

Enhanced Visible-Light Photocatalytic Hydrogen Evolution over a g-C₃N₄/SrTiO₃/Zn-TFBDC Ternary Composite

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Abstract: The development of efficient visible-light-responsive photocatalysts is essential for sustainable hydrogen (H₂) production. Herein, a ternary SrTiO₃/g-C₃N₄/Zn-TFBDC metal–organic framework heterojunction was fabricated through a facile solvent-assisted self-assembly strategy. Structural, morphological, optical, and surface characterization confirmed the successful integration of SrTiO₃, g-C₃N₄, and Zn-TFBDC and the formation of intimate interfacial contact among the three components. The photocatalytic H₂ evolution activity was evaluated under visible-light irradiation using aqueous isopropanol as a sacrificial electron donor. Among the prepared samples, the optimised SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite achieved the highest H₂ evolution rate of 642.78 μmol g⁻¹ h⁻¹, corresponding to approximately 2.03-, 2.06-, and 1.81-fold enhancements over pristine SrTiO₃, g-C₃N₄, and Zn-TFBDC, respectively. The improved performance is attributed to the synergistic interaction among the three components, which enhances visible-light absorption, promotes interfacial charge separation and migration, and suppresses the recombination of photogenerated charge carriers. Moreover, the porous Zn-TFBDC framework provides abundant accessible active sites and interconnected pathways for charge transport. These results demonstrate that rational integration of oxide, carbon nitride, and MOF components is an effective strategy for constructing efficient ternary photocatalysts for visible-light-driven H₂ production.

Keywords: Perovskite, photocatalysts, g-C₃N₄, Zn-MOF, water splitting, H₂ evolution.

1. Introduction

The decreasing reserves of fossil fuels, along with growing awareness of climate change and environmental damage, have made clean, renewable and carbon-neutral energy technologies of great interest [1,2]. The high gravimetric energy density, carbon-free utilisation, and compatibility with fuel-cell technologies make hydrogen (H_2) a promising energy carrier [3,4]. The environmental advantages of a hydrogen energy system are, however, very dependent on the method used to produce hydrogen. The production of industrial hydrogen is mostly based on fossil fuels, such as steam methane reforming, which is energy intensive and releases significant amounts of CO_2 [4]. Therefore, sustainable hydrogen production based on renewable energy sources is still one of the biggest scientific and technological challenges.

One of the potentially attractive pathways is the photocatalytic hydrogen production process, which will convert solar energy into storable chemical energy [5, 6]. The groundbreaking research by Fujishima and Honda showed that water splitting can be achieved by photoelectrochemical processes involving a semiconductor oxide such as TiO_2 [7], and has led to a wide range of research into semiconductors as materials for solar-fuel production. A semiconductor photocatalyst works by absorbing photons having energy equal to or higher than the bandgap that can be absorbed and excite electrons from the valence band to the conduction band, creating positively charged holes in the valence band. The photogenerated electrons and holes can then be transported to the surface reaction sites where they can be involved in the reduction and oxidation reactions, respectively [5, 8]. However, several common problems limit the photocatalytic efficiency: (1) insufficient light absorption in the solar light, (2) fast bulk and surface charge recombination, (3) slow interfacial carrier migration, and (4) limited number of accessible catalytic sites [9, 10]. Therefore, a good photocatalyst must possess characteristics of wide light absorption, suitable band-edge potentials, high charge separation and transport efficiency, chemical stability, and high surface-active sites.

Strontium titanate ($SrTiO_3$) is a perovskite-type oxide that is extensively studied and has several desirable properties for photocatalytic and photoelectrochemical applications, which include chemical stability, photocorrosion resistance, and a conduction band potential suitable for proton reduction [9, 11]. Initial investigations showed overall water decomposition in cocatalyst-modified $SrTiO_3$ systems, making it a potential candidate to develop as a powerful photocatalytic platform [11]. However, pure $SrTiO_3$ has a large band gap of 3.2 -3.3 eV and

thus is mainly sensitive to ultraviolet radiation. This photo response is restricted, and this reduces its efficiency in absorbing the visible portion of the solar spectrum. One way to overcome this limitation is to introduce a dopant, such as Kato and Kudo's SrTiO₃ doped with both antimony (Sb) and chromium (Cr), which demonstrated visible light absorption and photocatalytic activity [12]. Takata et al. reported the external quantum efficiency of up to 96% at 350–360 nm for the overall water splitting of suitably modified Al-doped SrTiO₃, further demonstrating the high intrinsic potential of SrTiO₃ [13]. Although such success under UV illumination, it is still necessary to expand the optical response of SrTiO₃ and retain the efficient charge separation and high redox activity, which are required for applications based on visible light.

Since Wang et al. [14] first reported the use of graphitic carbon nitride (g-C₃N₄) for photocatalytic hydrogen production from water, it has been one of the most researched metal-free visible-light photocatalysts. It contains carbon and nitrogen, which are ubiquitous on Earth, has a moderate bandgap of about 2.7 eV, and can absorb light up to about 460 nm [14,15]. It is located in a position of its conduction band that promotes proton reduction, and has a polymeric heptazine framework with high chemical and thermal stability. Furthermore, g-C₃N₄ can be easily prepared by the thermal polymerisation of low-cost nitrogen-containing starting materials such as melamine, urea, and dicyandiamide [16]. However, bulk g-C₃N₄ exhibits a high electron-hole recombination rate, low electron mobility, a tendency to restack within the sheets, a relatively low accessible surface area, and limited utilisation of the solar spectrum [15-17]. Thus, morphological control, defect engineering, element engineering, cocatalyst loading and heterojunction construction have been extensively explored to enhance its photocatalytic activity [15,17,18].

Another important group of materials are metal–organic frameworks (MOFs) for photocatalytic uses. They are crystalline porous structures that are built from clusters of metal ions and organic linkers, which lead to extremely high surface areas, tunable pore architectures and chemically tunable frameworks [19-21]. MOFs may be used as light absorbers, porous hosts, charge transfer mediators, catalyst supports or as sources of accessible reaction sites [19,20]. Their structural tunability also allows them to be designed to be coupled with conventional semiconductors in close contact, which could help adsorption of reactants and migration of the photogenerated carriers. Many pristine MOFs, however, are not conductive and demonstrate fast charge recombination, which motivates integration with complementary semiconductors as a design strategy [19-21]. A porous MOF material based on Zn ions was chosen in the current study, which was a framework made from tetrafluoro terephthalate

linkers (Zn-TFBDC). It is hoped that its incorporation will create accessible pores and interfacial sites and will give an extra charge migration pathway. The photocatalytic H₂-evolution heterojunction containing Zn-TFBDC has not been fully explored.

The creation of heterojunctions is a good method to combine the complementary properties of various photocatalytic materials. The well-designed interfacial contact and band alignment can promote the directional movement of charge, decrease non-radiative electron-hole recombination and maintain the photogenerated carriers with appropriate redox potentials [18, 22]. Ternary heterostructures can offer more interfaces compared to single-component and binary systems and more complex pathways for the transport of carriers. But the more components, the more careful control is needed for the interfacial structure, composition, band positions, and charge-transfer mechanism, in order to improve activity. Rational interfacial engineering of SrTiO₃ and g-C₃N₄ has been proven to enhance the photocatalytic evolution of H₂ in previous studies of the systems of Pt/g-C₃N₄/SrTiO₃, Ag/g-C₃N₄/SrTiO₃, and Ti₃C₂/SrTiO₃/g-C₃N₄ [23-25]. The results suggest that SrTiO₃/g-C₃N₄ is an appropriate platform to be modified by a porous third component. However, the ternary heterojunction of SrTiO₃/g-C₃N₄/Zn-TFBDC is not well explored.

A convenient solvent-assisted self-assembly method was used to synthesise a ternary SrTiO₃/g-C₃N₄/Zn-TFBDC heterojunction photocatalyst. The amount of Zn-TFBDC was carefully raised to find the optimal composition of a composite. Structural, morphological, optical and surface properties of the obtained materials were characterised by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning and transmission electron microscopy, UV-visible diffuse reflectance spectroscopy, photoluminescence spectroscopy and X-ray photoelectron spectroscopy. The photocatalytic H₂-evolution activity was tested under visible light irradiation in an aqueous isopropanol solution with isopropanol used as a sacrificial electron donor. The study focused on understanding the role of each component of ternary interfacial coupling, visible-light absorption, charge-carrier separation and migration, porous active-site accessibility, and loading of the Zn-MOF on photocatalytic H₂ production. The results reveal how the rational design of MOF-engineered oxide/carbon-nitride heterostructures for visible-light-driven hydrogen production can be achieved.

