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Pt-Loaded Z-Scheme g-C₃N₄/Bi₄Ti₃O₁₂ Heterostructure for Enhanced Photocatalytic H₂ Evolution

Poonam Chaturvedi^{1,2}, Valerie Keller^{2,*} and Tapas Kumar Mandal^{1,3,*}

¹ Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India

² Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES), UMR 7515, CNRS/University of Strasbourg, 25 rue Becquerel, Cedex 2 67087 Strasbourg, France

³ Center for Nanotechnology, Indian Institute of Technology Roorkee, Roorkee 247667, India

* Correspondence: vkeller@unistra.fr (V.K.); tapas.mandal@cy.iitr.ac.in (T.K.M.); Tel.: +91-1332-285864 (T.K.M.)

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Abstract: Efficient photocatalytic H₂ evolution requires coordinated control of light absorption, interfacial charge transfer, and surface reduction kinetics. Here, g-C₃N₄/Bi₄Ti₃O₁₂ (CN/BTO) heterojunctions were constructed by *in-situ* thermal coupling and subsequently modified through *in-situ* photodeposition of Pt. Among the investigated compositions, 2.5-CN/BTO showed the highest activity before Pt addition. Structural, optical, and electrochemical analyses indicate effective coupling between CN and layered BTO, while EPR measurements and band-position analysis are consistent with a direct Z-scheme charge-transfer pathway. Pt nanoparticles were found preferentially on CN-rich regions, supporting electron accumulation at the CN side of the heterostructure during photocatalysis. Pt incorporation increased the H₂ production to 1278 μmol g⁻¹ during the first 5 h, approximately 39 times that of pristine CN and BTO under the same conditions. Reuse tests revealed a pronounced loss of activity after the first cycle, followed by a slower decline, with H₂ production of 360, 351, and 300 μmol g⁻¹ over 5 h in cycles 2–4. Post-reaction analyses indicate structural and surface modification of the CN component, accompanied by localized Pt clustering, whereas the crystalline BTO phase remains largely preserved. The study therefore establishes the beneficial role of CN/BTO interfacial coupling and Pt cocatalysis in promoting H₂ evolution, while revealing the structural evolution that limits sustained photocatalytic performance.

Keywords: Aurivillius bismuth titanate; layered perovskite titanate; g-C₃N₄; heterojunction; photocatalytic H₂ evolution

1. Introduction

The global transition toward sustainable energy systems has intensified research into sacrificial-agent-assisted photocatalytic H₂ evolution as an environmentally benign approach for hydrogen production. Hydrogen is widely regarded as a clean and sustainable energy carrier due to its high gravimetric energy density and environmentally benign combustion, making it a promising solution for future energy and environmental challenges [1–4]. To date, numerous renewable-energy-based strategies have been developed for hydrogen production. Among them, semiconductor-driven photocatalytic hydrogen evolution through water splitting is particularly appealing because it enables the direct conversion of solar energy into chemical energy. This approach minimizes energy losses associated with multistep energy transformation processes and therefore represents a highly promising route for generating environmentally benign “green hydrogen” [5]. The performance of photocatalysts in this process is governed by their ability to efficiently absorb sunlight, generate electron–hole pairs, suppress recombination losses, and catalyze the hydrogen evolution reaction [6]. Layered bismuth titanate



($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) has attracted considerable interest as a photocatalyst owing to its Aurivillius-type structure, suitable bandgap, and intrinsic chemical robustness [7–13]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a layered Aurivillius oxide corresponding to the $n = 3$ member of the general $(\text{Bi}_2\text{O}_2)[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ family, with Bi and Ti occupying the A and B sites, respectively. Its crystal structure is formed by alternating positively charged $(\text{Bi}_2\text{O}_2)^{2+}$ layers and negatively charged $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ perovskite-like slabs stacked along the c -axis. The perovskite-like block contains three TiO_6 octahedral layers, which gives $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ its characteristic three-layered architecture [14]. However, the wide bandgap and rapid charge recombination significantly limit its activity under visible-light irradiation, restricting its overall photocatalytic efficiency.

To overcome these shortcomings, constructing semiconductor heterojunctions has emerged as an effective strategy to enhance light utilization and facilitate spatial charge separation [15–22]. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), a metal-free polymeric semiconductor with a moderate bandgap and excellent photochemical stability, has proven to be a highly suitable partner for oxide-based photocatalysts [20,23–33]. Recent developments in carbon-nitride photocatalysts further demonstrate the importance of controlling their structural and electronic properties for H_2 evolution. Defect regulation in melon-based carbon nitride has been shown to improve photocatalytic performance, while ultrathin twisted carbon-nitride nanoplates can extend light absorption and facilitate charge migration [34,35]. Coupling $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with $\text{g-C}_3\text{N}_4$ can form a type-II or Z-scheme heterostructure that promotes directional carrier migration across the interface and broadens the response into the visible-light region. Such architectures benefit not only from improved charge separation but also from enhanced interfacial redox kinetics. $\text{g-C}_3\text{N}_4/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunction, prepared by physical mixing, ball milling and hydrothermal route have been explored for photocatalytic dye degradation [7,36–39]. To the best of our knowledge, photocatalytic hydrogen evolution over a binary $\text{g-C}_3\text{N}_4/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunction prepared via *in-situ* thermal polymerization has been scarcely explored.

In addition to improving charge separation, heterojunction construction offers several further advantages that contribute to enhanced photocatalytic performance. Carefully matched band structures across the semiconductor interface help to establish an internal electric field that promotes directional carrier transfer and reduces recombination losses [31,40,41]. The intimate interfacial contact formed during heterojunction assembly frequently increases the density of catalytically active sites, partly due to lattice mismatch and defect formation at the interface. Moreover, modified surface electronic states within the heterostructure often improve reactant adsorption and accelerate interfacial reaction kinetics [1,42]. In systems incorporating carbon nitride, the presence of conjugated π -structures and electron-mediating surface nitrogen species further makes it highly applicable in photocatalysis, improving both the thermodynamics and kinetics of the reaction [1]. Collectively, these effects allow semiconductor heterojunctions to outperform their single-component counterparts by delivering higher activity, faster charge-transfer dynamics, and superior long-term stability [15,43–46].

Further enhancement can be realized by incorporating noble metal co-catalysts [12,20,47–51]. Platinum is highly effective for hydrogen evolution due to its lower overpotential and high work function, resulting in a strong ability to capture photogenerated electrons [52]. Photodeposition enables Pt nanoparticles to anchor directly to reactive sites on the heterojunction surface, creating an intimate metal–semiconductor contact that accelerates interfacial charge extraction and promotes rapid hydrogen formation. Recent work has also highlighted the importance of engineering the Pt–semiconductor interfacial electronic environment to promote charge separation and interfacial H_2 -evolution kinetics [53].

In this work, $\text{g-C}_3\text{N}_4/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunction photocatalyst was synthesized via *in-situ* thermal coupling followed by *in-situ* photodeposition of Pt. Comprehensive structural, optical, and morphological analyses were conducted to elucidate heterojunction formation and examine the structural evolution of the photocatalyst during repeated reaction cycles. The optimized Pt modified 2.5-CN/BTO heterojunction achieves H_2 production of $1278 \mu\text{mol g}^{-1}$ during the first 5 h compared to the individual components. In addition, the structural evolution of the polymeric $\text{g-C}_3\text{N}_4$ component during repeated photocatalysis is examined, since CN frameworks are known to undergo reconstruction/defect formation under irradiation, which can influence co-catalyst anchoring and long-term kinetics. The findings provide insights into rational strategies for designing high-efficiency photocatalysts for hydrogen production.

2. Experimental Section

2.1. Materials

Bismuth oxide (Bi_2O_3 , 99.9%, Sigma Aldrich), titanium oxide (TiO_2 , 99.8%, Sigma Aldrich), methanol (Sigma Aldrich), melamine ($\text{C}_3\text{H}_6\text{N}_6$, 99.0%, Sigma Aldrich), dihydrogen hexachloroplatinate (IV) hydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.999%, Alfa-Aesar), poly(vinylidene fluoride) (PVDF) (Alfa Aesar), N-methyl-2-pyrrolidone

(NMP) (99.0%, Himedia), and 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) ($C_6H_{11}NO$, 97.0%, BLD Pharma) were purchased and used as received without any further purification. Ultrapure water (Millipore Milli-Q grade) with a resistivity of 18.2 M Ω .cm (25 °C) was used in all experiments.

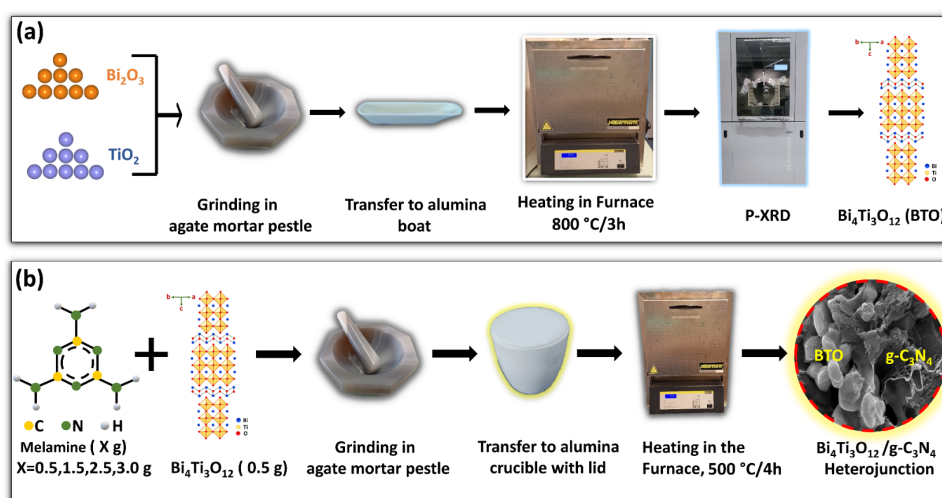
2.2. Catalyst Preparation

2.2.1. Synthesis of $Bi_4Ti_3O_{12}$ (BTO)

$Bi_4Ti_3O_{12}$ was synthesized through a conventional solid-state reaction [54,55]. Stoichiometric amounts of Bi_2O_3 and TiO_2 were weighed and thoroughly ground in an agate mortar for 60 min to ensure homogeneous mixing of the precursors. The mixed powder was transferred to an alumina boat and calcined in a muffle furnace at 800 °C for 3 h in air with a heating rate of 10 °C min⁻¹. After cooling to room temperature, the resulting product was gently crushed to obtain a fine powder. The synthesized $Bi_4Ti_3O_{12}$ is represented as BTO here. The synthesis method is shown in Scheme 1a. The physical appearance of the synthesized sample is shown in Figure S1 (see Supplementary Materials).

