



Highly selective solar CO₂ conversion into ethanol over metal-free sulfonated g-C₃N₄/nitrogen doped reduced graphene oxide hybrid photocatalyst

Sachin G. Ghugal^a, Amol U. Pawar^a, Park Kyoung Mo^a, Poonchi Sivasankaran Ramesh^a, Harish Reddy Inta^a, Sanjeev Gupta^a, Sung-hoon Oh^a, Muhammad Zaeem Azam Khan^a, Young Seok Son^a, Hyunchul Shin^b, Hongxian Han^c, Young Soo Kang^{a,*}

^a Carbon Resources Conversion Research Center, Environmental & Climate Technology, Korea Institute of Energy Technology (KENTECH), 21 Kentech-gil, Naju, 58330, Republic of Korea

^b EST Energy, Jinsun Building, 28, Tekeunosaneop-ro 81beon-gil, Nam-gu, Ulsan, Republic of Korea

^c Laboratory of Catalysis for Energy and Resources, College of Sciences, Yanbian University, Yanji, Jin Province, 133002, PR China

ARTICLE INFO

Keywords:

Photocatalytic CO₂ reduction
SO₃H-g-C₃N₄/N-rGO hybrid
Proton-electron transport pathways
Ethanol selectivity
Solar fuel production

ABSTRACT

Photocatalytic conversion of CO₂ into C₂ fuels such as ethanol is more valuable compared to C₁ products owing to their higher energy density and commercial value. Achieving high C₂ selectivity requires tuning the thermodynamic CO₂ reduction reaction (CO₂RR) energy landscape and enabling sequential transfer of twelve electrons and twelve protons for ethanol formation, which demands efficient CO₂ capture and activation, a lowered activation barrier for the rate-determining step, and independently tailored, high-conductivity electron and proton transport pathways. In this study, a hybrid photocatalyst comprising sulfonated g-C₃N₄ (SO₃H-g-C₃N₄) and nitrogen-doped reduced graphene oxide (N-rGO) was designed to establish these two distinct transport pathways. Sulfonate (-SO₃H) groups on g-C₃N₄ provide a high-conductivity proton transport channel, while nitrogen sites on rGO, bearing a non-bonding electron pair, adsorb and activate CO₂ while enabling efficient multi-electron accumulation and transfer. The synergistic integration of tuned conduction band energetics with these dual transport pathways enabled the optimized 2S-g-C₃N₄/1N-rGO-10 hybrid to achieve a CO₂RR overpotential of 1.25 kJ mol⁻¹ compared to 4.63 kJ mol⁻¹ for pristine g-C₃N₄ and an activation energy of 57.11 kJ mol⁻¹ compared to 74.21 kJ mol⁻¹, delivering ethanol as the dominant liquid product at 10.6 μmol g⁻¹ h⁻¹. DFT calculations identified pyridinic-N as the most active CO₂ adsorption site and established a thermodynamically favourable reaction pathway toward ethanol, while *in-situ* ATR-IR spectroscopy confirmed key intermediates, including *COOH, *CHO, and *CO-*CHO, consistent with the proposed mechanism. These findings provide a rational design strategy for dual-pathway photocatalysts for selective solar-driven CO₂ to liquid fuel conversion.

1. Introduction

A major reason for climate change is assumed to be the rising atmospheric carbon dioxide (CO₂) concentration levels caused by human activity, which requires creative approaches for carbon capturing, storage and conversion [1,2]. Photocatalytic CO₂ conversion into fuels holds promise as a sustainable way for mitigating CO₂ emissions and producing renewable energy sources, through upcycling of atmospheric CO₂, capturing and conversion into value-added fuels and chemicals [3,4]. To accomplish high efficiency in CO₂ reduction reaction (CO₂RR),

it is crucial to design a system that possesses highly active sites capable of effectively capturing and activating CO₂ in the reactant state while simultaneously lowering the transition state energy of rate determining step, thereby reducing both reaction energy and activation energy of CO₂RR. The product selectivity can be controlled by two most critical parameters, such as the number of electrons and protons for CO₂RR and the thermodynamic CO₂RR energy optimization of the transporting electrons, matching with the selected CO₂RR product. The thermodynamic CO₂RR energy and different transporting numbers of electrons and protons can enhance the efficiency of CO₂RR and its product

* Corresponding author.

E-mail address: yskang@kentech.ac.kr (Y.S. Kang).

