension-matched g-C₃N₄-based heterojunction photocatalysts with high-efficiency charge separation for solar-driven H₂ production.

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1. Introduction

With the vigorous development of the world economy, burning of fossil energy, energy crises, and increasingly severe environmental pollution seriously endanger human health, so it is vital to research and develop green and sustainable energy to replace fossil fuels.^{1–4} Hydrogen is an excellent energy carrier with a high energy density and causes zero pollution.^{5,6} Inspired by the theory of artificial photosynthesis mechanism, photocatalytic water-splitting to produce clean and nontoxic hydrogen is a very promising technology for converting light energy into chemical energy.⁷ It offers a straightforward, environmentally friendly, and recyclable approach to producing hydrogen energy.^{8,9} The development of stable and effective photocatalysts is essential to this technology.

In recent years, polymer carbon nitride (g-C₃N₄) has the advantages of nontoxicity, no secondary pollution, visible light

response, stability, and low cost; moreover it has been widely used in the photocatalytic conversion of solar energy, such as hydrogen and oxygen production from photocatalytic water-splitting, selective organic photosynthesis, and degradation of organic pollutants, thus attracting people's attention.^{10–13} However, bulk g-C₃N₄ suffers from poor charge separation, insufficient visible light absorption, and few catalytic sites, which significantly reduces the photocatalytic efficiency.^{14–16} One of the prevailing approaches in photocatalytic studies involves the integration of g-C₃N₄ nanosheets with other semiconductors to fabricate heterojunctions. However, the coupling of commonly used classic metal oxide semiconductors, including WO₃ and Fe₂O₃, consistently produces poor dimension matching, and charge separation is still constrained by the weak electron transport capacity.^{17,18}

Metal–organic frameworks (MOFs) represent a novel class of porous crystalline materials that have attracted considerable attention from various academic fields. These MOFs possess numerous appealing features, including high porosity, a sizable specific surface area, tunable functionality, and potential catalytic capabilities. Their versatile properties have sparked their widespread exploration and application in diverse fields.^{19–21} Recently, the potential of certain MOFs in photocatalysis has garnered significant attention due to their semiconductor-like behavior and efficient visible-light absorption.^{22,23} As a subclass of MOFs, conductive MOFs have

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emerged as a promising area of study. The periodic porosity architecture and electrical conductivities of conductive MOFs with graphene-like 2D structures have attracted a lot of interest.^{24,25} In particular, the p-d 2D structures of conductive MOFs based on triphenylene-fused metal catecholates (M-CAT) endow them with strong electrical conductivity and a large specific surface area.^{26,27} Importantly, M-CAT has a conjugated structure similar to that of carbon nitride, and its matching interactions can be used to establish tight interfaces that greatly contribute to photocatalytic reactions by promoting charge transfer.^{28,29} Therefore, M-CAT is a suitable material for building heterostructures based on g-C₃N₄. By constructing dimension-matched M-CAT/g-C₃N₄ heterojunctions the efficient transfer of photogenerated electrons can be achieved, leading to significantly enhanced charge transfer kinetics and extended visible-light absorption.

Herein, we fabricated dimension-matched Ni-CAT-1/g-C₃N₄ heterojunction photocatalysts by utilizing interface interactions. Compared the ratio-optimized M-CAT/g-C₃N₄ heterojunctions with pristine g-C₃N₄, the visible-light efficiency for H₂ generation was 3.6 times higher. This remarkable photocatalytic performance could be primarily attributed to the facilitated transfer of high-level-energy electrons (HLEEs) *via* the heterojunction structure. Various analyses, including steady-state surface photovoltage spectroscopy, single-wavelength photocurrent interaction spectroscopy, and photoelectrochemical curves, time-resolved photoluminescence spectroscopy, supported this conclusion. The resulting heterojunctions demonstrated enhanced carrier separation, prolonged carrier lifetime, and strengthened interface contacts through matching interface interactions. Compared with previously reported semiconductor polymer/g-C₃N₄ nanocomposites, the M-CAT/g-C₃N₄ heterojunctions exhibited clear advantages. This study presents a feasible approach for designing and manufacturing g-C₃N₄-based nanoheterojunctions with exceptional visible-light performance for hydrogen evolution.

2. Experimental section

2.1. Material preparation

The materials used in this study were of analytical grade and were employed without any additional purification steps. Deionized water was consistently used throughout all the experimental procedures.