2.2.2. Fabrication of $g-C_3N_4/Bi_4Ti_3O_{12}$ (CN/BTO) Heterojunction

The $g-C_3N_4/Bi_4Ti_3O_{12}$ heterojunction photocatalyst was prepared using a solid-state thermal condensation approach, where melamine served as the carbon-nitride precursor [24]. A fixed amount of $Bi_4Ti_3O_{12}$ (0.5 g) was mixed with different amounts of melamine (0.5–3.0 g) and manually ground in an agate mortar until a uniform mixture was obtained. The mixture was then placed in a covered alumina crucible to maintain a semi-closed environment during polymerization and heated at 500 °C for 4 h in air with a heating rate of 2 °C min⁻¹. Under these conditions, melamine undergoes thermal polymerization to form $g-C_3N_4$, which grows in intimate contact with the $Bi_4Ti_3O_{12}$ particles, resulting in the formation of the $g-C_3N_4/Bi_4Ti_3O_{12}$ heterojunction, denoted here as X-CN/BTO, where X represents the addition mass of melamine ($X = 0.5, 1.5, 2.5$, and 3.0 g). The final product was ground to produce a homogeneous powder suitable for characterization and photocatalytic testing. The masses obtained for 0.5-CN/BTO, 1.5-CN/BTO, 2.5-CN/BTO, and 3.0-CN/BTO were 0.66 g, 1.22 g, 1.78 g, and 2.23 g, respectively. It should be mentioned that 0.5 g of BTO was heated under the same conditions (500 °C for 4 h in air with a heating rate of 2 °C min⁻¹) without the addition of melamine, resulting in the negligible mass loss of the calcined BTO (0.498 g). Thus, it is reasonable to calculate the mass% of CN in 0.5-CN/BTO, 1.5-CN/BTO, 2.5-CN/BTO, and 3.0-CN/BTO to be 24.2%, 59.0%, 71.9% and 77.6%, respectively, based on the formula of $(m_c - 0.5)/m_c$, where m_c represents the mass of synthesized X-CN/BTO heterojunction (Table S1). For comparison, pure CN was also prepared from melamine under the same condition (500 °C for 4 h in air with a heating rate of 2 °C min⁻¹) without the addition of BTO. The synthesis method is shown in Scheme 1b. The physical appearance of all the synthesised samples is shown in Figure S1.



Scheme 1. Synthesis process of (a) BTO, (b) CN/BTO heterojunction.

2.3. Characterization

Powder X-ray diffraction (P-XRD) measurements were carried out using a Bruker D8-Advance diffractometer equipped with a Lynx Eye detector operating at 40 kV and 40 mA, using Cu K α ($\lambda = 1.5418$ Å)

radiation. The angle range (2θ) was set to 5° to 90° with a step size of 0.0092° and a counting time of 0.4 s per step, during the measurement. A Zeiss Gemini SEM 300 (Carl Zeiss AG, Oberkochen, Germany), equipped with a FEG Schottky source and an energy-dispersive X-ray spectroscopy (EDS) detector, was used for scanning electron microscopy to understand morphology. High-resolution transmission electron microscopy (HR-TEM) images were collected with a JEM-3200FS field-emission electron microscope (JEOL Ltd., Tokyo, Japan) operated at an accelerated voltage of 300 kV. For TEM sample preparation, a small amount of sample (~ 2 mg) was dispersed in ethanol and drop-cast onto a carbon-coated copper grid. Nitrogen adsorption-desorption isotherms at 77 K were obtained using a Micromeritics ASAP 2420 porosimeter (Micromeritics Instrument Corp., Norcross, GA, USA). Samples were first degassed at 100°C under primary vacuum for 5 h to remove adsorbed water and impurities from their surface. Specific surface areas were calculated by using the Brunauer, Emmett, and Teller (BET) method in the relative pressure (P/P_0) range of 0.05–0.3. The BJH method, specifically for mesoporous solids, calculated the pore size distribution. To investigate the optical properties of the samples, the diffuse reflectance spectra were recorded in the range of 200–800 nm on a Lambda 950 UV–visible spectrophotometer (PerkinElmer, Waltham, MA, USA) equipped with a 100 mm diffuse reflectance integrating sphere using BaSO_4 as reference. ATR-FTIR spectra were recorded using a Thermo Scientific Nicolet iS10 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) fitted with a Smart Orbit single-bounce diamond ATR accessory, operating over the $400\text{--}4000\text{ cm}^{-1}$ range. Photoluminescence spectra were recorded at room temperature by using a Shimadzu RF-6000 spectrofluorophotometer (Shimadzu Corp., Kyoto, Japan). Time-resolved photoluminescence decay measurements were performed on FLS 1000 (Edinburgh Instruments, Livingston, UK). For this, a picosecond pulsed light-emitting diode source (EPLED-340 Model) with a wavelength of 336.1 nm was used. The emission decay was monitored at the photoluminescence maximum ($\lambda_{\text{em}} = 460\text{ nm}$). The decay profiles were collected using a time-correlated single-photon counting (TCSPC) detector, and the decay curves were fitted using a bi-exponential function to extract the characteristic carrier lifetimes. Electron paramagnetic resonance (EPR) spectra were collected on an EMXmicro A200-9.5/12/S/W spectrometer (Bruker Biospin, Rheinstetten, Germany), operating at the X-band microwave frequency. The spectrometer was running under Bruker WIN EPR software for acquisition and processing. Spectra were recorded at room temperature. Ultraviolet photoelectron spectroscopy (UPS) analyses were performed on a Thermo Scientific NEXSA photoemission spectrometer using the photon source, an unfiltered He-I (21.22 eV) gas discharge lamp. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ultrahigh-vacuum (UHV) Thermo-VG Scientific Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using Al $K\alpha$ X-ray radiation (1486.6 eV). C 1s reference peak at 284.8 eV was used for the binding energy correction, and CASA XPS software was used to deconvolute the peaks. The Pt content of the recovered photocatalyst was quantified using an Agilent 4210 microwave plasma–atomic emission spectrometer (MP-AES) (Agilent Technologies, Santa Clara, CA, USA).

2.4. Electrochemical Measurement

Electrochemical impedance spectroscopy (EIS) was performed in a three-electrode system on a Metrohm electrochemical workstation (Multi Autolab/M204). For the EIS measurement, the experiment was performed in the frequency range of 0.1 to 45,000 Hz at 0.215 V, using a mixture of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (10 mM) and KCl (0.1 M) in a 1:1 ratio as the electrolyte. The circuit fitting was performed by the NOVA 2.1 software. For all measurements, the electrode was prepared by making a homogeneous slurry of the sample with polyvinylidene fluoride (PVDF) binder in a 90:10 (optimized) ratio, respectively, in N-methyl-2-pyrrolidone (NMP) solvent. Then, the slurry was spin-coated on a piece of indium tin oxide (ITO) glass ($1\text{ cm} \times 1\text{ cm}$). The sample-coated ITO was used as the working electrode, a Pt wire served as the counter electrode, and Ag/AgCl was used as the reference electrode.

2.5. Photocatalytic H_2 Evolution

Photocatalytic hydrogen evolution experiments were conducted in an inner-irradiation quartz reactor (with a capacity of 550 mL) equipped with a 250 W medium-pressure mercury lamp (MP-MVL), a magnetic stirrer, and a water-circulation jacket to maintain the reaction temperature at near-ambient conditions. In a typical run, 100 mg of the photocatalyst was dispersed in 250 mL of a 20 vol% methanol–water solution, which served as a sacrificial electron donor system. The suspension was purged with high-purity N_2 for several minutes to remove dissolved oxygen prior to illumination. For samples requiring platinum as a co-catalyst, *in-situ* photodeposition was carried out directly in the reaction medium. A calculated volume (10.25 μL) of 0.25 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution, corresponding to a nominal Pt precursor dosage of 0.5 wt% with respect to the catalyst mass, was introduced into the reactor using a microsyringe. The mixture was stirred at 450 rpm under continuous N_2 bubbling for 30 min to

allow uniform dispersion of the Pt precursor. Illumination was then initiated, during which Pt photodeposition and hydrogen evolution occurred simultaneously.

The produced gases were periodically sampled by injecting the gas sample with a gastight syringe and analyzed using a Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity detector (TCD), a 5 Å molecular-sieve column, and nitrogen as the carrier gas. A picture of the photocatalytic set-up used for the photocatalytic H₂-evolution tests is provided in Figure S2.

3. Results and Discussion

3.1. P-XRD and Structural Analysis

The P-XRD patterns of BTO, g-C₃N₄ and CN/BTO heterojunctions are shown in Figure 1a. The powder XRD pattern of Bi₄Ti₃O₁₂ (BTO) can be indexed to the orthorhombic Aurivillius phase (ICSD 15-9929), and no extra reflections from secondary oxides are detected, indicating that the BTO is phase-pure [56]. Pure carbon nitride (CN) shows the typical two reflections at about 12.9° and 27.2° (ICSD 87-1526), which are assigned to the in-plane structural packing of the tri-s-triazine units corresponding to (100) and the interlayer stacking of the conjugated aromatic system conforming to (002) planes, respectively [29]. In the CN/BTO composites, all characteristic peaks of BTO are retained, demonstrating that the introduction of CN does not alter the crystal structure of the oxide. With increasing CN content, an additional broad feature appears around 27.4° (Figure 1a), which becomes more pronounced at higher CN loading and overlaps with the BTO reflections in this region. This evolution of peaks confirms the successful incorporation of CN and the formation of CN/BTO composites without any other detectable crystalline impurity phases.

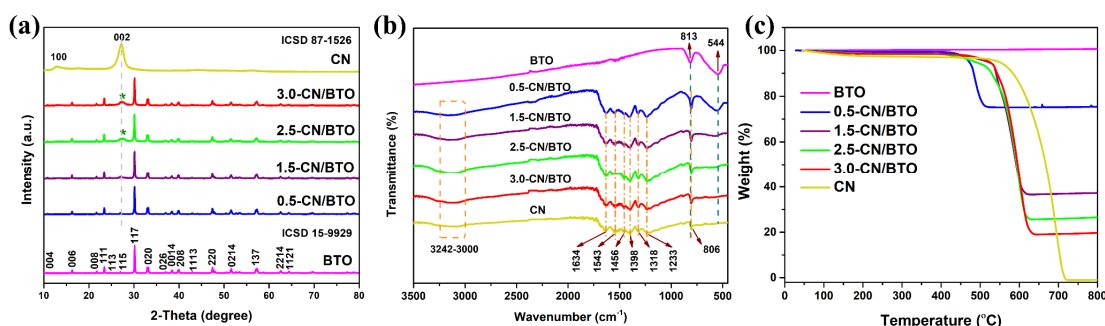


Figure 1. (a) Powder XRD patterns, (b) FT-IR spectra and (c) TGA of BTO, CN, and CN/BTO heterojunctions.

3.2. FT-IR Analysis

FT-IR spectra were recorded to further understand the presence of both BTO and CN in the heterojunction system. As shown in Figure 1b, the FT-IR spectrum of CN exhibits the well-known series of bands between 1200 and 1650 cm⁻¹, attributed to the stretching vibrations of C–N and C=N in the heptazine (tri-s-triazine) rings, together with a characteristic breathing mode of the s-triazine units at around 806 cm⁻¹. A broad absorption in the 3242–3000 cm⁻¹ region arises from overlapped N–H and adsorbed O–H stretching modes [26]. The BTO spectrum shows an absorption at 813 and 544 cm⁻¹ related to the characteristic internal Bi–O and Ti–O stretching vibration of BTO, respectively [54]. In the heterojunction system, these characteristic peaks of BTO and CN are clearly present, indicating both components preserve their fundamental structural motifs in the heterojunction.

3.3. Thermal Analysis

Thermogravimetric analysis was performed to assess the thermal stability of BTO, CN, and the CN/BTO composites (Figure 1c). BTO shows negligible weight loss up to 800 °C, confirming its high thermal stability. In contrast, CN exhibits a major decomposition step that begins around 550 °C and is almost completely oxidized by 700 °C, consistent with the thermal behavior of polymeric carbon nitride. The CN/BTO composites exhibit weight-loss profiles that are intermediate between those of the two individual components. All composites show minor mass loss below 200 °C, attributed to physically adsorbed moisture and surface volatiles. A pronounced decomposition step appears between 500 and 650 °C, corresponding to the thermal degradation of CN within the composite. The residual mass at high temperature increases with decreasing CN content, reflecting the higher fraction of thermally stable BTO. The onset of CN decomposition in the composites is slightly shifted to a lower

temperature compared with bare CN, which is consistent with the literature, showing that oxide species can catalyze the degradation of CN and weaken interlayer interactions [57,58].