2. Experimental section

2.1 Materials

Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Strontium hydroxide octahydrate (Sr(OH)₂·8H₂O), Potassium chloride (KCl), Lithium Chloride (LiCl), Zinc perchlorate

hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), TFBDC (Tetrafluoro phthalic acid), N, N-dimethylformamide (DMF, 99.9%), Toluene (99.5%), Ethyl acetate, (EtOAc, 99.5%), Urea (NH_2CONH_2 99%), Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.5%), Methanol (CH_3OH , 99.9%), and Isopropanol ($\text{C}_3\text{H}_8\text{O}$, 99.5%) were purchased from Aladdin. Ultrapure water and deionised water were used in these experiments. All the chemicals were used without further purification.

2.2 Synthesis of Perovskite SrTiO_3 Nanofibers

All synthesis was conducted in an ambient environment using commercially available solvents. SrTiO_3 nanofibers were synthesised via a two-step hydrothermal process [26]. Briefly, 1.25 g of TiO_2 was dispersed in 60 mL of 10 M NaOH solution and stirred at 600 rpm for 40 min. The resulting suspension was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. After naturally cooling to room temperature, the precipitate was collected and treated with 50 mL of 0.2 M HCl under continuous stirring for 4 h. The product was subsequently separated by centrifugation and washed several times with deionised water and absolute ethanol until the pH reached approximately 7. The obtained material was dried at 70 °C for 12 h.

The dried intermediate was then dispersed in an aqueous solution containing 0.05 M $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and stirred for 30 min. Subsequently, the suspension was transferred into a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 210 °C for 85 min. After cooling to room temperature, the resulting white precipitate was collected by centrifugation and repeatedly washed with deionised water and absolute ethanol until a neutral pH was attained. Finally, the product was dried at 70 °C for 12 h to obtain SrTiO_3 nanofibers. The synthesis procedure is shown in Fig.S1

2.3 Synthesis of g- C_3N_4

5g of urea was weighed and placed in a 50 mL crucible, sealed, placed in a muffle furnace, heated to 550 °C at 0.5 °C /min, and calcined for 3 hours to obtain a light-yellow block of g- C_3N_4 [27]. The synthesis procedure is illustrated in Fig. S2.

2.4 Synthesis of Zn-TFBDC

Zn-TFBDC was prepared by solvothermal synthesis [28]. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.86 mg) and tetrafluoro phthalic acid (TFBDC, 0.4 mmol) were dissolved in 40 mL of N, N-dimethylformamide (DMF) under magnetic stirring for 1 h. The homogeneous solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 120 °C for 12 h. After naturally cooling to room temperature, the resulting crystalline product was isolated by filtration through a 0.45 μm membrane and successively washed with DMF, deionised water,

and ethanol to remove residual reactants and solvents. Finally, the purified sample was dried at 60 °C to obtain the Zn-TFBDC framework. The preparation procedure is illustrated in Fig. S3.

2.5 Synthesis of g-C₃N₄/SrTiO₃/Zn-TFBDC Composite

A series of g-C₃N₄/SrTiO₃/Zn-TFBDC ternary composites were synthesised via a facile solution-assisted self-assembly method. Briefly, g-C₃N₄ and SrTiO₃ were mixed at a fixed mass ratio of 55:35 and dispersed in anhydrous methanol under ultrasonication for 10 min to obtain a homogeneous suspension [27]. Subsequently, different amounts of Zn-TFBDC corresponding to 10, 20, 30, and 40 wt% with respect to the g-C₃N₄/SrTiO₃ support were added to the suspension. The resulting mixtures were magnetically stirred at room temperature for 48 h to facilitate the formation of intimate interfacial contact among the three components. Thereafter, the precipitates were collected by centrifugation, washed twice with anhydrous ethanol to remove residual impurities, and dried at 80 °C for 12 h. The as-prepared composites were denoted as CN/ST/ZT-10, CN/ST/ZT-20, CN/ST/ZT-30, and CN/ST/ZT-40, where the numerical values represent the loading amount of Zn-TFBDC relative to the g-C₃N₄/SrTiO₃ matrix.

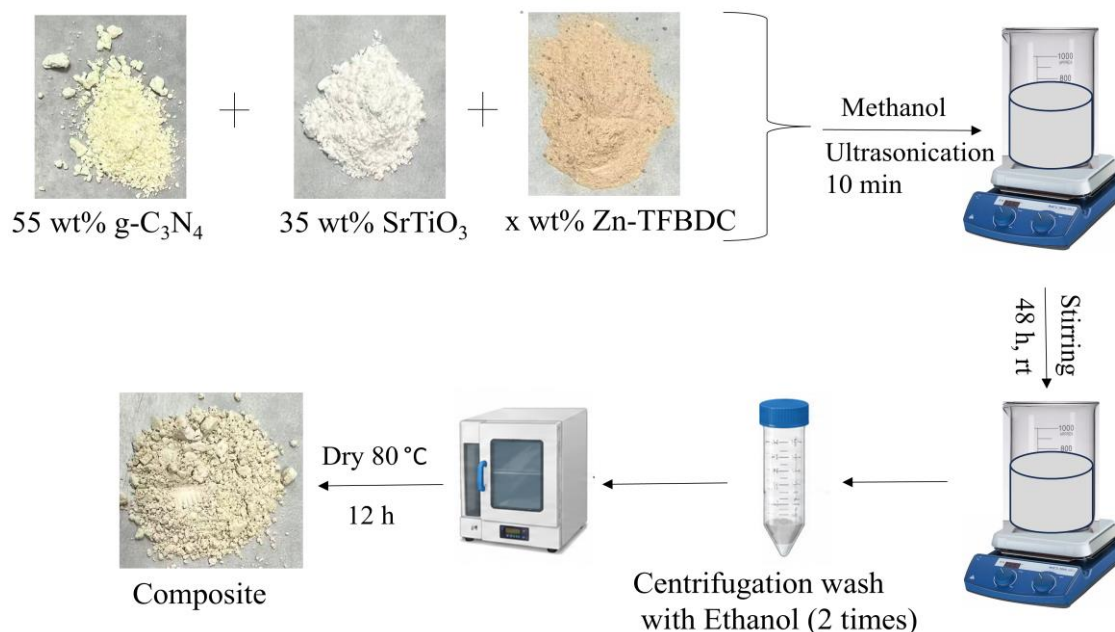


Figure 1. Preparation of g-C₃N₄/SrTiO₃/Zn-TFBDC Ternary Composite.

2.6 Photocatalytic hydrogen production

The performance evaluation process of different photocatalysts for the photocatalysis of aqueous hydrogen is as follows [21]. The 0.05 g photocatalyst was fully dispersed in a 40 mL aqueous solution containing 5% isopropanol. The photocatalyst was then suspended in DI water by ultrasonic treatment for 10 min. A rubber stopper and sealing film sealed a quartz tube containing the catalyst and solution. Next, a xenon lamp was used as the light source; the agitator was switched on before lighting; the reactor air was released; and the reaction began after the value stabilized. The reading was taken every hour. Hydrogen production readings were taken every hour for three consecutive hours.

2.7 Characterization

The crystal structure of the samples was analysed using a Bruker D8 diffractometer (Bruker, Germany) with Cu-K α radiation. The morphology and composition of the samples at the nanoscale level were examined using a Verios G4 field emission scanning electron microscope (FEI), and further characterized with a Talos F200X transmission electron microscope (TEM). Solid UV absorption spectra of the samples were recorded using a U-3900H spectrophotometer (HITACHI), while fluorescence spectra were obtained using an F-7100 fluorometer (HITACHI). Electrochemical impedance spectroscopy (EIS) was conducted on a CHI700E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.), utilizing a three-electrode system with DMF as the solvent. The photocatalytic experiments were performed using a DS-GHX-V photochemical reactor (Shanghai Dusi Instrument Co., Ltd.), with each step employing a 600 W xenon lamp for visible light illumination. The material's surface chemical characteristics were obtained using Al K α radiation and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD).

3. Results and discussion

3.1 Characterization

To study the crystalline phase and chemical bonding properties of the pristine components and SrTiO₃/g-C₃N₄/Zn-TFBDC composites, the samples were subjected to X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy, shown in Fig. 2 (a, b), respectively. Fig. S4a shows the complete XRD pattern of the as-prepared SrTiO₃ nanofibers and compares it with the standard diffraction pattern (PDF#84-0444). The unique diffraction reflections of the SrTiO₃ nanofibers indicate the formation of crystalline SrTiO₃ at 22.8°, 32.4°, 39.9°, 46.5°, and 57.8° (Fig. 2a). The diffraction pattern (PDF#84-0444) matches the pattern typically

observed for SrTiO₃ [29]. The reflection of the pristine g-C₃N₄ is broad and intense at 27-28°, reflecting a (002) plane that originates from the interlayer stacking of conjugated carbon-nitride layers, while the reflection at 13° reflects an in-plane structural ordering and is a weaker feature. [29,30] On the other hand, the reflections of Zn-TFBDC can be found in more than one way, which means that the Zn-based coordination framework has a crystalline structure [31].