2.1.1 Synthesis of the g-C₃N₄ nanosheets. In a typical experiment, 30 g of urea was placed in a ceramic crucible, and bulk g-C₃N₄ was obtained by heating the urea to 550 °C for 180 minutes while ramping the temperature up by 5 °C min⁻¹. Next, bulk g-C₃N₄ was thermally heated to 520 °C and burned again for 240 minutes at a rate of 5 °C min⁻¹. Ultimately, a pale yellow g-C₃N₄ nanosheet was obtained after cooling to ambient temperature.

2.1.2 Synthesis of Ni-CAT-1. 4.0 mL of deionized water and 7 mg of 2,3,6,7,10,11-hexahydroxy triphenylene and 10 mg of Ni(OAc)₂·4H₂O were added to a 10 mL glass vial and sonicated

for a certain time. The reaction mixture was heated to 85 °C for 12 hours and then cooled to room temperature. The product was vacuum dried at 60 °C for 12 hours after being rinsed with deionized water and acetone to obtain dark blue Ni-CAT-1.

2.1.3 Synthesis of the Ni-CAT-1/g-C₃N₄ nanocomposite. A certain amount of g-C₃N₄, 4.0 mL of deionized water, and 7 mg of 2,3,6,7,10,11-hexahydroxy triphenylene, and 10 mg of Ni(OAc)₂·4H₂O were added to a 10 mL glass vial and sonicated for a certain time. The reaction mixture was heated to 85 °C for 12 hours and then cooled to room temperature. The product was vacuum dried at 60 °C for 12 hours after being rinsed with deionized water and acetone to obtain Ni-CAT-1/g-C₃N₄ nanocomposites.

2.2. Characterization

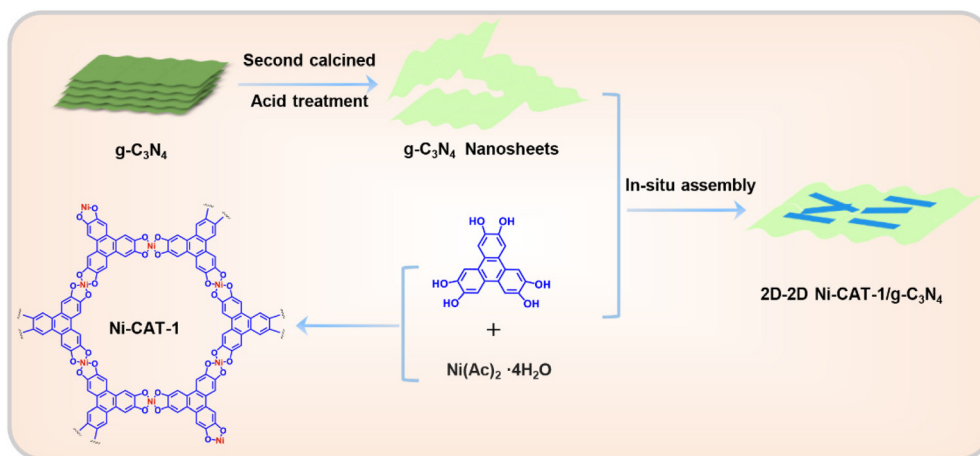
The morphology and microstructures were investigated using scanning electron microscopy (Apreo C SEM), transmission electron microscopy (HAADF-STEM), and high-resolution transmission electron microscopy (HRTEM, JEOL, NEM-2100F) equipped with an X-ray energy dispersive spectrometry unit (EDS, X-MaxN80T IE250). Powder X-ray diffraction (PXRD) patterns were obtained using a X'Pert PR diffractometer with Cu K α radiation (λ = 0.154 nm) over the range of 2–50° at 45 kV and 200 mA. Fourier transform infrared (FT-IR) spectra were recorded using a Spectrum 100 spectrometer. The thermal stability of the materials was measured by thermogravimetric analysis (TGA, SDTA851e). N₂ adsorption-desorption isotherms were recorded on a Micromeritics ASAP 2020 analyzer at 77 K, and the samples were dried under vacuum at 120 °C for 3 days before testing. The elemental composition and valence distribution information were characterized by X-ray photoelectron spectroscopy (Thermo ESCALAB 250Xi) using an Al K α micro focused X-ray source. UV-Vis diffuse reflectance spectroscopy (DRS) was performed by a UV-vis spectrophotometer (Lambda 35 spectrometer) and used BaSO₄ as a reference. Photoluminescence (PL) spectroscopy analysis was performed on an SPEX Fluorolog-3 spectrofluorometer using 370 nm as the excitation source. The surface photovoltage spectroscopy (SPS) measurements for the samples were implemented on a home-built apparatus equipped with a lock-in amplifier (SR830, USA) synchronized with a light chopper (SR540, USA). The transient-state surface photovoltage (TPV) spectra were measured at room temperature, excited by a 355 nm radiation pulse. Time-resolved photoluminescence (TR-PL) spectra were recorded using a single photon counting spectrometer (Edinburgh Instrument, FLS 920) with a 1 μ s pulse lamp as the excitation source.