3.4. XPS Analysis

XPS analysis was performed to further investigate the surface chemical composition and chemical states of elements in BTO, CN, and the heterojunction systems. The survey spectra (Figure S3) confirm the elemental composition of the samples. BTO shows only Bi, Ti and O core levels, indicating a single-phase oxide surface. CN displays only C 1s and N 1s signals. In the 2.5-CN/BTO heterojunction, all characteristic elements of both components appear simultaneously, confirming successful heterojunction formation. The weaker intensity of Bi and Ti peaks in the heterojunction arises from partial surface coverage of BTO by CN. The high-resolution Bi 4f spectra (Figure 2a) for BTO show two main peaks at 158.7 eV (Bi 4f_{7/2}) and 164.0 eV (Bi 4f_{5/2}), characteristic of Bi³⁺ in an oxide lattice [13]. Notably, two weak bands at ~157.3 and ~162.9 eV belonging to metallic Bi are detected in pristine BTO [15] but are markedly suppressed in the 2.5-CN/BTO heterojunction, indicating that coupling with CN reduces the fraction of surface-reduced (metallic) Bi species. Ti 2p spectrum (Figure 2b) of BTO exhibits a well-defined doublet at 457.6 (Ti 2p_{3/2}) and 463.1 eV (Ti 2p_{1/2}), typical of Ti⁴⁺ in a perovskite-like oxide [54,59]. The Ti 2p region partially overlaps with the Bi 4d_{3/2} contribution; therefore, the Ti 2p spectra were fitted by considering this overlapping contribution, particularly in the Ti 2p_{1/2} region. For BTO, the O 1s spectrum (Figure 2c) can be deconvoluted into three peaks. The peaks at ~529.5 and ~530.9 eV are attributed to the stronger Bi–O and Ti–O bonds, respectively [15], while a low-binding-energy shoulder ~528.1 eV in BTO and ~526.6 eV in 2.5-CN/BTO originates from defective lattice oxygen associated with locally reduced metal–O environments. The high-binding-energy O 1s component at ~532.0 eV in 2.5-CN/BTO becomes more pronounced after CN incorporation and can be attributed to an increased contribution from surface hydroxyls/adsorbed oxygenated species and/or defect-related oxygen environments. This change suggests a more hydroxylated/defect-rich surface, which may enhance interfacial adsorption and charge-transfer steps compared with bare BTO.

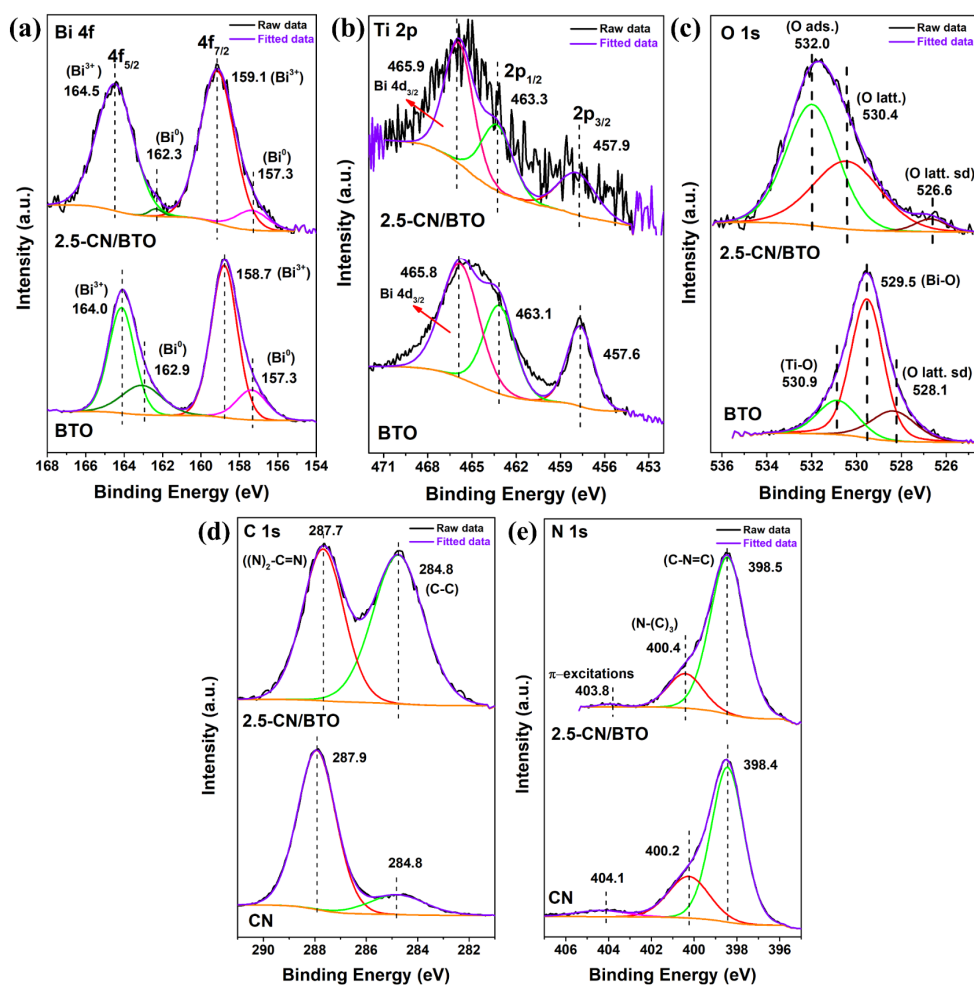


Figure 2. XPS spectra of the pure BTO, CN, and 2.5-CN/BTO heterojunction: (a) Bi 4f; (b) Ti 2p; (c) O 1s; (d) C 1s; and (e) N 1s.

The C 1s spectrum of CN (Figure 2d) is dominated by a peak at 287.9 eV, characteristic of sp^2 -hybridized C bonded to N atoms ($(N)_2C=N$) in the carbon-nitride matrix, with a minor contribution at 284.8 eV assigned to graphitic carbon impurities (C–C) [60]. In 2.5-CN/BTO, the $(N)_2C=N$ component appears at 287.7 eV and the C–C peak at 284.8 eV becomes more evident, reflecting the CN framework and some surface carbon species. The nearly unchanged positions indicate that CN maintains its polymeric structure but is in electronic contact with the oxide. The N 1s spectra of CN and 2.5-CN/BTO exhibit three main components. In Figure 2e, the dominant peak at 398.4 eV is assigned to sp^2 -hybridised N in C–N=C units of the heptazine (tri-s-triazine) ring. A second peak at 400.2 eV corresponds to tertiary nitrogen ($N-(C)_3$) linking the heptazine units, and a higher-binding-energy component at 404.1 eV is attributed to the π -excitation peaks [61,62]. Binding-energy shifts of Bi 4f, Ti 2p, O 1s, N 1s and C 1s in 2.5-CN/BTO point to interfacial charge redistribution between BTO and CN (Table S2).

3.5. FE-SEM Analysis

FE-SEM analysis of BTO, CN and CN/BTO heterojunctions were used for the initial assessment of the microstructure. SEM image of pristine BTO in Figure 3a shows agglomerates of crystallites, consistent with the layered nature of the Aurivillius structure. In contrast, CN shows a stacked, lamellar morphology composed of thin sheets and flakes, typical of thermally condensed carbon nitride in Figure 3b. After composite formation, morphology evolves with CN content. At low loading (0.5-CN/BTO), the BTO particles are partially wrapped by crumpled CN sheets, and both phases can still be distinguished as shown in Figure 3c. For the intermediate composition (1.5-CN/BTO), a more intimate contact between BTO grains and CN lamellae is observed, with CN coating the oxide particles and forming a continuous interfacial network that is favorable for charge transfer (Figure 3d). When the CN content is further increased (2.5- and 3.0-CN/BTO), the surface becomes increasingly covered by aggregated CN layers, and the underlying BTO grains are less exposed (Figure 3e,f). This morphological evolution confirms the formation of CN/BTO heterojunctions and suggests that an optimum CN loading is required to balance interfacial contact with light absorption and surface accessibility.

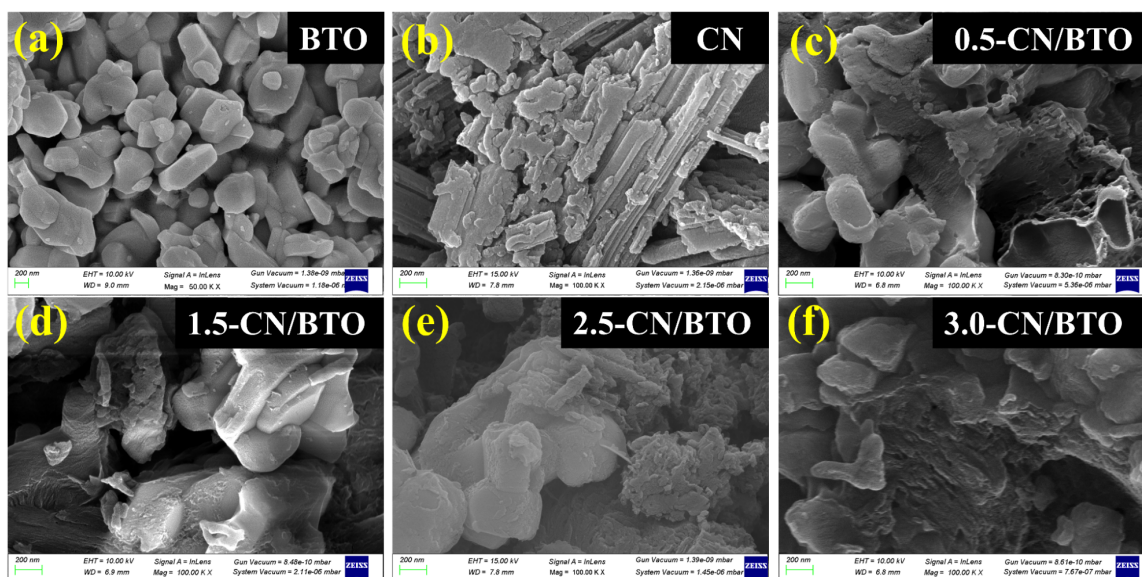


Figure 3. FE-SEM images of (a) BTO; (b) CN; (c) 0.5-CN/BTO; (d) 1.5-CN/BTO; (e) 2.5-CN/BTO; (f) 3.0-CN/BTO.

3.6. TEM Analysis

TEM analysis provides direct evidence of the heterostructure architecture. In Figure 4a,b, CN appears as low-contrast, fluffy aggregates composed of thin, wrinkled nanosheets. In Figure 4c, dense BTO particles with higher electron contrast are observed in close contact with the CN matrix. Enlarged image (Figure 4d) shows BTO crystallites embedded at the edges or surfaces of CN sheets, indicating that the oxide and carbon nitride are intimately interfaced rather than simply mixed physically. A high-resolution TEM image (Figure 4e) and corresponding IFFT patterns (Figure 4f,f') of the 2.5-CN/BTO sample display clear lattice fringes in the BTO region with an interplanar spacing of ~ 0.272 nm and ~ 0.270 nm, which can be indexed to the (200) and (020) planes of orthorhombic BTO [54]. The adjacent CN region appears largely disordered with an amorphous nature, characteristic of graphitic carbon nitride. The continuous contact between the crystalline BTO domains and the

CN matrix, together with the well-resolved lattice fringes, confirms the formation of a CN/BTO heterojunction interface that is expected to facilitate interfacial charge separation during photocatalysis.