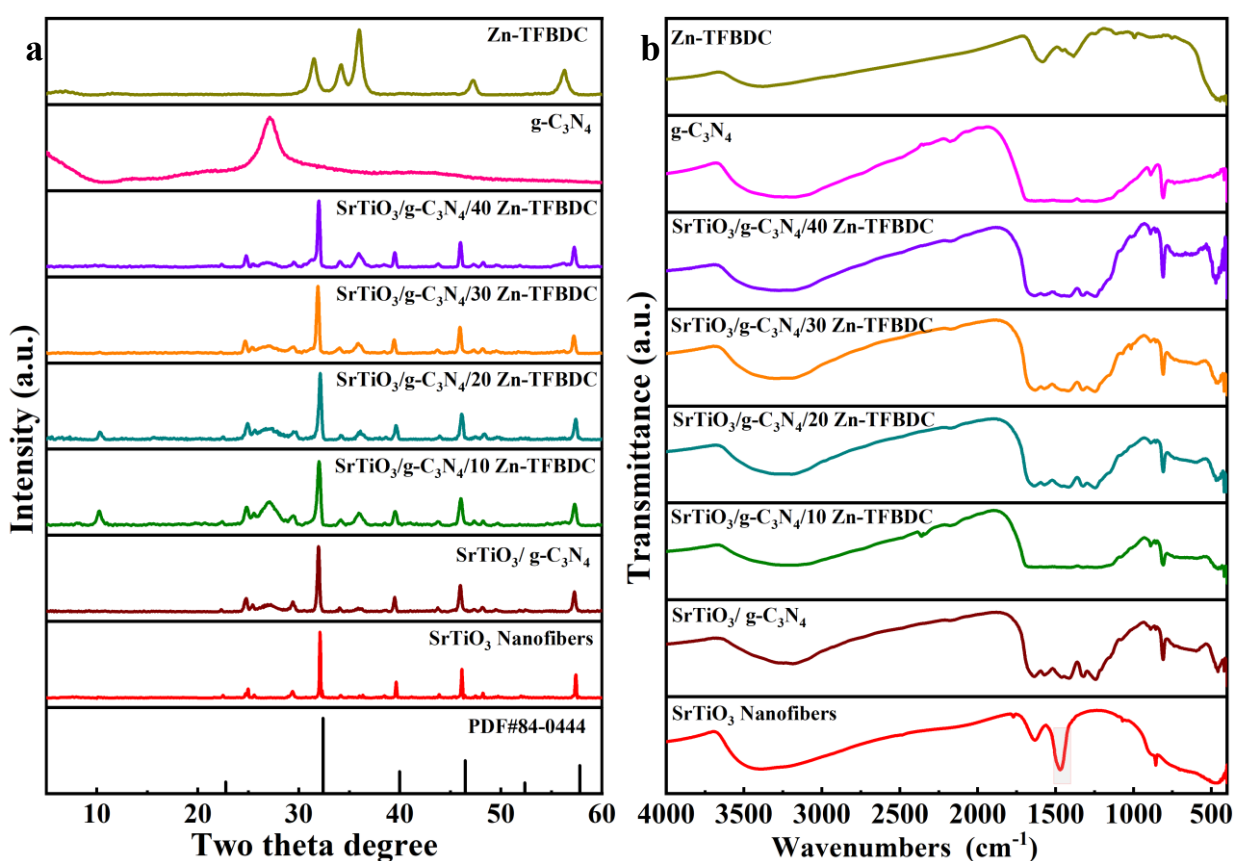


Figure 2. (a) XRD patterns, (b) FTIR patterns of g-C₃N₄/SrTiO₃/Zn-TFBDC Ternary Composite

The binary SrTiO₃/g-C₃N₄ composite was then formed, and the peaks of SrTiO₃ are easily recognized, whereas the peak of g-C₃N₄ is kept in the region of its characteristic (002) reflection. Studies on heterostructured photocatalysts have demonstrated that the unique diffraction properties can be preserved upon coupling SrTiO₃ with g-C₃N₄ [29]. The bulk structure of the SrTiO₃ phase does not change significantly upon the addition of g-C₃N₄ and Zn-TFBDC, as the main SrTiO₃ peaks remain at the same 2θ values throughout the ternary series. Changes in relative peak intensities and reduced diffraction features as the Zn-TFBDC loading increases are primarily attributed to changes in the relative proportion of the phases and to overlap of diffraction features. The XRD results show that when the two materials, g-C₃N₄ and Zn-

TFBDC, are mixed with SrTiO₃, they form a ternary composite without destroying the SrTiO₃ crystal structure.

Further insight into the chemical bonding environments of the pristine components and composite photocatalysts was obtained using FTIR spectroscopy (Fig. 2b), with the characteristic vibration regions annotated in the spectrum (Fig. S6). The nanofibers of SrTiO₃ have a wide absorption band in the 3300-3000 cm⁻¹ region, which is believed to be due to -OH stretching vibrations from the surface hydroxyl groups and/or physically adsorbed water. Furthermore, the low wave number absorption below about 600 cm⁻¹ is related to the characteristic lattice vibrations of the SrTiO₃ framework, primarily Ti-O and Sr-O bonds [29]. A well-defined feature is observed around 1500-1400 cm⁻¹, which is tentatively assigned to surface carbonate species, which may be due to the adsorption of CO₂ from the atmosphere or surface carbonate-containing species on Sr-based oxide surfaces. This assignment is not an intrinsic SrTiO₃ lattice vibration and is therefore shown as a potential surface carbonate assignment in Fig. S6.

The pristine g-C₃N₄ spectrum features the typical vibrational modes of polymeric graphitic carbon nitride. The bands of absorption, which are distributed over the whole range of 1650-1200 cm⁻¹, are primarily attributed to the stretching vibrations of C-N and C-N bonds in the conjugated heptazine structure. Moreover, the strong band at 800-810 cm⁻¹ is attributed to the breathing mode vibration of tri-s-triazine/heptazine units, and the broad band in the region of 3300-3000 cm⁻¹ is attributed to N-H groups in the terminal position and adsorbed hydroxyl-containing species [30]. These are typical features that indicate that the polymeric carbon-nitride framework is well preserved.

In the case of Zn-TFBDC, several bands are observed in the fingerprint region and relate to vibrations of the coordinated tetrafluoro terephthalate linker. The absorption bands in the range of approximately 1200-1000 cm⁻¹ are attributed primarily to the vibrations of C-F and other vibrations associated with the linker of the fluorinated aromatic framework, while those in the range of approximately 1600-1400 cm⁻¹ are attributed to the vibrations associated with asymmetric and symmetric stretching of the coordinated carboxylate groups [31,32]. These characteristic carboxylate- and fluorinated-linker vibrations help to support the formation of the Zn-TFBDC coordination structure.

The binary and ternary composites have the main FTIR characteristics of both the individual components. After coupling SrTiO₃ with g-C₃N₄, the main FTIR characteristics of both individual components were retained, and by adding different amounts of Zn-TFBDC, the main FTIR characteristics of the composite remain preserved. The region in the mid-infrared spectrum between 3300-3000 cm⁻¹ (O-H/N-H), 1650-1200 cm⁻¹ (C-N/C=N) and the carboxylate-related region at 1200-800 cm⁻¹ (linker/heptazine fingerprint) are still visible throughout the composite series, as is the low-wavenumber region of the SrTiO₃ lattice contribution. The optimized SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite has its characteristic regions clearly identified in Fig. S6. The relative amounts of the three components and perhaps changes in their local chemical environments can be inferred from changes in band intensity and band broadening as the amount of Zn-TFBDC loading increases.

In combination, the FTIR data confirm successful incorporation and coexistence of SrTiO₃, g-C₃N₄, and Zn-TFBDC in the ternary composites and confirm that the main vibrational features of the components are preserved upon composite preparation. The findings of these observations are additional evidence for successful assembly of the multicomponent photocatalytic system and are complementary to the XRD results.

Fig. 3 shows SEM and TEM images of the pristine components, binary composite, and optimized ternary photocatalyst. SEM and TEM images of the pristine components, binary composite, and optimized ternary photocatalyst are depicted in Fig. 3. Pristine SrTiO₃ is one-dimensional, presenting elongated nanofiber or nanorod-like structures (Fig. 3a, b). The shape of g-C₃N₄ is wrinkled and uneven (Fig. 3c, d), which shows the layered structure of polymeric carbon nitride. The elongated SrTiO₃ structures are well connected with the g-C₃N₄ sheets in the binary SrTiO₃/g-C₃N₄ composite (Fig. 3e, f), indicating excellent physical integrity between the two phases. The intimate contact between morphologically distinct semiconductor domains facilitates the previously reported SrTiO₃/g-C₃N₄ heterostructures, which leverage this contact to enhance carrier transport efficiency at the interface [33, 34]. Pristine Zn-TFBDC has an aggregated nanostructured morphology (Figs. 3g, h). The optimized SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite is a heterogeneous structure that comprises elongated SrTiO₃ structures and sheet-like carbon-nitride domains, along with smaller features related to Zn-TFBDC (Fig. 3i, j). TEM also shows that there is close spatial association between these structurally distinct components. Ternary photocatalysts that contain SrTiO₃ and g-C₃N₄ with similar

multicomponent interfacial designs have been reported for the hydrogen evolution reaction [35].