The other detailed experimental analyses are described in the ESI.†

3. Results and discussion

3.1. Synthetic route and structural characterization

In this work, we rationally designed and synthesized Ni-CAT-1/g-C₃N₄ composites with a well-defined interface using an



Scheme 1 Synthetic illustration of the Ni-CAT-1/g-C₃N₄ composites.

in situ method. Scheme 1 shows a schematic diagram of the synthesis process. Ni-CAT-1 was incorporated onto the surface of g-C₃N₄ by *in situ* growth. Various Ni-CAT-1/g-C₃N₄ composites were effectively synthesized by carefully modifying the raw material ratio.

Scanning electron microscopy (SEM) was used to observe the Ni-CAT-1/g-C₃N₄ composites, whereby g-C₃N₄ displayed a layered nanosheet shape, as shown in Fig. 1a, while Ni-CAT-1 possessed a rod-like shape with a diameter of approximately 50 nm, as seen in Fig. 1b. Also, it is evident from Fig. 1c that Ni-CAT-1 grew on the g-C₃N₄ surface. Simultaneously, the Ni-CAT-1/g-C₃N₄ composite photocatalyst underwent EDS element analysis, and the results are displayed in Fig. 1d. All the C, N, and Ni elements showed a uniform distribution in the aggregation state. Combined with the EDS energy spectral results (Fig. S1†), it was evident that the Ni-CAT-1/g-C₃N₄ composite had mass fractions of 64.50%, 24.18%, 10.25%, and 1.07% for the elements C, N, O, and Ni, respectively. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to describe the morphology of the sample, as shown in Fig. 1e and f. From Fig. 1e,

rod-like Ni-CAT-1 was observed on the layered g-C₃N₄ framework. Furthermore, distinct lattice fringes of Ni-CAT-1 could be seen in the HRTEM image in Fig. 1f, where the lattice spacing of 1.90 nm corresponded to the (010) crystal face of Ni-CAT-1.³⁰ These observations verified that the Ni-CAT-1/g-C₃N₄ heterojunction was successfully constructed.

For all of these materials, powder X-ray diffraction (PXRD) investigation was done to ascertain their structures. As illustrated in Fig. 2a, the two-dimensional layer repeat unit (100) and interlayer stacking reflection (002) crystal faces of g-C₃N₄ were at positions with 2θ of 12.7° and 27.6°, respectively.³¹ The diffraction peaks at 2θ of 4.6°, 9.3°, 13.9°, and 16.2° were related to the (010), (020), (121), and (022) crystal faces of Ni-CAT-1, respectively.^{32,33} By adding g-C₃N₄ *in situ* to the Ni-CAT-1 synthesis system, different proportions of Ni-CAT-1/g-C₃N₄ composites were obtained. A series of Ni-CAT-1/g-C₃N₄

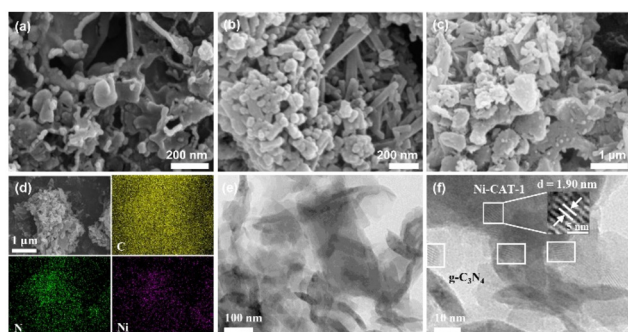


Fig. 1 SEM images of (a) g-C₃N₄, (b) Ni-CAT-1, and (c) Ni-CAT-1/g-C₃N₄. (d) SEM image of Ni-CAT-1/g-C₃N₄ and the corresponding elemental mappings of C, N, and Ni. (e) TEM image and (f) HRTEM image of Ni-CAT-1/g-C₃N₄.