<https://doi.org/10.1016/j.cej.2026.179827>

Received 26 January 2026; Received in revised form 17 July 2026; Accepted 22 July 2026

Available online 24 July 2026

1385-8947/© 2026 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

selectivity [5]. The highly efficient CO₂RR system and pathways during CO₂RR also critically affect the efficiency and product selectivity [5,6].

The organic semiconductors made of earth-abundant and light-weight elements are potential candidates for photocatalytic CO₂RR. Among them, two-dimensional (2D) layered semiconductor graphitic carbon nitride (g-C₃N₄) is a promising photocatalyst as its metal-free composition, visible-light-responsive organic semiconductor with a moderate bandgap (~2.7 eV), superior chemical and thermal stability, low cost, environmentally friendly intrinsic and appropriate electronic properties with sufficiently strong CO₂ reducing potential [7,8]. However, practical application of g-C₃N₄ in photocatalytic CO₂RR is hindered by inherently low surface area, poor electron transport charge capacity and insufficient proton transporting ability, which hinders and suppresses the formation of liquid fuel product of CO₂RR [9–11]. To overcome these limitations, integrating a nitrogen-doped reduced graphene oxide (N-rGO) layer with a g-C₃N₄ layer in a hybrid photocatalytic system can offer a promising strategy, providing the benefits of a metal-free catalyst that can significantly enhance CO₂RR efficiency for the production of selective liquid fuels [6,12,13].

Surface functionalization with sulfonate groups plays a vital role in enhancing proton transport ability into the CO₂RR site. The introduction of -SO₃H groups provides Brønsted acidic sites that act as local proton transporting media by diffusion, facilitating proton-coupled electron transfer (PCET) processes for CO₂RR [14–16]. This modification creates more favourable proton transport pathways, which are essential for generating liquid fuel products during CO₂RR, ultimately improving catalytic efficiency. In parallel, N-rGO can serve as an ideal functional layer for constructing a hybrid with g-C₃N₄ due to its excellent electrical conductivity, high charge storage capacity, large specific surface area, and chemically adaptable surface functionalities [12,17]. These properties enable N-rGO to act as an efficient charge mediator, promoting rapid separation of photogenerated charge carriers. This facilitates efficient photoelectron transfer and accumulation, enabling effective multi-electron shuttling for the enhanced CO₂RR [14,16]. Nitrogen doping into reduced graphene oxide (rGO) introduces nitrogen active sites for CO₂RR, which can play a crucial role in CO₂ capturing and activation for enhancing CO₂RR efficiency [18]. The lone electron pair on nitrogen facilitate efficient CO₂ capturing by making a Lewis base-Lewis acid complex with linear CO₂ molecule, resulting in an activated bent CO₂ molecule in the reactant state, weakening the C=O bonds and transforming it into a more reactive intermediate by resulting partial charge separated complex [16,19]. This activation step is critical in facilitating the transformation of linear CO₂ into reactive intermediates as a bent structure, thus enhancing CO₂RR efficiency through the multi-electron and multi-proton transport for efficient CO₂RR for liquid fuel production.

This study aims to develop a highly efficient and selective solar-driven CO₂ conversion system based on a sulfonate-functionalized g-C₃N₄ (SO₃H-g-C₃N₄)/N-rGO hybrid photocatalyst. The system is designed to create different proton and electron transport channels by introducing -SO₃H groups on g-C₃N₄ to facilitate proton transport and integrating an N-rGO functional layer for multi-electron transport. These modifications aim to enhance the efficiency and selectivity of CO₂RR for liquid fuel ethanol production. The surface concentration of sulfonate groups on g-C₃N₄ was optimized by varying the amount of chlorosulfonic acid (0.5–3 mL), with the final content determined via titration. Similarly, the nitrogen content in N-rGO was adjusted by controlling the amount of urea, which served as a nitrogen source, calculated based on the weight percentage of graphene oxide (GO) and verified using XPS analysis. The SO₃H-g-C₃N₄/N-rGO hybrid photocatalyst was prepared by integrating the SO₃H-g-C₃N₄ layer with an optimum concentration of sulfonate groups at the interface junction with N-rGO, featuring an optimized N atom concentration for efficient CO₂ capturing and activation, along with high conductivity and large charge capacity. The weight ratio of the N-rGO layer to the SO₃H-g-C₃N₄ layer was further optimized to maximize photocatalytic CO₂RR