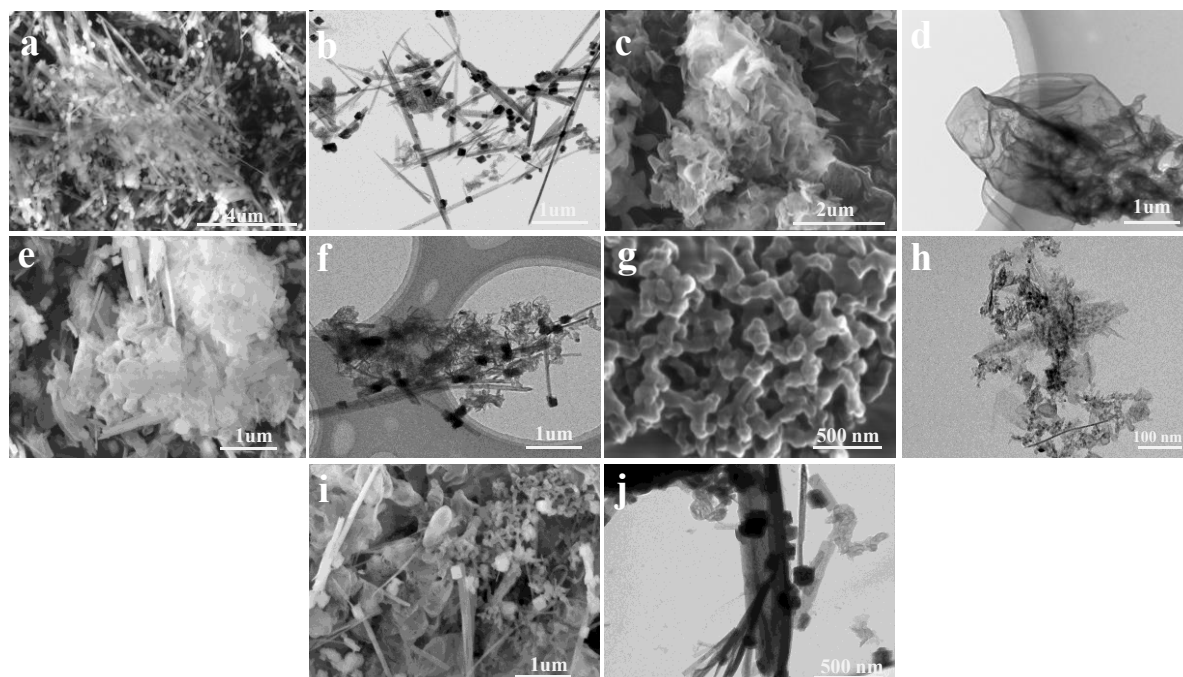


Figure 3. Morphological characterization of the pristine components and composites, (a) SEM, (b) TEM images of SrTiO₃ nanofibers, (c) SEM, (d) TEM images of g-C₃N₄, (e) SEM, (f) TEM images of g-C₃N₄/SrTiO₃, (g) SEM, (h) TEM images of Zn-TFBDC, (i) SEM, (j) TEM images of g-C₃N₄/SrTiO₃/ 20 Zn-TFBDC Ternary Composite.

However, we use the SEM/TEM data only to illustrate morphology and interfacial contact, and we assess the efficacy of light-induced charge separation independently by PL and EIS. To further investigate the elemental composition of the constituent materials, we performed EDS analysis and elemental mapping (Supporting Information, Figure Number????). The predicted Sr, Ti, and O signals are apparent in SrTiO₃, and the characteristic C and N distributions are apparent in the g-C₃N₄. The detected elements Zn, F, C, and O represent the fluorinated Zn-tetrafluoro terephthalate coordination framework for virgin Zn-TFBDC. The recent study of Zn-TFBDC showed the elemental and spectroscopic fingerprints of Zn, F, C, and O [36]. The newly added Zn EDS images of the SrTiO₃/g-C₃N₄/x Zn-TFBDC ternary series illustrate the incorporation of Zn into the SrTiO₃/g-C₃N₄ at different loadings of Zn-TFBDC. The signal of Zn is observed for the optimised composite (20%), in particular, in concert with the SEM/TEM data, and is consistent with the XPS-detected signals of Zn 2p and F 1s. The SEM, TEM, and EDS analyses verify the successful assemblage of the ternary SrTiO₃/g-C₃N₄/Zn-TFBDC structure and the proximity of the different phases. The resulting interfaces become the

structural basis for the subsequent study of the carrier migration and recombination behavior. The resulting interfaces serve as the structural basis for the subsequent study of carrier migration and recombination behavior.

3.2 Photocatalytic activity

The optimized SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite was characterized by the XPS method to determine the surface elemental composition and chemical states of the composite (Fig. 4). The survey spectrum (Fig. 4a) presents the general features of Sr, Ti, C, N, O, F and Zn, which indicates the presence of the three constituents in the ternary composite. The SrTiO₃/g-C₃N₄-based heterostructures have been reported to have a similar chemical environment with Sr, Ti, C, N and O [29,25]. Zn-TFBDC has been observed to display unique Zn, F, C and O, XPS signals [31]. The high-resolution C 1s spectrum (Fig. 4b) contains a higher binding energy component that originates from C-N environments (N-C=N bond in g-C₃N₄ and O-C=O in the TFBDC linker) along with a significant contribution from C-C/C=C species. In recent photocatalysts that contain g-C₃N₄ [29,25] with a similar N environment can be identified. The N 1s spectrum (Fig. 4c) is mostly linked to nitrogen atoms in the conjugated C-N framework of g-C₃N₄. The O 1s envelope (Fig. 4d) is the signature of the presence of several oxygen habitats associated with the surface oxygen-containing species, as well as the presence of the lattice oxygen in SrTiO₃. The spectrum of Fig. 4f corresponds to the Ti 2p level and is consistent with the presence of Ti⁺ in the SrTiO₃ lattice [29,25], while the spectrum of Fig. 4e is the characteristic spin-orbit doublet of Sr²⁺. The F 1s signal (Fig. 4g) is attributed to the fluorinated tetrafluoro terephthalate linker, while the Zn 2p signal (Fig. 4h) displays the Zn 2p_{3/2} and Zn 2p_{1/2} characteristics that are typical of the presence of Zn²⁺ species. These designations are consistent with those found in the earlier XPS characterization of Zn-TFBDC, which determines the elemental composition and chemical environment of the fluorinated Zn coordination framework using the Zn 2p, F 1s, and C 1s spectra [31].