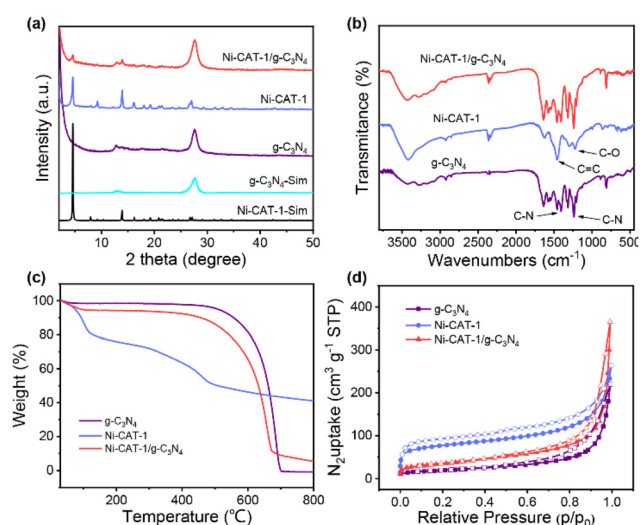


Fig. 2 (a) XRD patterns, (b) FT-IR spectra, (c) TGA curves, and (d) N₂ adsorption and desorption curves of g-C₃N₄, Ni-CAT-1, and Ni-CAT-1/g-C₃N₄.

composites of various proportions were successfully constructed, as can be observed from Fig. S2,[†] where the typical peaks of the Ni-CAT-1 composites were slightly enhanced with the increase in the Ni-CAT-1 mass fraction. Fig. 2b displays the FT-IR spectra of the g-C₃N₄, Ni-CAT-1, and Ni-CAT-1/g-C₃N₄ composites. The C–N stretching vibration peaks are represented by the peaks seen in the g-C₃N₄ spectra at 1248, 1325, and 1412 cm^{−1}.^{34,35} The stretching vibrations of C=C and C–O were responsible for the absorption peaks that are seen in the Ni-CAT-1 spectra at 1462 and 1220 cm^{−1}, respectively.³⁰

Interestingly, there is a close alignment between the peak positions of Ni-CAT-1/g-C₃N₄ and the corresponding stretching vibration peaks of g-C₃N₄. However, because of their overlap with g-C₃N₄, the distinctive peaks of Ni-CAT-1 are difficult to identify in the composite.

Fig. 2c shows the thermogravimetric analysis (TGA) results for Ni-CAT-1, g-C₃N₄, and Ni-CAT-1/g-C₃N₄, respectively. It can be analyzed that g-C₃N₄ has good thermal stability, with almost no weight loss before 500 °C, and a sharp weight loss after 500 °C, which combines the pyrolysis temperature of g-C₃N₄. The weight of Ni-CAT-1 gradually drops as the temperature rises, suggesting that the frame gradually collapses with the temperature. When the temperature reaches 800 °C, Ni-CAT-1 completely transforms into NiO, and the weight stays at 40%. Because Ni-CAT-1 is used in such small amounts, the Ni-CAT-1/g-C₃N₄ composite nonetheless exhibits good stability. To evaluate the Brunauer–Emmett–Teller (BET) surface areas of g-C₃N₄, Ni-CAT-1, and Ni-CAT-1/g-C₃N₄ composites, N₂ adsorption and desorption studies were carried out at 77 K (Fig. 2d). The specific BET surface areas of g-C₃N₄, Ni-CAT-1, and Ni-CAT-1/g-C₃N₄ were measured, and the results showed that the values were 68, 281.1, and 113.37 m² g^{−1}, respectively. The addition of Ni-CAT-1 to the Ni-CAT-1/g-C₃N₄ composites resulted in a notable increase in their specific surface area.