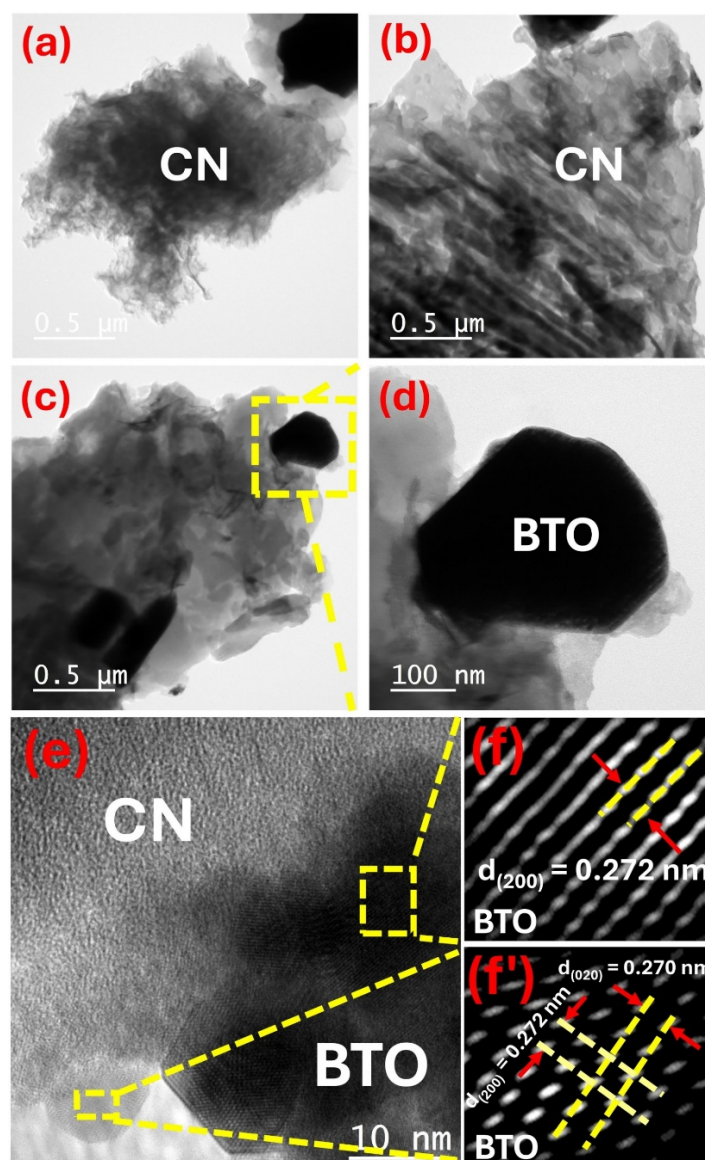


Figure 4. TEM images (a–d); HR-TEM image (e); and corresponding IFFT patterns (f and f') of 2.5-CN/BTO heterojunction.

3.7. UV–Vis DRS Analysis

The optical absorption properties of BTO, CN, and the CN/BTO composites were examined using UV–Vis diffuse reflectance spectroscopy (Figure 5). Pure BTO exhibits a sharp absorption edge around 385 nm, consistent with its wide bandgap. In contrast, CN exhibits a broader absorption profile that extends into the visible region, with an absorption edge located at approximately 445 nm. Upon forming the CN/BTO composites, the absorption edges shift progressively toward longer wavelengths with increasing CN content, reflecting the contribution of the carbon nitride component and the enhanced visible-light response of the heterostructures. The sample 2.5-CN/BTO displays the most significant broadening in the visible region, indicating improved light-harvesting capability due to the interfacial interaction between CN and BTO.

The optical band gaps were estimated from Tauc plots assuming indirect transitions (Figure 5b). The bandgap of pure BTO is approximately 3.15 eV, while g-C₃N₄ exhibits a narrower bandgap of about 2.70 eV, consistent with literature report [24]. For the CN/BTO heterostructures, direct extrapolation of the conventional Tauc plot was avoided because their optical response contains contributions from both semiconductor components. Instead, the optical transition energies were estimated using the baseline-intersection approach recommended for multicomponent semiconductor systems [63]. The estimated values were 2.72, 2.73, 2.71, and 2.76 eV for 0.5-

CN/BTO, 1.5-CN/BTO, 2.5-CN/BTO, and 3.0-CN/BTO, respectively (Table S3). These values lie close to that of CN, while the diffuse-reflectance spectra show an extension of the absorption response of BTO toward the visible region after incorporation of CN. The optical changes in the heterostructures are therefore attributed to the combined absorption contributions of BTO and CN rather than to a direct narrowing of the BTO band gap.

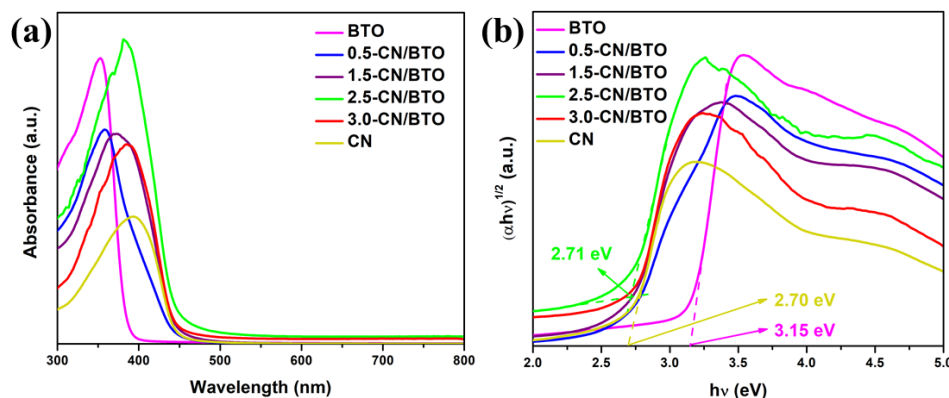


Figure 5. (a) UV-vis absorbance converted from DRS data using the Kubelka–Munk function, of as-prepared samples; and (b) Tauc plot of BTO, CN, and CN/BTO heterojunction.

3.8. UPS Measurement

The electronic structures of BTO and CN were examined using ultraviolet photoelectron spectroscopy (Figure 6). For BTO, the secondary electron cut-off appears at 15.85 eV, corresponding to a work function of 5.37 eV. The linear extrapolation of the valence region yields a Fermi level position 1.70 eV above the valence band maximum. Using the optical bandgap, the valence and conduction band positions can be placed at -7.07 eV and -3.92 eV versus the vacuum level, respectively. Similar analysis for CN gives a secondary electron cut-off of 16.10 eV and a work function of 5.12 eV, while the Fermi level lies 1.30 eV above the valence band edge. Based on the measured bandgap, the valence and conduction band levels of CN are estimated to be -6.42 eV and -3.72 eV, respectively. The overall band alignment indicates that CN has slightly higher-lying valence and conduction band edges compared to BTO, supporting the formation of a favorable interface for charge transfer within the CN/BTO heterojunction.

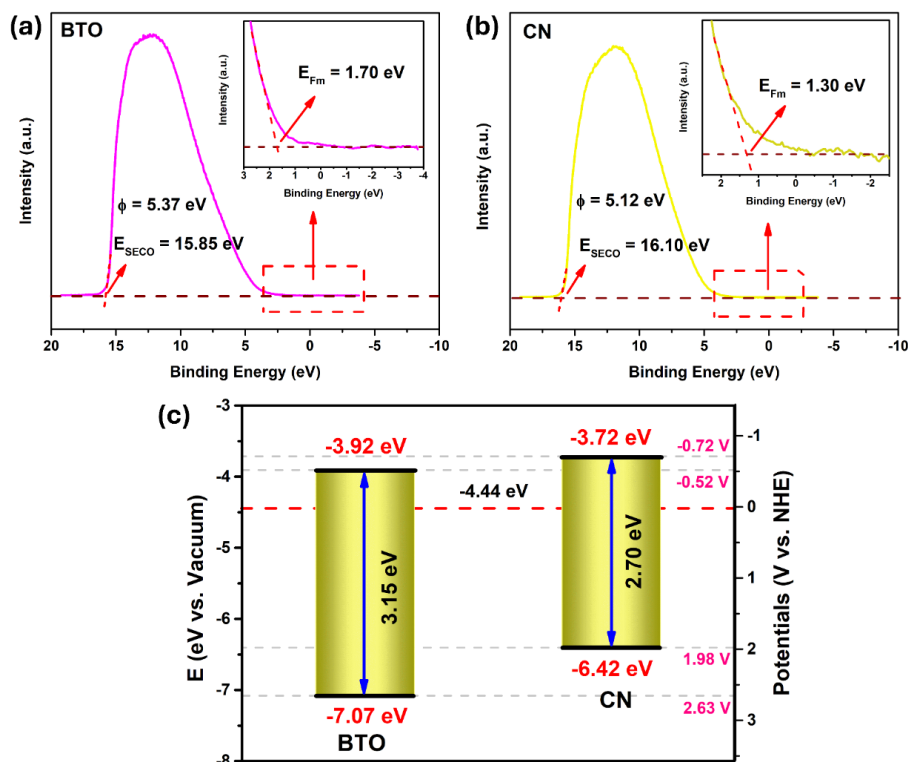


Figure 6. UPS spectra of (a) BTO; (b) CN; and (c) band structure of BTO and CN.

3.9. BET Surface Area and Porosity Measurements

The N₂ adsorption–desorption isotherms of BTO, CN, and the CN/BTO composites are presented in Figure 7a. All samples exhibit type-IV isotherms with an H3-type hysteresis loop according to the IUPAC classification [44]. BTO shows a very low adsorption capacity across the full relative pressure range, indicating its dense, non-porous nature. In contrast, CN exhibits a markedly higher uptake together with a typical type-IV isotherm profile associated with mesoporous structures. Upon forming the CN/BTO composites, the adsorption behaviour evolves between those of the individual components. All composite samples show substantially enhanced adsorption volumes relative to BTO, and the uptake increases progressively with higher CN content. The 2.5-CN/BTO sample displays the highest surface uptake ($S_{\text{BET}} = 9 \text{ m}^2 \text{ g}^{-1}$), suggesting the formation of a more accessible pore structure when an optimal amount of CN is incorporated (Table S4).

The corresponding pore size distributions derived from the BJH model (Figure 7b,c) reveal a broad mesoporous range for CN, centred between 20 and 60 nm. BTO shows negligible porosity, confirming its essentially non-porous nature and consistent with its isotherm behaviour. In contrast, CN and the CN/BTO composites show progressively higher uptake at high P/P_0 , indicating the presence of meso- and macro-porosity originating from the layered CN structure and its interaction with BTO. The BJH pore-size distributions (Figure 7b,c) reveal two characteristic pore ranges across the CN-containing samples. First, a dominant mesoporous region between $\sim 30\text{--}70 \text{ nm}$, attributed to interparticle voids among stacked CN nanosheets and CN/BTO aggregates. Second, a secondary mesoporous region between $\sim 2\text{--}10 \text{ nm}$, typically associated with surface slits formed within partially exfoliated CN domains or at CN–BTO interfaces.

Among all samples, 2.5-CN/BTO exhibits the highest pore volume, consistent with its highest nitrogen uptake, suggesting that this composition undergoes the most effective CN dispersion or partial thermal exfoliation during synthesis.