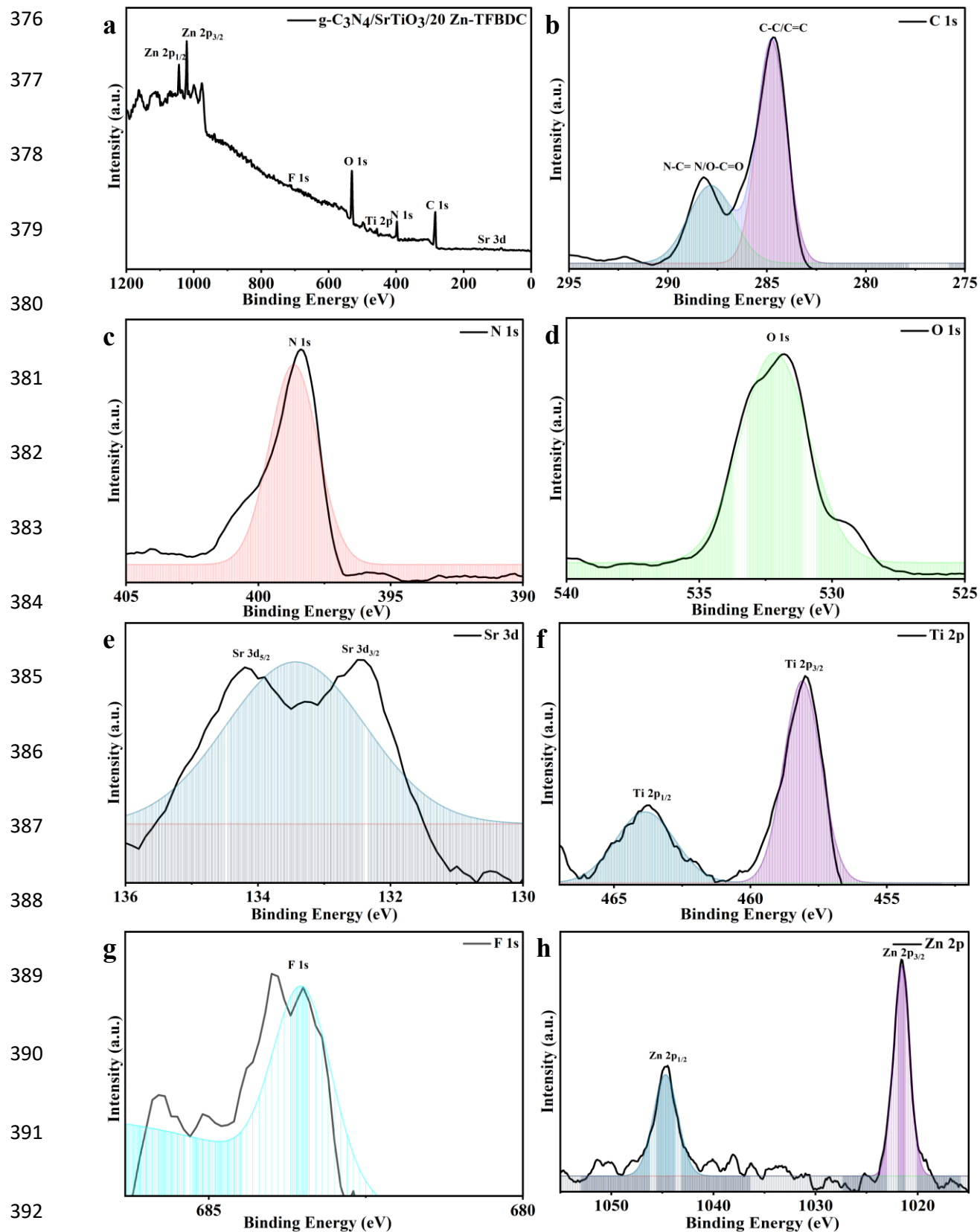


Figure 4. XPS characterization of the optimized $\text{SrTiO}_3/\text{g-C}_3\text{N}_4/20\% \text{ Zn-TFBDC}$ ternary composite: (a) survey spectrum and high-resolution spectra of (b) C 1s, (c) N 1s, (d) O 1s, (e) Sr 3d, (f) Ti 2p, (g) F 1s, and (h) Zn 2p.

The optical absorption properties of the pure and composite photocatalysts were assessed using UV-Vis spectroscopy, as depicted in Fig. 5a. The optical absorbance of pristine SrTiO₃ is very strong in the ultraviolet region and drops considerably at longer wavelengths, suggesting a rather wide band gap. On the contrary, g-C₃N₄, Zn-TFBDC and SrTiO₃/g-C₃N₄/Zn-TFBDC composites have a wider absorption in the visible-light spectrum. The ternary system can make use of a wider range of incident light spectra due to changes in the optical response of SrTiO₃ induced by the addition of g-C₃N₄ and Zn-TFBDC. Light-harvesting enhancement of SrTiO₃/g-C₃N₄ based photocatalytic device can be obtained due to interfacial coupling [33,37]. The related absorbance-derived Tauc maps are shown in Figure S13. Optical band gap energies of the chosen absorption edge areas of the SrTiO₃ nanofibers, g-C₃N₄, Zn-TFBDC and optimised SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite are approximately 3.06 eV, 2.81 eV, 3.01 eV, and 2.96 eV, respectively. The apparent band-gap value of the optimised ternary composite is smaller than that of pure SrTiO₃, suggesting that the former changes in its optical response as a consequence of the multicomponent coupling. These values are hence more meaningful as apparent optical band gaps derived from absorbance spectra analysis (Tauc) than Kubelka-Munk derived band gaps since the present spectra were measured in absorbance mode. Furthermore, the behaviour of the recombination of photogenerated charge carriers was studied via steady state photoluminescence spectroscopy (Fig. 5b). Pristine SrTiO₃ has a reasonably high PL, however, the emission intensity of binary or ternary composites is strongly affected. The PL emission of the SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite is much lower than that of SrTiO₃ and other composites, suggesting that the electron-hole recombination at the multicomponent interface is less for the composite SrTiO₃/g-C₃N₄/20% Zn-TFBDC. However, recent investigations revealed that heterojunctions of SrTiO₃-g-C₃N₄ have a reduction in PL emission and enhancement of separation of the photogenerated carriers [33, 37]. The intensity of the PL of the present composite series is, however, not proportional to the photocatalytic activity in a linear manner. The PL quenching for some samples with higher loadings is comparable to or better than that of the optimised 20% Zn-TFBDC composite. Therefore, only PL quenching alone cannot be used as an indicator of the most efficient photocatalytic performance, as the decrease in steady-state PL intensity can be due to non-radiative relaxation or carrier trapping. The enhanced H₂-evolution capability of the 20% composite may be attributed to optimal light harvesting, charge separation, interfacial carrier transport, and the availability of reaction-active sites. The superior performance of the MOF/g-C₃N₄-based photocatalysts is attributed to the heterointerface assembly, which promotes the

generation and separation of carriers, although numerous kinetic parameters still influence the overall activity [38].

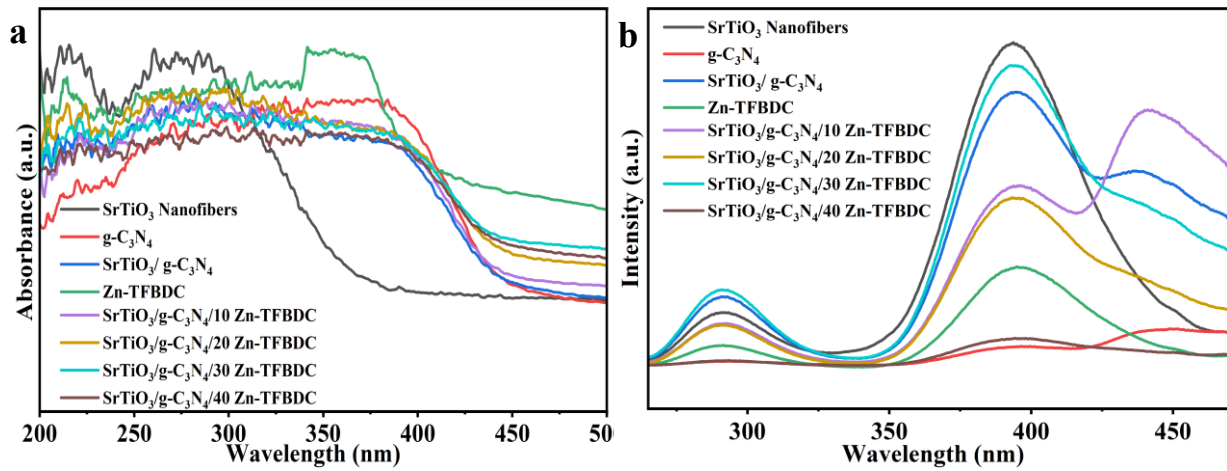


Figure 5. (a) UV absorbance (b) PL intensity of g-C₃N₄, SrTiO₃ nanofibers, Zn-TFBDC and their ternary composites.

The electrochemical impedance spectra were used to investigate the interfacial carrier transport, and the obtained Nyquist plots are shown in Fig. 6. The impedance responses of several samples demonstrate that the interfacial electrochemical behavior is significantly changed by changing the content of the Zn-TFBDC and coupling SrTiO₃ with g-C₃N₄. The smaller Nyquist arc is usually correlated to lower interfacial charge transfer resistance, and to more favorable carrier migration under equal measurement conditions. A few recently published SrTiO₃/g-C₃N₄ heterojunctions demonstrated that the PL and EIS analyses can be complementary to understand the change in carrier recombination and charge-transfer behavior after the connection between two materials [37]. However, in this situation the semicircular arcs are not completely resolved in the range of the presented impedances, and the optimum composite containing 20% Zn-TFBDC does not clearly demonstrate the smallest apparent arc across the entire range of measurement. Therefore, the EIS data have been used mainly to point out the effect of ternary design on the interfacial carrier-transport properties and is not used to give a clear-cut lowest charge-transfer resistance (CTR) without fitting the equivalent circuit. Impedance parameters can then be fitted to quantify the R_{ct} . The separation and transport behaviour of the photogenerated charge carriers is also drastically affected when combined with the PL results, with the EIS measurements confirming the above conclusion. The VB-XPS of the individual components was also investigated, as shown in Fig. S14, to determine the valence-band electronic structures of the different components. The linear extrapolation of

the leading edges of these plots to the baseline resulted in approximate band gaps of 2.20 eV for SrTiO₃ nanofibers, 2.36 eV for g-C₃N₄ and 3.13 eV for Zn-TFBDC. Recently, SrTiO₃/g-C₃N₄ heterojunctions were investigated using VB-XPS, optical band-gap analysis, PL spectroscopy and electrochemical characterization to determine the electrical structure and carrier behaviour of the heterojunctions [37]. In conjunction with VB-XPS data (shown in Fig. S13), the apparent optical band-gap values give additional insights into the relative electronic structure of the constituent materials. It should be noted that the VB-XPS onset energies are with respect to the Fermi level of the XPS measurement and therefore should not be taken as electrochemical valence band potentials (VVB) vs NHE or RHE directly without a suitable energy-reference conversion. Therefore, the VB-XPS data have been primarily employed here to assign the relative position of the valence bands, and to aid in the explanation of the proposed charge transfer mechanism at the interface.