The elemental composition and valence distribution of the synthesized Ni-CAT-1, g-C₃N₄, and Ni-CAT-1/g-C₃N₄ composite were ascertained using X-ray photoelectron spectroscopy (XPS). The existence of C, N, O, and Ni elements was confirmed by the XPS full spectrum (Fig. S3[†]), which was comparable with the composition of the g-C₃N₄ and Ni-CAT-1 composites. The C 1s spectra (Fig. 3a) reveals binding energies of 284.79, 285.95, 286.16 and 288.19 eV, corresponding to C=C in the benzene ring and C–C outside the benzene ring, C–N, C–O, N–C=N, respectively.³⁴ Peaks at 531.4, 532.0, and 533.1 eV, corresponding to the Ni–O, C–O, and O–H bonds of Ni-CAT-1, were observed in the O 1s spectra (Fig. 3b). According to the N 1s spectra, the binding energies of C=N–C, bridging (C)₃–N, and N–H in g-C₃N₄ are 398.6, 399.9, and 401.2 eV, respectively (Fig. 3c). The spin orbit peaks of Ni 2p_{3/2} and Ni 2p_{1/2} were represented by spectral peaks of Ni 2p at 855.95 and 875.03 eV, respectively. Ni²⁺ was noted by the satellite peaks at 861.5 and 880.2 eV.^{36,37} All of these findings support the structural integrity of g-C₃N₄ throughout the synthesis process and the effective creation of the Ni-CAT-1/g-C₃N₄ composite.

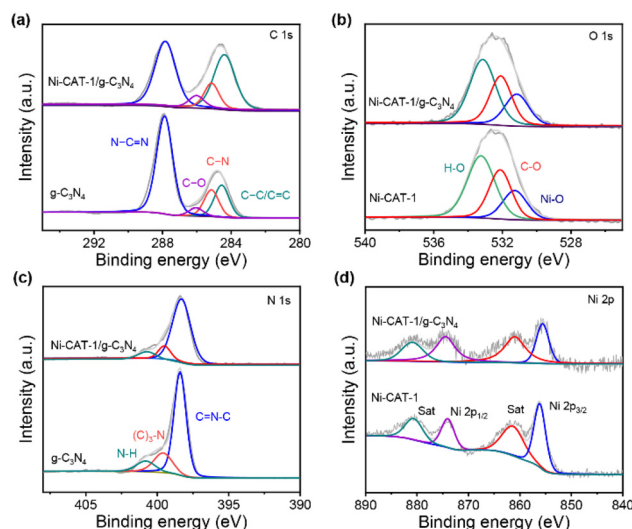


Fig. 3 XPS spectra with high-resolution plots for (a) C 1s, (b) O 1s, (c) N 1s, and (d) Ni 2p of g-C₃N₄, Ni-CAT-1, and Ni-CAT-1/g-C₃N₄.

3.2. Photocatalytic performance and charge separation

The optical absorption characteristics of the materials were ascertained using UV-Vis diffuse reflectance spectroscopy (DRS). According to Fig. 4a, g-C₃N₄ has an absorption band edge at approximately 450 nm. It is interesting to note that adding Ni-CAT-1 increases the capacity to absorb light from g-C₃N₄. Tauc plot analysis was used to calculate the band gaps of the photocatalysts, as depicted in Fig. S4 and S5.[†] g-C₃N₄ and Ni-CAT-1 have computed band gaps of 2.65 and 2.2 eV, respectively. The g-C₃N₄ and Ni-CAT-1 Mott–Schottky plots (Fig. 4b and S6[†]) show positive slopes, which is indicative of the typical n-type semiconductor behavior of these compounds. For g-C₃N₄ and Ni-CAT-1, the equivalent flat band potentials are −1.13 and −1.2 V, respectively. As such, the g-C₃N₄ and Ni-CAT-1 conduction bands (CBs) are located at −1.03 and −1.1 V, respectively.⁸ The valence bands (VBs) of g-C₃N₄ and Ni-CAT-1 are estimated to be 1.62 and 1.1 V, respectively, based on their band gaps. These results imply that both g-C₃N₄ and Ni-CAT-1 could satisfy the thermodynamic conditions needed for photocatalytic water-splitting to produce H₂ (−0.41 V vs. NHE, pH 7).

The photocatalytic performance of the Ni-CAT-1/g-C₃N₄ composites is displayed in Fig. 4c. Both g-C₃N₄ and Ni-CAT-1 individually exhibited low hydrogen production performances. However, the Ni-CAT-1/g-C₃N₄ composites demonstrated a significant improvement in photocatalytic hydrogen production. Among the composites, the highest hydrogen-production performance was achieved when the Ni-CAT-1 content was 11%, resulting in a rate of 2.76 mmol h^{−1} g^{−1}. A histogram of photocatalytic hydrogen production at different ratios of Ni-CAT-1/g-C₃N₄ is shown in Fig. 4d. Table S1[†] summarizes a comparison between reported g-C₃N₄-based heterojunctions and the ratio-optimized 11% Ni-CAT-1/g-C₃N₄ for visible-light photocatalytic H₂ production, highlighting the superiority of Ni-CAT-1/g-C₃N₄. Furthermore, the stability and recyclability of