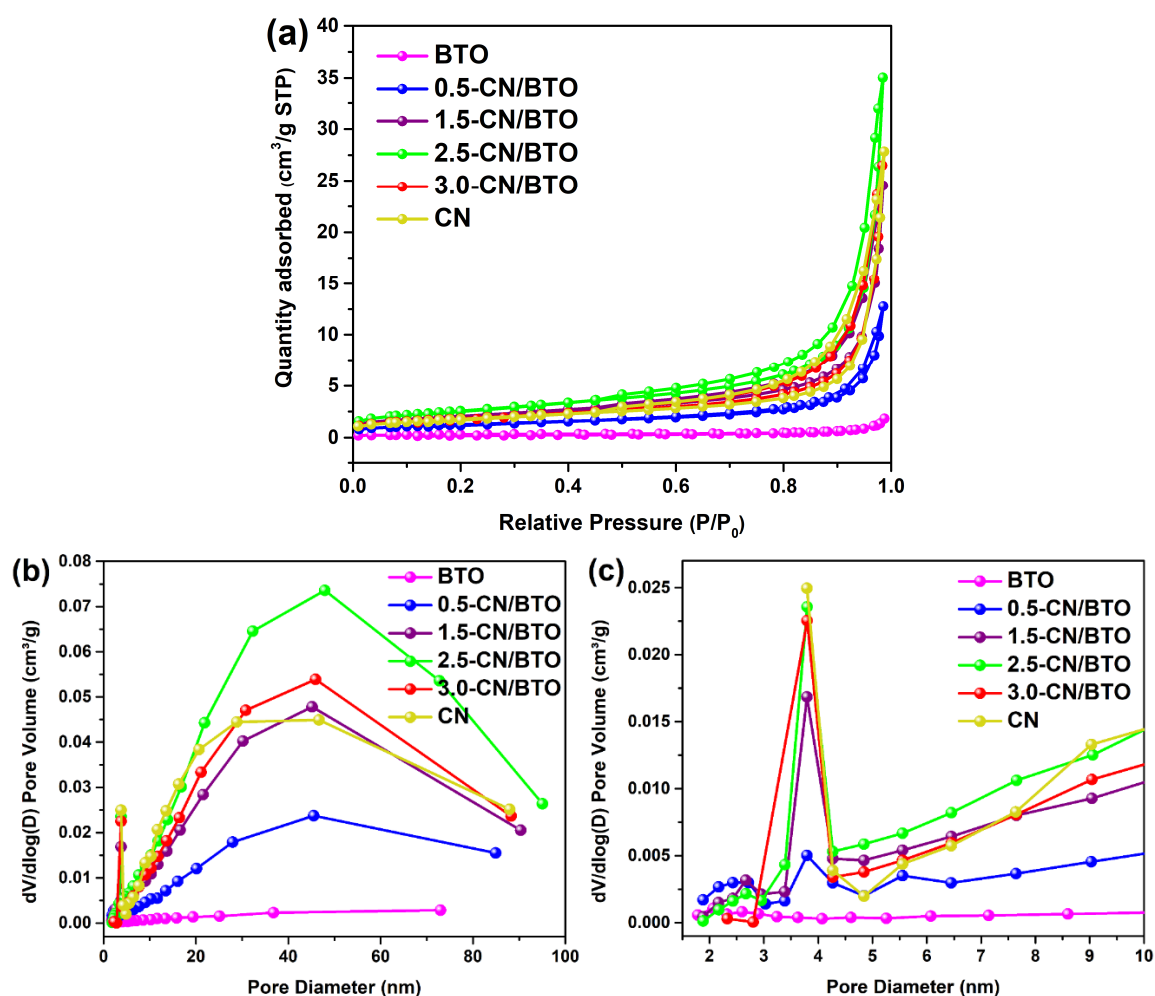


Figure 7. (a) Nitrogen adsorption-desorption isotherms; (b,c) Mean pore size distribution of BTO, CN, and CN/BTO heterojunctions.

3.10. Photoluminescence (PL) Spectra

The steady-state PL spectra recorded at an excitation wavelength of 350 nm are shown in Figure 8a. CN exhibits a strong emission band centered around 460 nm, originating from the high recombination rate of photogenerated charge carriers [1]. BTO shows almost no detectable emission due to low radiative recombination efficiency. Upon forming the CN/BTO composites, the PL intensity decreases compared with pure CN, with the 2.5-CN/BTO sample showing the most pronounced quenching. The quenching effect is attributed not only to spatial charge separation across the heterointerface but also to the formation of interfacial defect or band-bending regions that act as charge-transfer channels, reducing the probability of radiative recombination within the CN framework. The trend correlates well with the improved photocatalytic performance of these composites.

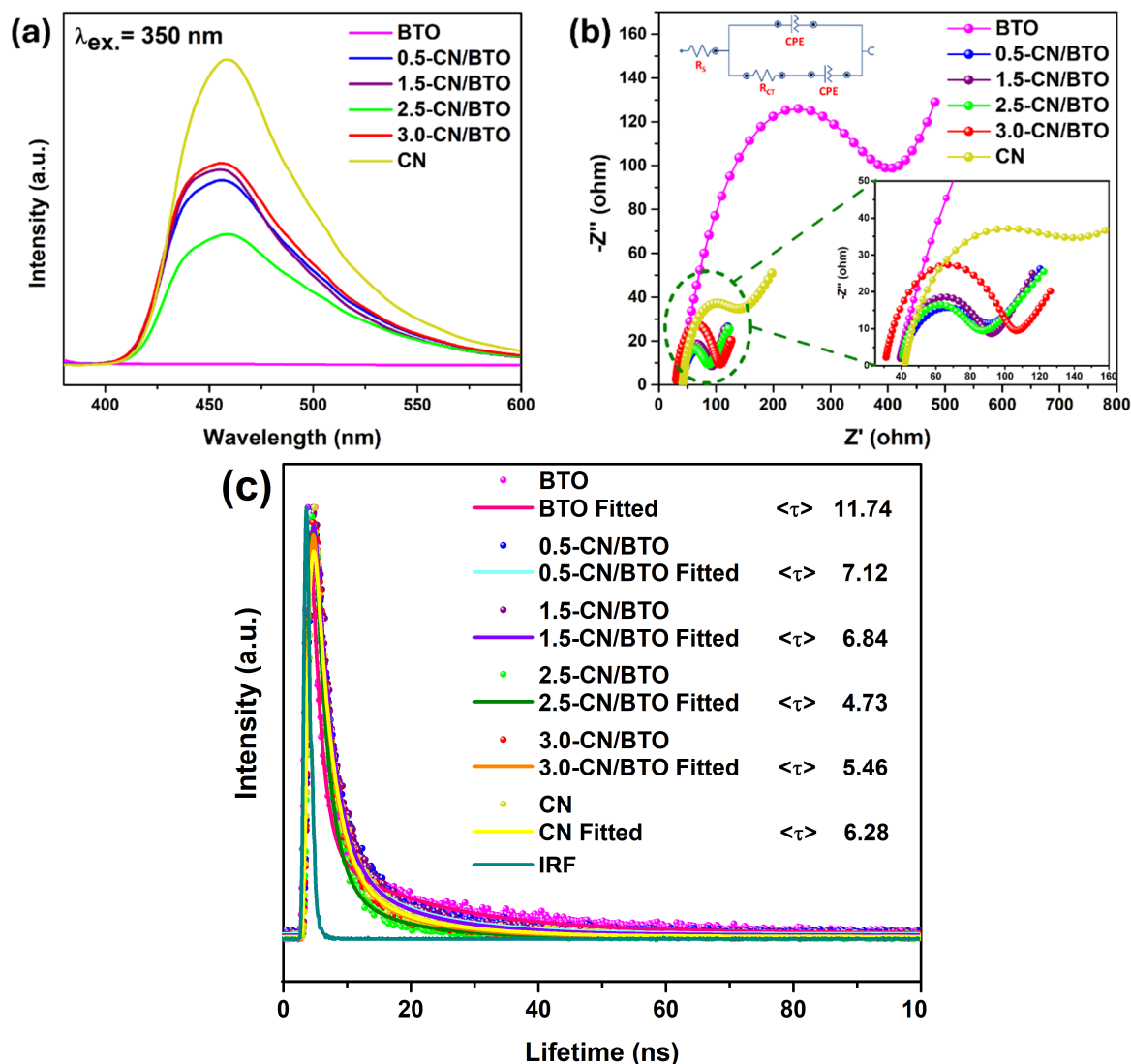


Figure 8. (a) PL spectra; (b) EIS spectra; and (c) FLS data of BTO, CN, and CN/BTO heterojunctions.

3.11. EIS Spectra

Electrochemical impedance spectroscopy further supports the enhanced charge transport in the composites (Figure 8b). Nyquist plots reveal that BTO exhibits the largest semicircle diameter, corresponding to a high charge-transfer resistance. CN also shows a relatively large impedance arc. In contrast, the CN/BTO composites display significantly smaller semicircles, with 2.5-CN/BTO showing the lowest resistance. The R_{ct} values for BTO, CN, 0.5-CN/BTO, 1.5-CN/BTO, 2.5-CN/BTO, and 3.0-CN/BTO are 363.3, 75.0, 48.0, 50.0, 38.0, and 70.0 Ω , respectively (Table S5). The reduced arc radius reflects faster interfacial charge transfer and lower recombination losses at the electrode–electrolyte interface [1,44]. These observations are consistent with the PL results and confirm that the CN/BTO heterojunction facilitates more efficient charge separation and transport than either component alone.

3.12. Time-Resolved Photoluminescence Decay

Time-resolved photoluminescence decay profiles of BTO, CN, and the CN/BTO heterojunctions were recorded to examine the charge-carrier dynamics (Figure 8c). Bi-exponential functions were used to fit the decay curve. The average lifetime was calculated by the following equation [17],

$$\tau_{avg} = \sum_{i=1}^2 A_i B_i^2 / \sum_{i=1}^2 A_i B_i \quad (1)$$

where, τ_{avg} is the average lifetime, and A_i and B_i are the amplitude and radiative lifetime, respectively. Time-resolved fluorescence lifetime spectroscopy reveals that all samples exhibit bi-exponential decay behavior, indicating the presence of two distinct recombination pathways (Table S6). The fast lifetime component (τ_1) is attributed to surface-related charge recombination, while the slower component (τ_2) corresponds to bulk or radiative recombination. Pristine BTO exhibits a relatively long average lifetime ($\tau_{ave} \sim 11.74$ ns), indicating a slow radiative recombination process. In contrast, CN shows a shorter lifetime of ~ 6.28 ns, reflecting faster recombination within the polymeric framework. Upon the formation of the heterojunction, the lifetimes decrease markedly, with $\langle \tau \rangle$ values of 7.12, 6.84, 4.73, and 5.46 ns for 0.5-CN/BTO, 1.5-CN/BTO, 2.5-CN/BTO, and 3.0-CN/BTO, respectively. The pronounced reduction in lifetime, particularly for 2.5-CN/BTO, likely reflects the opening of additional non-radiative pathways associated with interfacial charge transfer rather than solely increased recombination, as evidenced by the concurrent increase in photocatalytic activity [64].