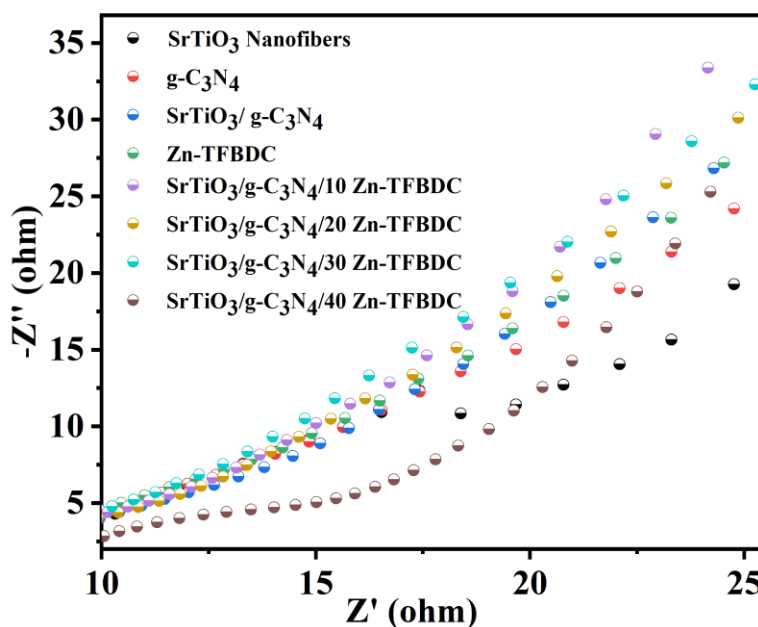


Figure 6. Comparison of g-C₃N₄, SrTiO₃ nanofibers, Zn-TFBDC and their ternary composites.

Based on the results of the UV-Vis, PL, EIS, Tauc, and VB-XPS, it can be seen that the optical response and the photogenerated carrier dynamics of the system were influenced by the SrTiO₃/g-C₃N₄/Zn-TFBDC ternary interface. The optimized 20% Zn-TFBDC composite has superior photocatalytic performance for H₂ evolution by breaking the balance of the competing processes, which is attributed to a combination of three effects: (1) higher visible-light utilization, (2) lower radiative recombination, and (3) changed interfacial transport behavior. From this, the following possible interfacial charge transfer is proposed.

The photocatalytic H₂ evolution activity of pristine components, binary heterostructure and ternary SrTiO₃/g-C₃N₄/x Zn-TFBDC composites were examined under visible light irradiation (Fig. 7a-c). For all the photocatalysts that were studied, the amount of developed H₂ increased with increasing irradiation time (Fig. 7a). But there were considerable differences in activity, depending on composition. Moderate activities of H₂ evolution have been seen for SrTiO₃, g-C₃N₄ and Zn-TFBDC. The photocatalytic response was significantly enhanced, however, by a combination of SrTiO₃ and g-C₃N₄ and the introduction of Zn-TFBDC.

The SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite showed the best photocatalytic activity with an H₂ evolution rate of 642.78 μmol g⁻¹ h⁻¹ (Fig. 7b). The value is around 2.03 times the value of pristine SrTiO₃, as illustrated in the figure. The improvement in the ternary composite is reasonably believed to be due to the synergistic contribution of increased light utilization, intimate multi-component interfacial contact, and modified photogenerated-carrier separation and transport as revealed by the above-mentioned characterization techniques. In order to optimize the H₂ evolution efficiency, the extension of heterointerfaces in ternary photocatalysts with SrTiO₃ and g-C₃N₄ is necessary to achieve a high utilization of carriers and an efficient charge transfer at the interface [35, 39].

An increase in the Zn-TFBDC content beyond the optimum did not further increase the photocatalytic reactions, whereas the 30% and 40% composites decreased the H₂ evolution reactions when compared with the 20% composite. This is because such behavior indicates that the photocatalytic activity is not directly affected by the more MOF component. Too much Zn-TFBDC may be able to partially cover photoactive surface, affect light penetration, decrease the accessibility of catalytically active sites or create new trapping/recombination pathways. In MOF/g-C₃N₄ heterojunctions, the optimal composition of the interface is a tradeoff between light harvesting, access to the active site, and carrier separation [40,41]. Independent tests were used to determine the reliability of photocatalytic measures (Fig. 7c). The activity trend observed, and especially the higher activity of the 20% Zn-TFBDC composite, is reproducible in that it is possible to observe relatively small dispersion among the repeated measurements. Combined, our observations demonstrate that achieving optimal loading of Zn-TFBDC leads to a more desirable multicomponent design instead of maximizing a given property, such as PL quenching or the impedance response. The schematic photocatalytic process in figure 7d is based on the structural, optical and electrical characterizations. When visible light is applied to light-sensitive components, a pair of charge carriers is formed inside the components. The intimate interfaces between SrTiO₃, g-C₃N₄ and Zn-TFBDC facilitate the movement of carriers

at the interface. In proton reduction, photogenerated electrons help to generate H₂, and the photogenerated holes are lost through oxidation of the sacrificial isopropanol donor. This schematic is only meant to illustrate the proposed interfacial carrier-transfer mechanism and does not represent an absolute electrochemical band diagram because the VB-XPS onset potentials are not separately referenced to NHE/RHE.

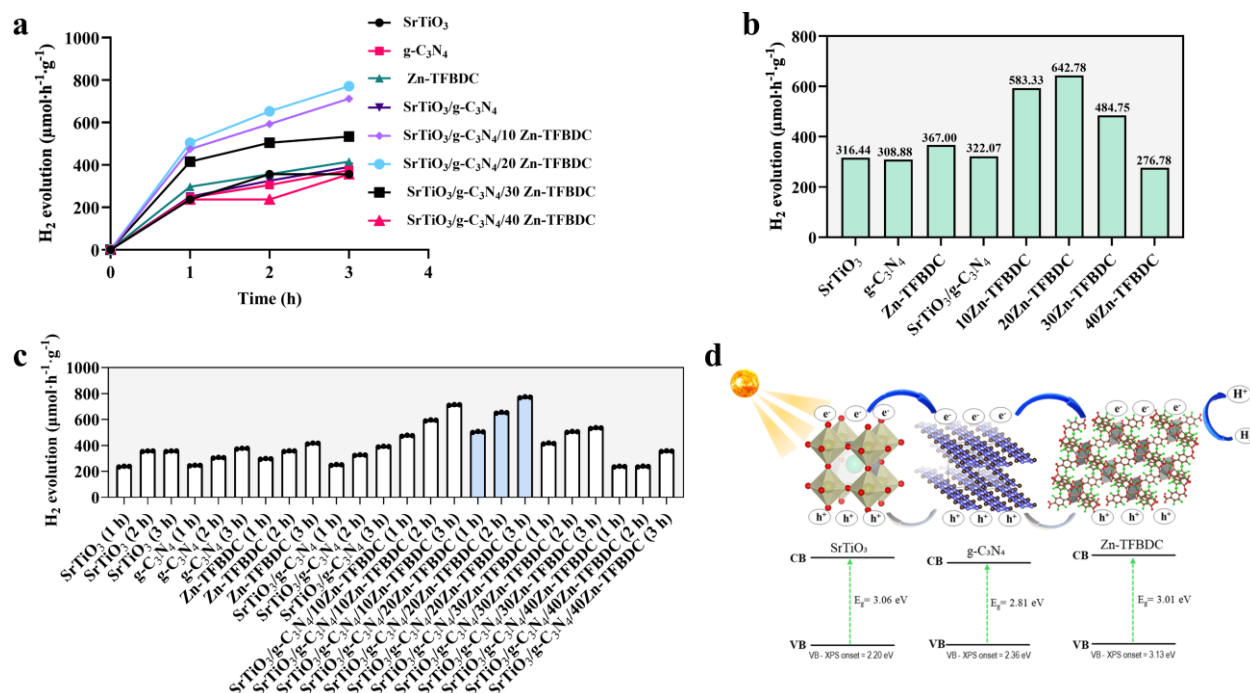


Figure 7. (a) Photocatalytic activity and (b) the rate of hydrogen (H₂) evolution. (c) the average rate of hydrogen (H₂) evolution from the g-C₃N₄, SrTiO₃ nanofibers, Zn-TFBDC and their ternary composites. (d) Charge transport in the as-prepared g-C₃N₄, SrTiO₃ nanofibers, Zn-TFBDC ternary composite. Error bars in (c) represent mean ± SD (*n*=3) calculated in GraphPad Prism 10.4.0 (621) software.