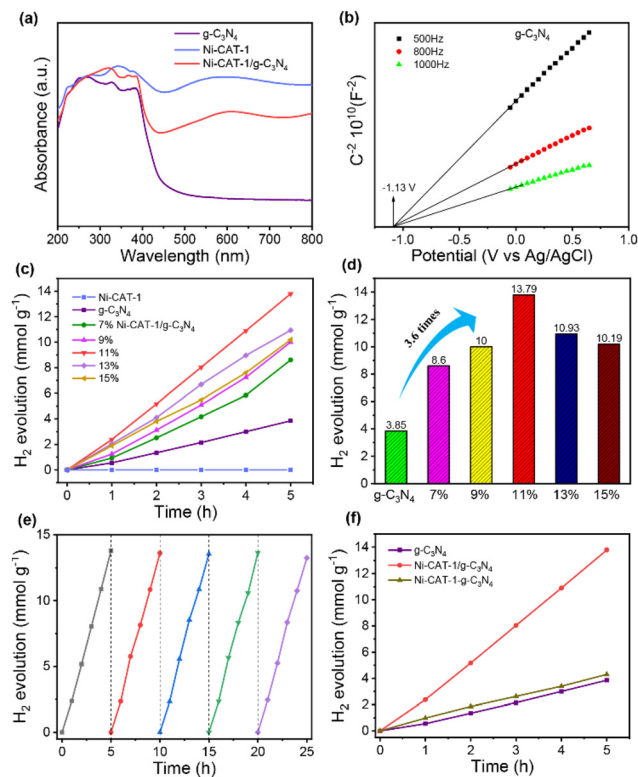


Fig. 4 (a) DRS of g-C₃N₄, Ni-CAT-1, and Ni-CAT-1/g-C₃N₄. (b) Mott-Schottky plots of g-C₃N₄. (c) Photocatalytic hydrogen-production rate diagram for Ni-CAT-1/g-C₃N₄ series of materials. (d) Histogram of Ni-CAT-1/g-C₃N₄ photocatalytic hydrogen-generation yield at various ratios. (e) Hydrogen-production rate graph for the Ni-CAT-1/g-C₃N₄ cycle stability tests. (f) *In situ* preparation of Ni-CAT-1/g-C₃N₄ versus physical mixing of Ni-CAT-1-g-C₃N₄ and hydrogen-production rate.

Ni-CAT-1/g-C₃N₄ were thoroughly investigated. Fig. 4e shows that no inactivation occurs even after five runs. After the photocatalytic reaction, PXRD and XPS studies were carried out on the post-reaction samples to evaluate the structural stability of Ni-CAT-1/g-C₃N₄ (Fig. S7 and S8†). Remarkably, the XRD patterns and XPS spectra of the photocatalyst following the process showed no appreciable variations from the original sample. The remarkable stability of Ni-CAT-1/g-C₃N₄ during the photocatalytic hydrogen-generation process was thus confirmed by this observation. In order to explore the difference between *in situ* preparation and the physical mixing of Ni-CAT-1/g-C₃N₄, a hydrogen-production comparison experiment was conducted between 11% Ni-CAT-1/g-C₃N₄ prepared *in situ* and that prepared by physical mixing. As illustrated in Fig. 4f, in contrast to 11% Ni-CAT-1-g-C₃N₄ synthesized *in situ*, the hydrogen-generation rate of 11% Ni-CAT-1-g-C₃N₄ prepared by physical mixing was only 0.859 mmol h⁻¹ g⁻¹. This discrepancy could be explained by an inadequate contact between the two materials, which would prevent electrons from easily moving from g-C₃N₄ to Ni-CAT-1 and reduce the photocatalytic activity. This result provides additional evidence that the two constituents of the Ni-CAT-1/g-C₃N₄ composite were successfully combined.