3.13. Photocatalytic Performance

The photocatalytic activities of the samples were evaluated for sacrificial-agent-assisted H_2 evolution under light irradiation. Because methanol can contribute to H_2 formation even in the absence of a photocatalyst, a blank experiment was performed. In the absence of a photocatalyst, methanol produced 3 μmol of hydrogen over 5 h. Figure 9a–c compares the photocatalytic H_2 evolution activities of pristine BTO, CN, CN/BTO composites with different CN loadings, and Pt-decorated heterojunction under identical conditions. Bare BTO and CN exhibit low hydrogen production (33 $\mu\text{mol g}^{-1}$ in 5 h), confirming their limited charge separation efficiency when used individually. After coupling CN with BTO, a clear enhancement in hydrogen evolution is observed, demonstrating the beneficial role of heterojunction formation. Among all composites, 2.5-CN/BTO shows the highest intrinsic activity (5.6 times higher than CN and BTO), indicating that this composition provides the most favorable balance between light absorption, interfacial charge transfer, and active surface sites.

Upon *in-situ* photodeposition of Pt, the photocatalytic activity is markedly enhanced. The sample denoted as 0.5-Pt/2.5-CN/BTO was prepared using a nominal Pt precursor dosage of 0.5 wt%, while MP-AES analysis of the catalyst recovered after four photocatalytic cycles gave a Pt content of 0.39 wt%. Under identical reaction conditions, Pt-free 2.5-CN/BTO produces 186 $\mu\text{mol g}^{-1}$ H_2 over 5 h (37.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$), whereas 0.5-Pt/2.5-CN/BTO produces 1278 $\mu\text{mol g}^{-1}$ during the first 5 h (255.6 $\mu\text{mol g}^{-1} \text{h}^{-1}$), corresponding to an approximately 6.9-fold enhancement. This initial enhancement reflects the cocatalytic role of Pt in facilitating electron extraction and proton reduction [52]. However, the average activity of the Pt-containing catalyst during cycles 2–4 decreases to 67.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$, approximately 1.8 times the initial 5 h activity of Pt-free 2.5-CN/BTO. Thus, although Pt substantially enhances the initial activity, its advantage becomes considerably smaller during repeated operation and does not prevent progressive catalyst deactivation.

The time-dependent H_2 evolution of the Pt-modified 2.5-CN/BTO catalyst is distinctly non-linear, with H_2 production values of 768, 1023, 1119, 1179, and 1278 $\mu\text{mol g}^{-1}$ after 1–5 h, respectively (Table 1). Thus, the corresponding incremental production decreases markedly after the first hour, indicating a high initial activity followed by a lower H_2 -evolution regime. It should be noted that Pt photodeposition and H_2 evolution occur simultaneously in the present system; therefore, the first-hour value represents an initial reaction period involving *in-situ* formation of the Pt cocatalyst rather than a steady-state rate for a preformed Pt/CN/BTO catalyst. Post-reaction characterization reveals modification of the CN component together with limited localized association of Pt nanoparticles, suggesting that evolution of the catalyst surface and cocatalyst distribution may contribute to the change in activity. Time-dependent deactivation associated with changes in Pt and carbon-nitride surfaces has been reported for Pt/g- C_3N_4 photocatalysts [65]. However, the present post-reaction measurements do not allow the decrease within the first reaction cycle to be assigned to a single mechanism.

Figure 9d shows the cycling behaviour of the 0.5-Pt/2.5-CN/BTO photocatalyst over four consecutive H_2 -evolution cycles. H_2 production decreases markedly from 1278 $\mu\text{mol g}^{-1}$ in the first cycle to 360 $\mu\text{mol g}^{-1}$ in the second cycle, followed by values of 351 and 300 $\mu\text{mol g}^{-1}$ in the third and fourth cycles, respectively. Thus, the

largest activity loss occurs after the first cycle, while a further, slower decrease persists during subsequent cycling. Post-reaction P-XRD, ATR-FTIR, FE-SEM, and XPS consistently indicate structural and surface modification of the CN component, while TEM reveals localized clustering of Pt nanoparticles with retention of the crystalline BTO phase. These changes may collectively contribute to the observed deactivation, although their individual contributions cannot be distinguished from the present data. Accordingly, the cycling results indicate progressive catalyst deactivation rather than stable long-term performance.

The 0.5-Pt/2.5-CN/BTO photocatalyst shows an average H_2 evolution rate of $67.4 \mu\text{mol g}^{-1} \text{h}^{-1}$, calculated from cycles 2–4 and used in Table S7 to represent the post-first-cycle activity rather than the substantially higher initial-cycle value. Because the reported systems were evaluated under different irradiation sources, catalyst loadings, sacrificial agents, and reaction conditions, this comparison is intended only as a general benchmark. A direct AQY-based comparison was not made because the wavelength-resolved incident photon flux was not measured under the present broadband irradiation conditions.

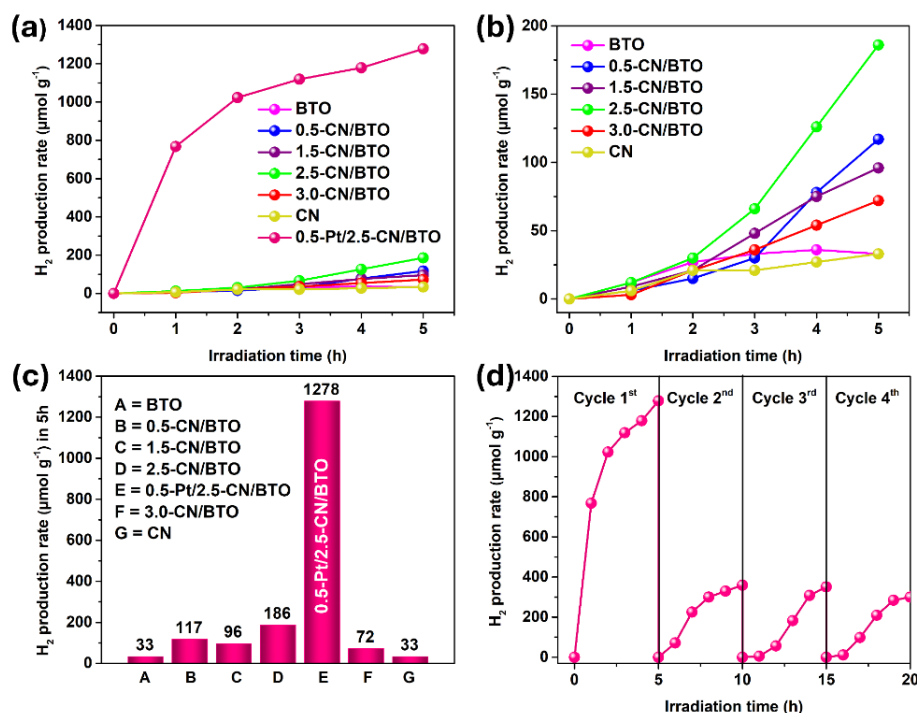


Figure 9. (a,b) Time-dependent production of H_2 in sacrificial-agent-assisted photocatalytic H_2 evolution; (c) Photocatalytic activity of the CN/BTO heterojunction, along with BTO and CN; (d) cycling behaviour of the 0.5-Pt/2.5-CN/BTO photocatalyst over four consecutive hydrogen-evolution cycles.

Table 1. Time-dependent H_2 production during 5 h of photocatalytic reaction in 20 vol% methanol–water solution under light irradiation.

Samples	H_2 Production ($\mu\text{mol g}^{-1}$)				
	1 h	2 h	3 h	4 h	5 h
BTO	12	27	33	36	33
0.5-CN/BTO	6	15	30	78	117
1.5-CN/BTO	9	21	48	75	96
2.5-CN/BTO	12	30	66	126	186
3.0-CN/BTO	3	21	36	54	72
CN	6	21	21	27	33
0.5-Pt/2.5-CN/BTO	768	1023	1119	1179	1278

3.14. Electron Paramagnetic Resonance (EPR) Analysis

The light-driven generation of reactive oxygen species (ROS) by the 2.5-CN/BTO photocatalyst was examined through EPR spectroscopy using DMPO as a spin-trapping agent (Figure 10). In the dark, no noticeable EPR signals are observed in either $\text{DMPO-O}_2^{\cdot-}$ and $\text{DMPO-}\cdot\text{OH}$ configurations, confirming that the composite does not spontaneously form radicals without illumination. Upon light exposure, distinct signals appear and progressively intensify with irradiation time, demonstrating efficient ROS generation under photocatalytic conditions.

In the DMPO- $\text{O}_2^{\cdot-}$ spectra (Figure 10a), a characteristic quartet with intensity variation (1:1:1:1) emerges after just 5 min of light exposure, indicating the formation of superoxide radicals by reduction of dissolved oxygen through photogenerated electrons (standard potential of $\text{O}_2/\text{O}_2^{\cdot-} = -0.33$ V vs. NHE) [66,67]. The signal becomes significantly stronger at 10 and 15 min, confirming continuous electron transfer to O_2 , a key step in maintaining charge flow within the heterojunction. The DMPO- $\cdot\text{OH}$ spectra (Figure 10b) also show the gradual appearance of the typical multiline hydroxyl radical pattern, with four distinct peaks in a 1:2:2:1 intensity ratio, as irradiation time increases. Formation of $\cdot\text{OH}$ arises from oxidation of surface-adsorbed water or hydroxide species by photogenerated holes (standard potential of $\text{H}_2\text{O}/\cdot\text{OH} = +1.99$ V vs. NHE) [66,67]. The stronger $\cdot\text{OH}$ signal at prolonged irradiation reflects the efficient utilization of holes and the high oxidative capability of the composite. The valence band of CN lies at a more negative potential (+1.98 V vs. NHE) than the $\cdot\text{OH}/\text{OH}^-$ (+2.38 V vs. NHE) and $\cdot\text{OH}/\text{H}_2\text{O}$ (+1.99 V vs. NHE) redox couples; it is therefore not thermodynamically capable of directly oxidizing water or hydroxide ions to generate hydroxyl radicals. As a result, direct $\cdot\text{OH}$ formation from water is unlikely. It suggests that photogenerated holes predominantly reside on BTO, which possesses a higher oxidation potential (+2.63 V vs. NHE), which is sufficiently oxidizing to convert H_2O or OH^- into $\cdot\text{OH}$, in agreement with the DMPO- $\cdot\text{OH}$ signals observed in water.

Thus, the detection of DMPO- $\text{O}_2^{\cdot-}$ and DMPO- $\cdot\text{OH}$ spin adducts, together with the measured band positions, is consistent with spatially separated redox sites in the CN/BTO system, which is consistent with a Z-scheme-like charge-transfer scenario, where electrons are preferentially available on CN and the holes are retained on BTO.

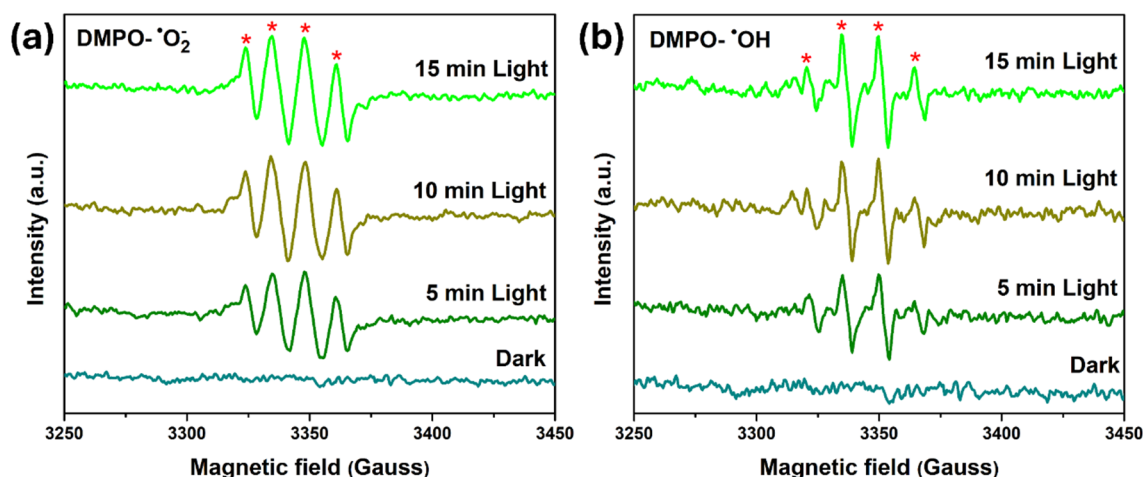


Figure 10. EPR spectra of (a) DMPO- $\text{O}_2^{\cdot-}$ (methanol dispersion) and (b) DMPO- $\cdot\text{OH}$ (aqueous dispersion) spin adduct under light irradiation with DMPO spin trapping.