The optimized photocatalytic system of SrTiO₃/g-C₃N₄/20%Zn-TFBDC was tested and compared with other photocatalytic systems reported in the literature (Table 1). The H₂ evolution rate of 642.78 μmol g⁻¹ h⁻¹ is comparable to Ag(3)@SrTiO₃/g-C₃N₄ (645.62 μmol g⁻¹ h⁻¹) [24] and slightly higher than the recently reported SrTiO₃/g-C₃N₄/ZnO ternary system (603.94 μmol g⁻¹ h⁻¹) [35]. Systems containing Pt or structurally designed systems such as 5% SrTiO₃/g-C₃N₄, TFBDC-modified g-C₃N₄/Pt, and crystalline g-C₃N₄ have been found to have higher activity [42-44]. For the first time, the SrTiO₃/g-C₃N₄/20% Zn-TFBDC photocatalyst

efficiently generates hydrogen without a noble metal cocatalyst under visible light. Absolute rates of H₂ evolution should be interpreted with caution because of variations in catalyst loading, sacrificial reagent, intensity of the light, concentration of cocatalyst and reactor configuration among the investigations.

Table 1. Comparison of the visible-light-driven photocatalytic H₂ evolution performance of the optimised SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite with related reported photocatalysts.

Photocatalyst	Visible-light condition / sacrificial system	H ₂ evolution rate μmol g ⁻¹ h ⁻¹	Year	Ref.
g-C ₃ N ₄	Visible light; 10 vol% TEOA; 3 wt% Pt	328.4	2019	[42]
5% SrTiO ₃ /g-C ₃ N ₄	Visible light; 10 vol% TEOA; 3 wt% Pt	966.8	2019	[42]
Ag(3)@SrTiO ₃ /g-C ₃ N ₄	Visible-light irradiation	645.62	2022	[24]
TFBDC-50/g-C ₃ N ₄ /Pt	420 nm; 10 vol% TEOA; Pt	764	2023	[43]
Crystalline g-C ₃ N ₄ (HPCN)	Visible-light irradiation	1846	2024	[44]
SrTiO ₃ /g-C ₃ N ₄ /ZnO (35%-STCZ)	Visible-light irradiation	603.94	2025	[35]
SrTiO ₃ /g-C ₃ N ₄ /20% Zn- TFBDC	Visible light; aqueous isopropanol; noble-metal-free	642.78	This work	

4. Conclusion

The solvent-assisted self-assembly method was successfully applied to prepare a ternary SrTiO₃/g-C₃N₄/Zn-TFBDC photocatalyst to perform visible-light-driven H₂ evolution. The structural and vibrational characteristics of SrTiO₃, g-C₃N₄, and Zn-TFBDC samples were found to largely remain unchanged after composite production, with no significant structural shift. XRD and FTIR investigations revealed that the characteristics of the produced composites, namely SrTiO₃, g-C₃N₄, and Zn-TFBDC, were mostly intact after the composite production process, without significant changes in structure. Intimate contact was revealed between the one-dimensional SrTiO₃ nanofibers, layered g-C₃N₄ and Zn-TFBDC domains

by SEM and TEM images. Successful incorporation of the components in the ternary architecture was confirmed with EDS and XPS investigations.

The optical and electrical characterization showed that the system was significantly affected by the ternary coupling. Compared with different reference samples, the optimized SrTiO₃/g-C₃N₄/20% Zn-TFBDC composite exhibited a lower PL emission, which demonstrated a lower radiative recombination of photogenerated carriers, and an optical band gap of around 2.96 eV. The composition-dependent changes in the charge-transport behavior at the interfaces were found using the EIS measurements, while information regarding the electronic structures of the individual components was obtained from the VB-XPS analysis. In general, the improvement of photocatalytic activity can be attributed to high utilization of the visible light, intimate interfaces of the multicomponent system, and enhanced charge-carrier separation and migration.

The composite 20% Zn-TFBDC showed the maximum value of H₂ evolution rate (642.78 μmol g⁻¹ h⁻¹) with aqueous isopropanol as a sacrificial electron donor under visible-light irradiation. This activity is 2.03 times higher than that of pure SrTiO₃ and is comparable with the recently reported photocatalysts of SrTiO₃/g-C₃N₄- and SrTiO₃/MOF-based visible-light-responsive photocatalysts. This reduction in activity at higher Zn-TFBDC loadings indicates that enhancing MOF content is not always the best approach to increasing photocatalytic effectiveness and that there is an optimal amount of MOF that maximizes the ability to absorb, contact, transport and present reactive surface sites for catalysis.

Furthermore, the optimized composite maintained its main diffraction features and characteristic vibrational bands after the reaction, showing excellent structural stability at [Fig.S15](#) under the reaction conditions mentioned above. Incorporating SrTiO₃ and g-C₃N₄ into a MOF whose metal is based on Zn is an effective noble-metal-free method to achieve highly stable photocatalytic multicomponent materials that have competitive H₂ evolution rates under visible light.

CRedit authorship contribution statement

Md Shohanur Rahman: Design of Methodology, Data analysis, Investigation, Data curation, Visualization, Writing. **Md Abdul Majed Patwary, Alexey Tarabarov:** Discussion, Writing-revision & editing. **Chuangang Qin** and **Syed Najeel-uz-zaman Haider**

(corresponding author): Conceptualization, Supervision, Ensuring the accuracy of description,
Writing-review & editing.

Conflicts of Interest

All authors declare that they have no conflicts of interest

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Data Availability Statements

- Conflicts of interest or competing interests: Not applicable
- Data and code availability: Not applicable
- Supplementary information: Applicable
- Ethical approval: Not applicable

Reference

- [1] S. Chu, A. Majumdar, Opportunities and challenges for a sustainable energy future, *Nature* 488 (2012) 294-303.
- [2] N.S. Lewis, D.G. Nocera, Powering the planet: Chemical challenges in solar energy utilization, *Proc. Natl. Acad. Sci. U.S.A.* 103 (2006) 15729-15735.
- [3] J.A. Turner, Sustainable hydrogen production, *Science* 305 (2004) 972-974.

605 [4] I. Dincer, C. Acar, Smart energy solutions with hydrogen options, *Int. J. Hydrogen Energy*
606 43 (2018) 8579-8599.

607 [5] X. Chen, S. Shen, L. Guo, S.S. Mao, Semiconductor-based photocatalytic hydrogen
608 generation, *Chem. Rev.* 110 (2010) 6503-6570.

609 [6] A. Kudo, Y. Miseki, Heterogeneous photocatalyst materials for water splitting, *Chem. Soc.*
610 *Rev.* 38 (2009) 253-278.

611 [7] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode,
612 *Nature* 238 (1972) 37-38.

613 [8] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of
614 semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69-96.

615 [9] F.E. Osterloh, Inorganic nanostructures for photoelectrochemical and photocatalytic water
616 splitting, *Chem. Soc. Rev.* 42 (2013) 2294-2320.

617 [10] Q. Wang, K. Domen, Particulate photocatalysts for light-driven water splitting:
618 Mechanisms, challenges, and design strategies, *Chem. Rev.* 120 (2020) 919-985.

619 [11] K. Domen, A. Kudo, T. Onishi, Mechanism of photocatalytic decomposition of water into
620 H_2 and O_2 over $NiO-SrTiO_3$, *J. Catal.* 102 (1986) 92-98.

621 [12] H. Kato, A. Kudo, Visible-light-response and photocatalytic activities of TiO_2 and $SrTiO_3$
622 photocatalysts codoped with antimony and chromium, *J. Phys. Chem. B* 106 (2002) 5029–
623 5034.

624 [13] T. Takata, J. Jiang, Y. Sakata, M. Nakabayashi, N. Shibata, V. Nandal, K. Seki, T.
625 Hisatomi, K. Domen, Photocatalytic water splitting with a quantum efficiency of almost unity,
626 *Nature* 581 (2020) 411-414.

627 [14] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M.
628 Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under
629 visible light, *Nat. Mater.* 8 (2009) 76-80.

630 [15] W.J. Ong, L.L. Tan, Y.H. Ng, S.T. Yong, S.P. Chai, Graphitic carbon nitride (g- C_3N_4)-
631 based photocatalysts for artificial photosynthesis and environmental remediation: Are we a step
632 closer to achieving sustainability? *Chem. Rev.* 116 (2016) 7159-7329.