The charge carrier properties of the representative samples were characterized using chemical and physical techniques. Fig. 5a shows the photocurrent responses of the g-C₃N₄ and Ni-CAT-1/g-C₃N₄ composite materials. The photocurrent under visible-light irradiation was greatly increased by the incorporation of Ni-CAT-1 in the composite as compared to g-C₃N₄. This enhancement can be ascribed to the enhanced capacity for charge transfer, which produces a more robust reaction to visible light. The results demonstrate that the Ni-CAT-1/g-C₃N₄ composite is more capable of photoelectric conversion and charge transfer than the single g-C₃N₄. Electrochemical impedance spectroscopy (EIS) is a powerful technique for determining the charge transfer resistance inside a photocatalyst material as well as the photogenerated electron-transfer ability, and it is an effective method that can intuitively judge the charge transfer resistance. As shown in Fig. 5b, the EIS spectra of Ni-CAT-1/g-C₃N₄ exhibit the smallest semi-circle diameter, indicating the lowest interfacial charge transfer resistance. Furthermore, the photoluminescence (PL) emission spectrum showed that the intensity of g-C₃N₄ was quenched after coupling with Ni-CAT-1, indicating that the charge recombination of g-C₃N₄ was effectively inhibited (Fig. 5c). The PL lifetimes were further determined by time-resolved fluorescence spectroscopy (TR-PL) (Fig. 5d). According to the fitted curve, the fluorescence lifetimes of g-C₃N₄ and Ni-CAT-1/g-C₃N₄ are 2.91 and 1.32 ns, respectively. The decay lifetime of g-C₃N₄ decreased with the introduction of Ni-CAT-1, which promoted the rapid migration of photogenerated charged. All of these findings support the result that the coupled Ni-CAT-1 is advantageous for speeding up charge transfer and separation.

3.3. Mechanism discussion

The constructed Ni-CAT-1/g-C₃N₄ heterojunctions were further evaluated to confirm their enhanced photogenerated carrier

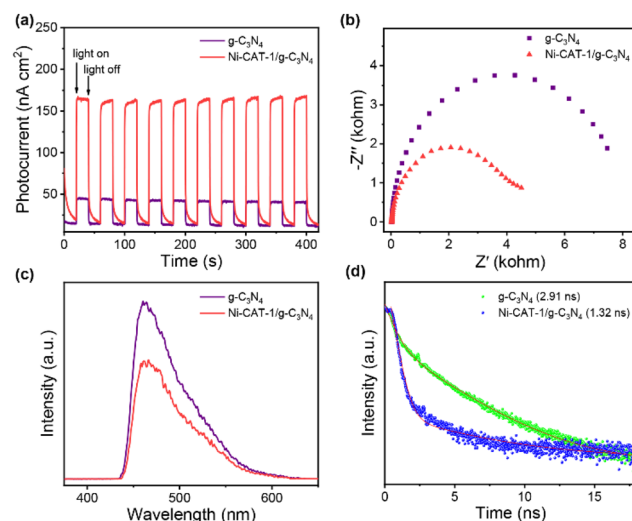


Fig. 5 (a) Transient photocurrent responses, (b) EIS Nyquist plots, (c) photoluminescence spectra, and (d) time-resolved PL spectra of g-C₃N₄ and Ni-CAT-1/g-C₃N₄.

transfer and separation. Surface photovoltage spectroscopy (SPS) measurements were conducted, and are displayed in Fig. 6a, showing that the Ni-CAT-1/g-C₃N₄ heterojunctions exhibited a significant SPS response, whereas no detectable SPS signal was observed for pure g-C₃N₄ and Ni-CAT-1 in the N₂ atmosphere. This result indicates that the Ni-CAT-1/g-C₃N₄ heterojunctions facilitated efficient charge separation and transfer. The dynamic processes of the photogenerated charge carriers were investigated using time-resolved surface photovoltage (TPV) spectroscopy. Ni-CAT-1 and g-C₃N₄ did not exhibit a TPV response in the N₂ atmosphere (Fig. 6b), suggesting a high rate of charge recombination. On the other hand, a distinct and discernible TPV response was noted for the Ni-CAT-1/g-C₃N₄ heterojunctions, suggesting that the photogenerated charges had a longer lifetime. The effective transfer of electrons from g-C₃N₄ to Ni-CAT-1 in the heterojunction structure is responsible for this increased charge lifetime.