3.15. Post-Reaction Characterization

3.15.1. P-XRD Analysis

The P-XRD patterns of the fresh and post-reaction samples are shown in Figure 11a. The characteristic reflections of the Aurivillius BTO phase remain clearly visible after photocatalysis, indicating retention of the crystalline BTO structure during the reaction. In contrast, changes are observed mainly in the diffraction features associated with the CN component. A reflection near 12.8° becomes more evident after photocatalysis and is associated with in-plane ordering of the heptazine-based units of carbon nitride [29]. The CN-related stacking reflection around 27.3° also changes in intensity after reaction, indicating modification of the stacking arrangement of the carbon-nitride layers.

An additional feature appears around 23.8° in the post-reaction samples. Since this reflection cannot be assigned unambiguously to a specific carbon-nitride-derived phase, it is denoted as a CN-derived feature in Figure 11a [68]. Its appearance, together with the changes observed at approximately 12.8° and 27.3° , indicates alteration of the structural organization of the CN component during photocatalysis. These results therefore support structural reorganization of carbon nitride rather than complete decomposition, while the precise molecular transformation cannot be determined from the XRD data alone.

No resolvable diffraction peaks corresponding to metallic Pt are observed in the sample recovered after four cycles. This is consistent with the low Pt content of the recovered catalyst (0.39 wt% by MP-AES) and the nanoscale Pt particles observed by TEM.

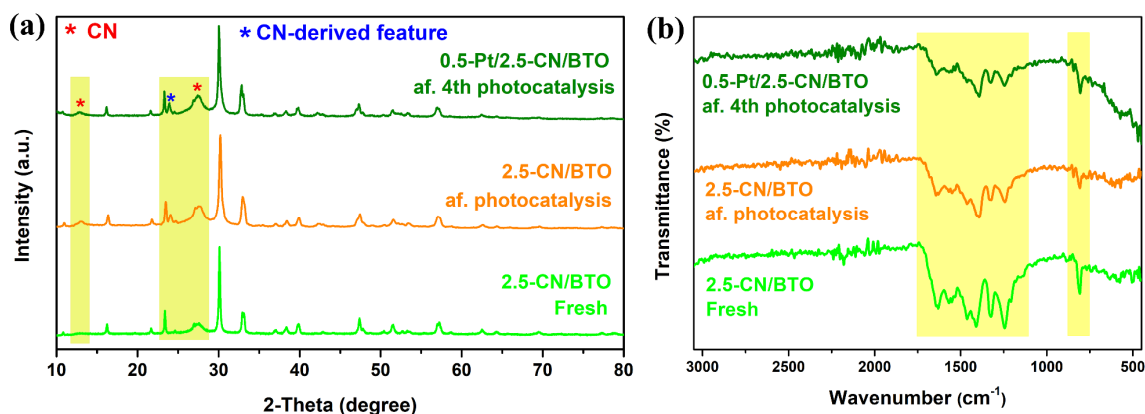


Figure 11. Structural and vibrational characterization of fresh and post-photocatalysis CN/BTO samples: (a) P-XRD patterns and (b) ATR-FTIR spectra of fresh 2.5-CN/BTO, Pt-free 2.5-CN/BTO recovered after one photocatalytic cycle, and 0.5-Pt/2.5-CN/BTO recovered after four photocatalytic cycles. The marked regions indicate changes associated with the CN component.

3.15.2. FT-IR Analysis

Complementary information on changes in the CN bonding environment was obtained from ATR-FTIR spectroscopy (Figure 11b). Fresh 2.5-CN/BTO exhibits the characteristic C–N/C=N stretching vibrations of the carbon-nitride framework in the 1200–1650 cm^{-1} region [46]. These vibrations remain present in the Pt-free 2.5-CN/BTO sample after one photocatalytic cycle and in the Pt-containing catalyst recovered after four cycles, showing that the carbon-nitride component is retained after photocatalysis. However, noticeable changes in the relative intensities and overall profile of these bands are observed after reaction, indicating modification of the local bonding environment and structural organization of the CN component.

The feature around 800 cm^{-1} also remains detectable after photocatalysis. Since this region contains overlapping contributions from the characteristic ring vibration of carbon nitride and Ti–O-related vibrations of BTO, changes in this band are not used independently to assign structural transformation of CN. Similarly, the broad changes observed at lower wavenumbers in the four-cycle Pt-containing sample are not assigned to the formation of a new phase because no distinct diagnostic vibration is observed.

Overall, the XRD and FT-IR results consistently show that the BTO crystalline phase is retained while the carbon-nitride component undergoes structural and bonding modifications during photocatalysis. Together with the post-reaction XPS and electron-microscopy results, these observations provide evidence for structural reorganization of CN during cycling, although the exact molecular transformation pathway cannot be established from the present data.

3.15.3. SEM Analysis

SEM imaging (Figure S4) provides additional information on the morphological changes observed after photocatalysis. Compared with the fresh composite (2.5-CN/BTO), the spent catalyst (0.5-Pt/2.5-CN/BTO) shows a more heterogeneous surface morphology, with thinner, wrinkled, and fragmented sheet-like regions becoming more apparent. Curled flakes and smaller platelet-like features are also observed in several areas. These morphological changes are consistent with modification of the CN component suggested by the post-reaction P-XRD results. However, phase-specific changes cannot be assigned solely from the SEM images, and the retention of the BTO phase is therefore discussed on the basis of the complementary XRD and TEM analyses.

3.15.4. TGA Analysis

The TGA profiles (Figure S5) of fresh composite (2.5-CN/BTO), and the spent catalyst (0.5-Pt/2.5-CN/BTO) indicate that the principal decomposition of the CN component occurs within the 500–650 $^{\circ}\text{C}$ range, confirming its retention after cycling. The post-reaction material displays a slightly earlier decomposition onset and a somewhat greater mass loss, indicating altered thermal behaviour of the CN-containing component after photocatalysis. This trend is consistent with the structural and morphological modifications observed by P-XRD and FE-SEM. Because TGA does not provide phase-specific molecular information, the change is not assigned to a particular CN-derived intermediate. The residual mass associated with BTO remains largely unchanged.

3.15.5. TEM Analysis

The TEM analysis of the spent 0.5-Pt/2.5-CN/BTO photocatalyst after four consecutive photocatalytic cycles is shown in Figure 12. The low-magnification image in Figure 12a provides an overview of the recovered catalyst, while the enlarged image in Figure 12b shows a CN-rich region with a more discontinuous and irregular nanosheet morphology than that observed in the fresh composite. This change is consistent with the structural modification of the CN component indicated by the post-reaction XRD and FE-SEM results. The dark-field image in Figure 12c highlights bright nanoscale features distributed within the CN-rich region, and HRTEM analysis in Figure 12d confirms the presence of Pt nanoparticles on CN. Some particles remain well separated, whereas localized groups of closely associated nanoparticles are also observed, indicating limited agglomeration in certain regions. The lattice-fringe analysis in Figure 12e gives an interplanar spacing of 0.196 nm, corresponding to the Pt (200) plane [69]. The particle-size distribution shown in Figure 12f gives an average Pt nanoparticle size of 2.8 ± 0.04 nm. Figure 12g shows well-resolved lattice fringes with a spacing of approximately 0.326 nm, which is assigned to the BTO (115) plane, confirming the presence of crystalline BTO after repeated photocatalytic cycling. Overall, the post-reaction TEM results show that nanosized Pt remains present on the CN-rich regions and that crystalline BTO is retained, while the CN morphology undergoes noticeable modification. The observed Pt localization on CN is consistent with preferential electron accumulation on the CN side of the heterostructure and, together with the EPR results and band-position analysis, supports the proposed direct Z-scheme charge-transfer pathway.

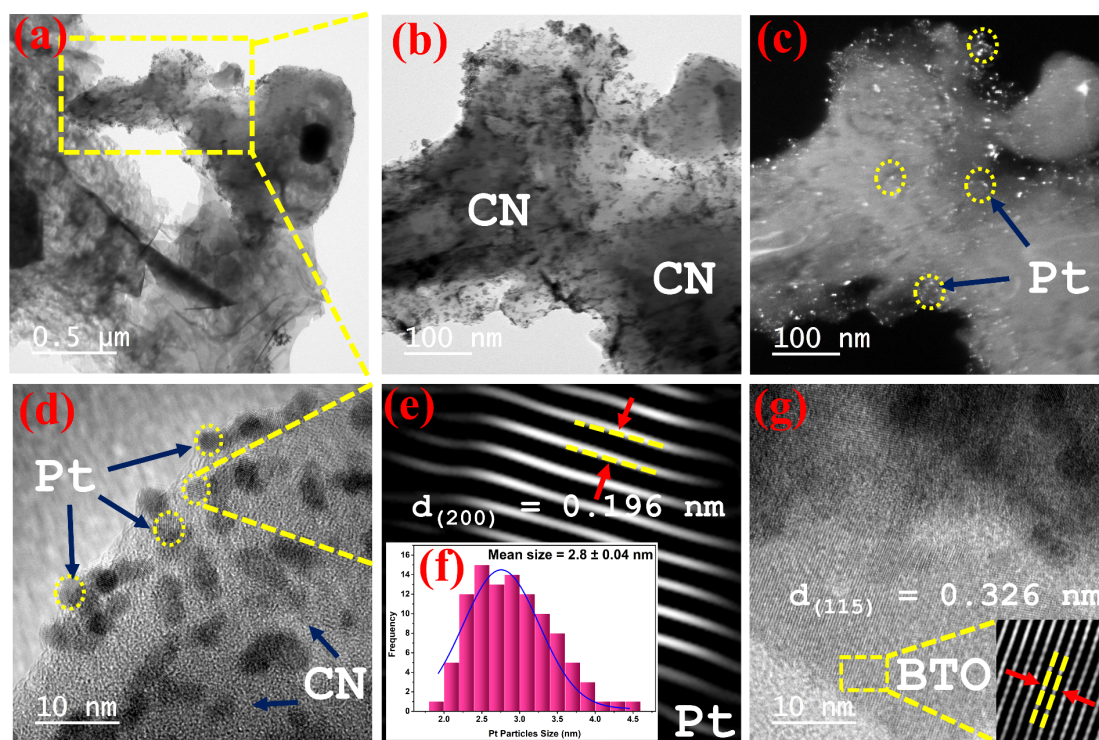


Figure 12. TEM analysis of spent 0.5-Pt/2.5-CN/BTO after four consecutive photocatalytic H₂-evolution cycles with in situ Pt photodeposition: (a,b) TEM images, (c) DF-TEM image, (d) HR-TEM image, (e) IFFT pattern showing lattice fringes of Pt NPs, (f) Gaussian-fitted histogram of Pt particle-size distribution, and (g) HR-TEM image with corresponding IFFT patterns.