633 [16] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S.Z. Qiao, Graphitic carbon nitride materials:
634 Controllable synthesis and applications in fuel cells and photocatalysis, *Energy Environ. Sci.*
635 5 (2012) 6717-6731.

636 [17] S. Yin, J. Han, T. Zhou, R. Xu, Recent progress in g- C_3N_4 -based low-cost photocatalytic
637 systems: Activity enhancement and emerging applications, *Catal. Sci. Technol.* 5 (2015) 5048-
638 5061.

- [18] J. Fu, J. Yu, C. Jiang, B. Cheng, g-C₃N₄-based heterostructured photocatalysts, *Adv. Energy Mater.* 8 (2018) 1701503.
- [19] A. Dhakshinamoorthy, Z. Li, H. Garcia, Catalysis and photocatalysis by metal–organic frameworks, *Chem. Soc. Rev.* 47 (2018) 8134–8172.
- [20] S. Wang, X. Wang, Multifunctional metal–organic frameworks for photocatalysis, *Small* 11 (2015) 3097–3112.
- [21] M.A. Nasalevich, M. van der Veen, F. Kapteijn, J. Gascon, Metal–organic frameworks as heterogeneous photocatalysts: Advantages and challenges, *CrystEngComm* 16 (2014) 4919–4926.
- [22] Q. Xu, L. Zhang, B. Cheng, J. Fan, J. Yu, S-scheme heterojunction photocatalyst, *Chem* 6 (2020) 1543–1559.
- [23] J.T. Lee, Y.J. Chen, E.C. Su, M.Y. Wey, Synthesis of solar-light-responsive Pt/g-C₃N₄/SrTiO₃ composite for improved hydrogen production: Investigation of Pt/g-C₃N₄/SrTiO₃ synthetic sequences, *Int. J. Hydrogen Energy* 44 (2019) 21413–21423.
- [24] T. Ahamad, S.M. Alshehri, Fabrication of Ag@SrTiO₃/g-C₃N₄ heterojunctions for H₂ production and the degradation of pesticides under visible light, *Sep. Purif. Technol.* 297 (2022) 121431.
- [25] X. Ye, H. Zhong, Y. Zhang, X. Liu, W. Tian, L.-A. Ma, Q. Wang, Ti₃C₂ MXene cocatalyst-supported Ti₃C₂/SrTiO₃/g-C₃N₄ heterojunctions with efficient electron transfer for photocatalytic H₂ production, *CrystEngComm* 26 (2024) 5440–5451.
- [26] J. Cao, Y. Jia, X. Wan, B. Li, Y. Zhang, S. Huang, H. Yang, G. Yuan, G. Li, X. Cui, Z. Wu, Strong tribocatalysis of strontium titanate nanofibers through harvesting friction energy for dye decomposition, *Ceram. Int.* 48 (2022) 9651–9657.
- [27] M.S. Rahman, R. Liu, C. Ye, M.T.N. Khan, C. Qin, T. Xu, Morphology effect of perovskite CsPbBr₃/g-C₃N₄ composite on photocatalytic water-splitting for hydrogen evolution, *Inorg. Chem. Commun.* 182 (2025) 115671.
- [28] X. Li, X. Wu, B. Li, et al., Efficient solar-driven water splitting enabled by perovskite photovoltaics and a halogen-modulated metal-organic framework electrocatalyst, *ACS Nano* 17 (2023) 23478–23487.
- [29] V. Gopal, G. Palanisamy, J. Lee, I.A. Abu-Yousef, A.F. Majdalawieh, A. Mahasneh, K.M. Prabu, S. Kanan, Fabrication of SrTiO₃-anchored rGO/g-C₃N₄ photocatalyst for the removal of mixed dye from wastewater: dual photocatalytic mechanism, *Sci. Rep.* 14 (2024) 16259.
- [30] M. Fiaz, N. Carl, M. Kashif, M.A. Farid, N.N. Riaz, M. Athar, Development of efficient bi-functional g-C₃N₄@MOF heterojunctions for water splitting, *RSC Adv.* 12 (2022) 32110–32118.

- [31] S. Hameed, D. Li, M.K. Aslam, S. Chen, J. Duan, Fluorine-confined catalytic sites for augmented p–d hybridization promoting flow-type aqueous Zn–CO₂ batteries, *Chem. Commun.* 61 (2025) 13636-13639.
- [32] C. Seidel, R. Ahlers, U. Ruschewitz, Coordination polymers with tetrafluoroterephthalate as bridging ligand, *Cryst. Growth Des.* **11** (2011) 5053-5063.
- [33] T.N.Q. Trang, N.T.G. Bao, T.T. Doanh, P.T. Trung, V.T.H. Thu, Manipulating interface-induced multi-channel charge transfers toward highly hierarchical synchronous g-C₃N₄/STO@Pt modulation for boosting artificial photosynthesis, *Int. J. Hydrogen Energy* 74 (2024) 346-360.
- [34] W. Zhang, Y. Li, L. Wang, F. Zhang, Y. Ai, G. Shao, P. Zhang, In situ construction of cyano-modified g-C₃N₄ nanolayer-coated SrTiO₃ nanotubes by gas-solid reaction for efficient photocatalytic solar fuel production, *Chem. Eng. J.* 469 (2023) 143817.
- [35] M.S. Alshammari, W.H. Hassan, M.M. Al-Zahiwat, H. Osman, H.A. El-Sabban, M.A. Diab, Z. Atamuratova, E. Saitov, A. Amari, Novel environmentally benign dual Z-scheme SrTiO₃/g-C₃N₄/ZnO heterojunction for efficient H₂ evolution and polluted water treatment: Optimization, mechanism interpretations and toxicity assessment, *FlatChem* 50 (2025) 100841.
- [36] S. Osman, R.A. Senthil, J. Pan, Y. Sun, A novel coral structured porous-like amorphous carbon derived from zinc-based fluorinated metal-organic framework as superior cathode material for high performance supercapacitors, *J. Power Sources* 414 (2019) 401-411.
- [37] F. Nan, S. Chen, S. Wang, Y. Lin, B. Fan, H. Li, L. Zhou, Construction of a Rh-doped SrTiO₃/g-C₃N₄ p–n heterojunction for enhanced photoelectrochemical performance, *RSC Adv.* 15 (2025) 9627-9635.
- [38] A. Jamma, B. Jaksani, C.S. Vennapoosa, S. Gonuguntla, S. Sk, M. Ahmadipour, M. Abraham B., I. Mondal, U. Pal, Defect-rich UiO-66@g-C₃N₄/Ni frameworks as efficient water splitting photocatalysts, *Mater. Adv.* 5 (2024) 2785-2796.
- [39] Y.T.H. Le, J.C.S. Wu, W.-Y. Yu, C.-L. Yeh, M. Maček Kržmanc, Photocatalytic whole H₂O splitting using Bi⁰-decorated g-C₃N₄/SrTiO₃ sheet-like catalyst under simulated sunlight, *Int. J. Hydrogen Energy* 130 (2025) 390-401.
- [40] X. Chu, B.-B. Luan, A.-X. Huang, Y. Zhao, H. Guo, Y. Ning, H. Cheng, G. Zhang, F.-M. Zhang, Controlled synthesis of 2D-2D conductive metal–organic framework/g-C₃N₄ heterojunctions for efficient photocatalytic hydrogen evolution, *Dalton Trans.* 53 (2024) 2534-2540.
- [41] W.A. Qureshi, R.N. Ali, S.N.-U.-Z. Haider, N. Ahmad, M.U. Khan, X. Hu, L. Wang, C. Cheng, S. Rao, A. Ali, Q.Q. Liu, J. Yang, Construction of B-doped g-C₃N₄/Ni-MOF-74 porous heterojunction with boosted carrier separation for photocatalytic H₂ generation, *Mater. Today Sustain.* 25 (2024) 100679.

- [42] Y. Luo, B. Deng, Y. Pu, A. Liu, J. Wang, K. Ma, F. Gao, B. Gao, W. Zou, L. Dong, Interfacial coupling effects in g-C₃N₄/SrTiO₃ nanocomposites with enhanced H₂ evolution under visible light irradiation, *Appl. Catal. B Environ.* 247 (2019) 1-9.
- [43] Y. Gu, H. Feng, J. Zhao, M. Cui, Y. Li, Z. Li, Rational construction of edge-grafted g-C₃N₄ via cross-linking aromatic compounds with C-F bonds for efficient photocatalytic H₂ evolution, *Chem. Eng. J.* 476 (2023) 146555.
- [44] L. Zhu, W. Zhang, G. Shi, X. Tian, P. Tang, P. Xia, Synthesizing crystalline g-C₃N₄ for enhanced photocatalytic hydrogen evolution under visible light, *CrystEngComm* 26 (2024) 599-603.