Determining the causes of the increased hydrogen production requires an understanding of the charge transfer mechanism in the Ni-CAT-1/g-C₃N₄ heterojunctions. To investigate this, as shown in Fig. 6c, wavelength-dependent photocurrent action spectra were acquired for g-C₃N₄, Ni-CAT-1, and Ni-CAT-1/g-C₃N₄. A progressive increase in the photocurrent density of g-C₃N₄ was seen as the excitation wavelength was lowered from 450 to 420 nm. However, Ni-CAT-1 displayed photocurrent generation from 500 to 420 nm, which was related to its absorption range. The photocurrent density of g-C₃N₄ was marginally higher than that of Ni-CAT-1 in the 450–420 nm region. The photocurrent density of Ni-CAT-1/g-C₃N₄ at 450 nm was nearly equal to the total photocurrent density induced by both Ni-CAT-1 and g-C₃N₄. This demonstrates that there was no efficient transfer between Ni-CAT-1 and g-C₃N₄. It is noteworthy that the Ni-CAT-1/g-C₃N₄ composite showed a significant

increase in photocurrent density beginning at 440 nm. Strong evidence for the transmission of HLEEs from g-C₃N₄ to Ni-CAT-1 can be seen in this observation. This novel insight sheds light on the charge transfer mechanism in the fabricated Ni-CAT-1/g-C₃N₄ heterojunction system.

We propose a novel mechanism for the transmission of HLEEs in the Ni-CAT-1/g-C₃N₄ heterojunction system on the basis of the research above. As depicted in Fig. 6d, the HLEEs of g-C₃N₄ are transferred to Ni-CAT-1 when the heterojunction is excited with a light beam shorter than 440 nm. The photocatalytic activities of g-C₃N₄ in the heterojunction are significantly enhanced by the greater charge separation enabled by this HLEE transfer. This new understanding of the charge transfer mechanism clarifies the improved performance of the Ni-CAT-1/g-C₃N₄ heterojunction.

4. Conclusions

In summary, we successfully synthesized tightly bound dimension-matched Ni-CAT-1/g-C₃N₄ heterojunctions *via* an interface-induced assembly process. A novel understanding of the charge transfer mechanism of excited HLEEs from g-C₃N₄ to Ni-CAT-1 elucidated the enhanced photocatalytic performance of the Ni-CAT-1/g-C₃N₄ heterojunction system. The optimized Ni-CAT-1/g-C₃N₄ heterojunction showed excellent photocatalytic activity and stability during hydrogen production, which were mainly due to the matching energy band of Ni-CAT-1 with g-C₃N₄ and the promotion of HLEE transfer through the heterojunction structure. This study presents a promising pathway for achieving efficient solar-driven hydrogen production.

Author contributions

Xiaoyu Chu: data curation, writing – review and editing, supervision, funding acquisition. Bing-Bing Luan: formal analysis, investigation, writing – review and editing. Ao-Xiang Huang: data curation, visualization. Yongkuo Zhao: methodology, visualization. Hongxia Guo: methodology. Yang Ning: visualization. Haojian Cheng: investigation. Guiling Zhang: methodology, supervision, funding acquisition. Feng-Ming Zhang: conceptualization, methodology, supervision, project administration, funding acquisition, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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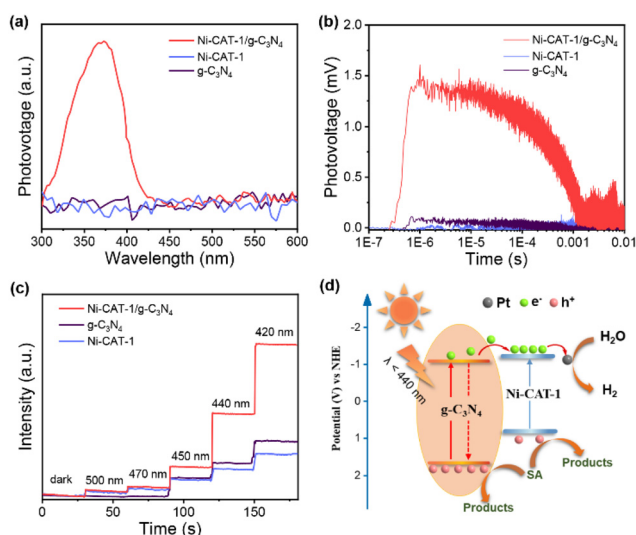


Fig. 6 (a) SPS responses in N₂ atmosphere, (b) TPV responses, (c) monochromatic photocurrent action spectra of Ni-CAT-1, g-C₃N₄, and Ni-CAT-1/g-C₃N₄. (d) Schematic of the charge transfer mode at the Ni-CAT-1/g-C₃N₄ heterojunction under light irradiation.

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