3.15.6. XPS Analysis

XPS analysis (Figure S6) provides further evidence of the changes occurring in the spent 0.5-Pt/2.5-CN/BTO photocatalyst after four cycles. After photocatalysis, the C 1s spectrum (Figure S6e) of 0.5-Pt/2.5-CN/BTO retains the characteristic carbon nitride features at ~288.0 eV, assigned to (N)₂C=N species in heptazine units, and at ~284.8 eV corresponding to adventitious or graphitic carbon. Additionally, two new components appear at ~286.2 eV and ~290.2 eV. The contribution at ~286.2 eV is assigned to C–NH₂ species, consistent with terminal amino groups at the edges of the carbon-nitride framework [70]. The high-binding-energy component at ~290.2 eV is attributed to a π – π^* shake-up satellite associated with the conjugated heptazine network. The emergence of these components after photocatalysis indicates a change in the local carbon environment of CN, with an increased contribution from

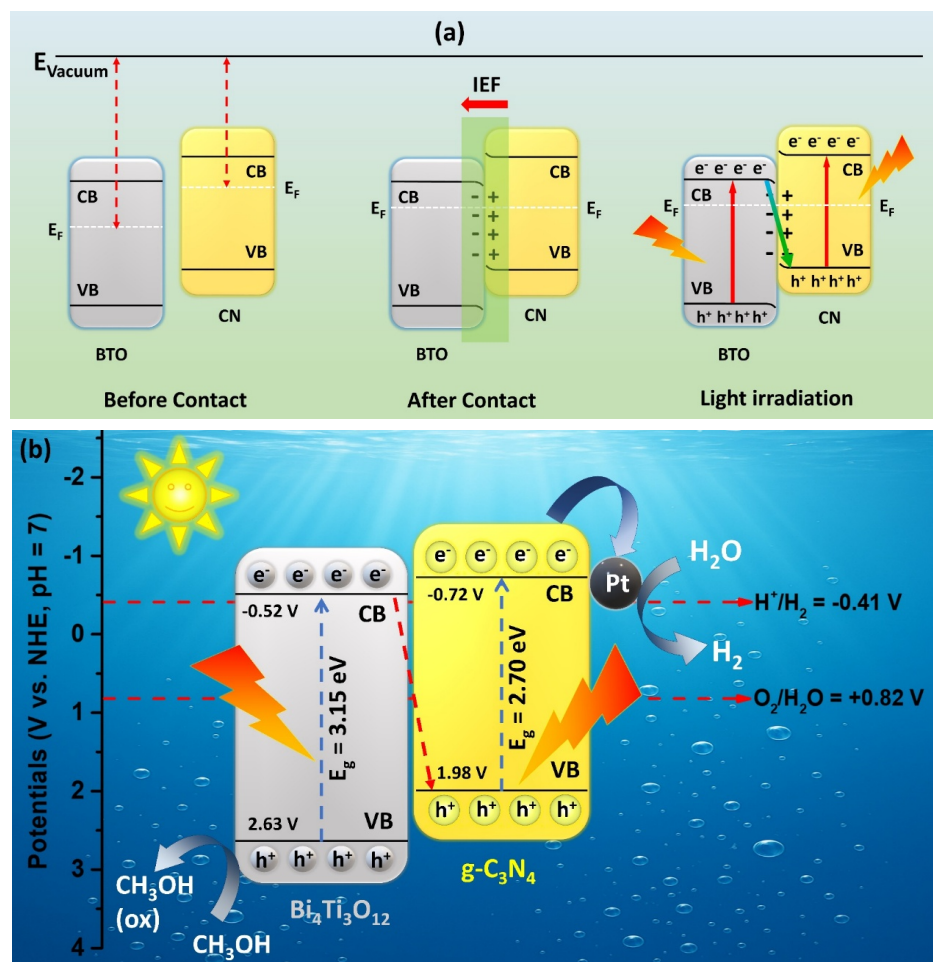
terminal amino functionalities and changes in the conjugated CN environment. This is consistent with the structural reorganization indicated by the P-XRD and FT-IR results.

Quantitative XPS analysis shows that the sensitivity-factor-corrected surface C/N atomic ratio decreases from 1.80 for fresh 2.5-CN/BTO to 1.50 for spent 0.5-Pt/2.5-CN/BTO after four photocatalytic cycles. Together with the changes in the C 1s spectrum, this decrease indicates a measurable modification of the CN surface composition and bonding environment during cycling.

The Bi 4f, Ti 2p and O 1s spectra retain the characteristic BTO-related chemical states after photocatalysis, supporting the persistence of the BTO component in the recovered catalyst. The metallic Bi⁰ feature observed in pristine BTO disappears after photocatalysis, consistent with re-oxidation of surface Bi species under the reaction conditions. Simultaneously, the low-binding-energy O 1s component, previously associated with lattice oxygen adjacent to reduced metal–O environments, vanishes, consistent with re-oxidation or modification of oxygen-deficient surface sites during photocatalytic operation. The appearance of metallic Pt⁰ signals in the Pt 4f region confirms the successful *in-situ* photodeposition of Pt nanoparticles on the heterojunction surface during hydrogen evolution [52].

3.16. Plausible Mechanism

A plausible sacrificial-agent-assisted photocatalytic H₂ evolution mechanism is shown in Scheme 2. Before contact, BTO and CN possess different work functions and Fermi-level positions, as determined from UPS measurements. BTO exhibits a higher work function (5.37 eV) than CN (5.12 eV), indicating that its Fermi level lies deeper below the vacuum level. Upon forming intimate contact in the heterojunction, electrons spontaneously flow from CN (higher Fermi level) to BTO (lower Fermi level) until thermodynamic equilibrium is reached. This charge redistribution results in Fermi-level alignment at the interface and induces band bending on both sides (upward band bending in CN and downward band bending in BTO at the interface), generating an internal electric field directed from CN to BTO [17,71].



Scheme 2. Schematic diagram of (a) charge transfer route between BTO and CN; (b) the mechanism of the Z-scheme g-C₃N₄/Bi₄Ti₃O₁₂ heterojunction for sacrificial-agent-assisted photocatalytic H₂ evolution.

Under light irradiation, both semiconductors are photoexcited. Due to the established Fermi level equilibrium and internal electric field, photogenerated electrons in BTO preferentially migrate toward the interface and recombine with holes in the valence band of CN. This interfacial recombination preserves the high reduction potential of electrons in the conduction band of CN (-0.72 V vs. NHE) and the strong oxidation ability of holes in the valence band of BTO ($+2.63$ V vs. NHE). Consequently, spatially separated charge carriers with strong redox power are retained, which is characteristic of a direct Z-scheme charge-transfer pathway. The conjugated π -network of CN provides delocalized electronic states capable of stabilizing photogenerated electrons, whereas the oxide lattice of BTO favors hole localization due to its deeper valence band. This charge carrier migration across the heterojunction interface underpins the observed carrier separation and subsequent photocatalytic activity.

During photocatalysis, Pt nanoparticles formed by *in-situ* photodeposition are selectively anchored on CN, indicating that photoexcited electrons are preferentially accumulated on the CN surface. These photoexcited electrons are efficiently transferred from CN to Pt, where they reduce protons to H_2 . The preferential Pt anchoring on CN supports electron accumulation on CN and is more consistent with a direct Z-scheme than a conventional type-II pathway. Simultaneously, holes retained in the VB of BTO are rapidly consumed by methanol, which acts as a sacrificial hole scavenger, suppressing charge recombination and accelerating continuous hydrogen evolution. This work provides a practical route to Z-scheme heterojunctions with improved H_2 evolution performance.

4. Conclusions

A Pt-modified CN/BTO heterojunction was successfully developed through thermal coupling of g- C_3N_4 with $Bi_4Ti_3O_{12}$ followed by *in-situ* photodeposition of Pt. Among the investigated compositions, 2.5-CN/BTO showed the most favorable photocatalytic response, reflecting an effective balance between light absorption, interfacial charge transfer, and accessible reaction sites. Pt incorporation further enhanced H_2 evolution, yielding $1278 \mu\text{mol g}^{-1}$ within the initial 5 h of irradiation. The cycling experiments, however, revealed a pronounced loss of activity after the first cycle, followed by a slower decline during subsequent operation, indicating that the enhanced initial activity is not fully retained on reuse. Post-reaction characterization shows that the BTO crystalline framework remains largely preserved, whereas the CN component undergoes structural and surface reorganization and the Pt nanoparticles exhibit localized clustering. These observations suggest that changes within the CN-rich surface environment and cocatalyst distribution contribute to the loss of photocatalytic performance during repeated operation. Overall, the study demonstrates the potential of combining layered $Bi_4Ti_3O_{12}$ with g- C_3N_4 and *in-situ* Pt deposition for promoting H_2 evolution, while highlighting the need to improve the structural durability of the CN-containing interface for sustained photocatalytic performance.

Supplementary Materials

The additional data and information can be downloaded at: <https://media.scilit.com/articles/others/2609111349569610/Photocatalysis-26060193-SM.pdf>. Figure S1: Optical images showing the physical appearance of (a) BTO; (b) 0.5-CN/BTO; (c) 1.5-CN/BTO; (d) 2.5-CN/BTO; (e) 3.0-CN/BTO; and (f) CN. Figure S2: Experimental set-up used for the photocatalytic H_2 -evolution tests. Figure S3: Survey XPS of BTO, CN, and 2.5-CN/BTO heterojunction. Figure S4: (a–d) FE-SEM images of the spent 0.5-Pt/2.5-CN/BTO heterojunction after four cycles of sacrificial-agent-assisted photocatalytic H_2 evolution. Figure S5: TGA of fresh 2.5-CN/BTO and spent 0.5-Pt/2.5-CN/BTO heterojunction catalyst. Figure S6: (a) XPS Survey scan and High-resolution XPS of (b) Bi 4f; (c) Ti 2p; (d) O 1s; (e) C 1s; (f) N 1s; and (g) Pt 4f for spent 0.5-Pt/2.5-CN/BTO heterojunction catalyst after four consecutive cycles of photocatalytic H_2 -evolution. Table S1: Mass% and weight% of g- C_3N_4 content in CN/BTO heterojunctions. Table S2: XPS binding energies of Bi4f, Ti2p, O1s, C1s, and N1s for BTO, 2.5-CN/BTO and CN. Table S3: Absorption edge and estimated optical transition energies of BTO, CN, and CN/BTO heterostructures. Table S4: Surface area, total pore volume, and mean pore size (pore diameter) of BTO, CN, and CN/BTO heterojunctions. Table S5: Equivalent circuit fitting parameters of EIS data of BTO, CN, and CN/BTO heterojunctions. Table S6: Summary of the photoluminescence decay time (τ) and their pre-exponential factor (B) of BTO, CN, and CN/BTO heterojunctions. Table S7: Comparison of the photocatalytic H_2 -evolution performance of representative g- C_3N_4 - and $Bi_4Ti_3O_{12}$ -based photocatalysts with and without Pt cocatalysts. References [72–76] are cited in supplementary materials.

Author Contributions

P.C.: Conceptualization, investigation, data analysis, and writing of the original draft. V.K.: Conceptualization, supervision, data analysis, reviewing, and editing of the manuscript. T.K.M.: Conceptualization, supervision, data analysis, reviewing, and editing of the manuscript. The manuscript was written through the contributions of all authors. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

Raw data are available from the authors upon request.

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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