performance. The optimized weight ratio (w/w, 90/10) of SO₃H-g-C₃N₄/N-rGO hybrid photocatalyst demonstrated the enhanced ethanol product selectivity in photocatalytic CO₂RR over formaldehyde as liquid products. Furthermore, *in-situ* ATR-IR analysis of photocatalytic CO₂RR over the SO₃H-g-C₃N₄/1N-rGO hybrid photocatalyst was performed to elucidate the intermediates involved in ethanol and formaldehyde formation. The designed SO₃H-g-C₃N₄/N-rGO hybrid photocatalyst offers a promising strategy to address current limitations of CO₂RR, offering a sustainable way for an efficient solar-to-fuel conversion system with high selectivity toward ethanol production.

2. Experimental section

2.1. Chemicals and materials

Urea (NH₂CONH₂, 99%, Sigma-Aldrich), chlorosulfonic acid (ClSO₃H, 99%, Sigma-Aldrich), potassium bicarbonate (KHCO₃, 99.7%, Sigma-Aldrich), dichloromethane (CH₂Cl₂, anhydrous, Sigma-Aldrich, 99.8%), *N,N*-Dimethylformamide (HCON(CH₃)₂, anhydrous, Sigma-Aldrich, 99.8%), methanol (Duksan, 99.8%), graphite flakes (Aldrich), KMnO₄, 99%, Sigma-Aldrich), H₃PO₄, Extra pure grade, Duksan), H₂SO₄, 95–98%, Sigma-Aldrich), HCl, 35–37%, Samchun), NaOH, > 98%, pellets, anhydrous), phenolphthalein indicator (Aldrich, 0.5 wt% ethanol: water (1:1), H₂¹⁸O (>97 atom% ¹⁸O, Sigma-Aldrich). All experiments were conducted using distilled water, and all chemicals used were of analytical grade and employed directly without any additional purification steps.

2.2. Synthesis of g-C₃N₄ and -SO₃H group functionalised g-C₃N₄

g-C₃N₄ was synthesised via thermally induced copolymerization using urea as a precursor [20]. Specifically, urea was heated in air at 550 °C for 2 h with the temperature increased at a controlled rate of 5 °C min⁻¹. The obtained pale-yellow solid product was then finely crushed using a mortar and pestle. The different SO₃H-g-C₃N₄ was synthesised by varying the volume of chlorosulfonic acid (0.5–3 mL). Briefly, g-C₃N₄ (~0.5 g) was dispersed in 25 mL of DCM in a glass beaker and stirred continuously to form a uniform suspension. A measured volume of chlorosulfonic acid (0.5–3 mL) was carefully introduced dropwise into the g-C₃N₄ suspension. Before the addition of chlorosulfonic acid, the g-C₃N₄ suspension in DCM was maintained below 5 °C through cooling with ice during the addition process. The suspension was then stirred at room temperature for 6 h, and washed with methanol thrice and dried in a vacuum oven for 6 h at 80 °C. The prepared sulfonated g-C₃N₄ were labelled as 0.5S-g-C₃N₄, 1S-g-C₃N₄, 1.5S-g-C₃N₄, 2S-g-C₃N₄, and 2.5S-g-C₃N₄, respectively.

2.2.1. Synthesis of graphene oxide (GO), reduced graphene oxide (rGO) and N-doped reduced graphene oxide (N-rGO)

GO sheets were synthesised by using graphite flakes via the Tour method, with fewer modifications [21]. In brief, 3 g of graphite flakes with 18 g of KMnO₄ were uniformly mixed. Separately, a 9:1 volume ratio mixture of H₂SO₄ (360 mL, 96%) and H₃PO₄ (40 mL, 75%) was prepared in a 500 mL beaker and added batch-wise to the prepared graphite-KMnO₄ mixture. After complete addition, the mixture was mixed at 50 °C for 12 h. After the reaction was completed, the reaction mixture was transferred into 400 mL of ice-cooled water, and an addition of 10 mL of hydrogen peroxide was performed in the reaction solution. The resulting dispersion was washed repeatedly with a mixed solution of HCl: water (v/v, 9:1) to remove metal ions and other residues. Ethanol washing was carried out to eliminate residual acid and oxide impurities, followed by freeze-drying the sample for 24 h.

Nitrogen doping into the synthesised GO samples was performed via a solvothermal reaction by taking a calculated amount of urea as a nitrogen source and reducing agent [18]. A measured amount of GO powder was dispersed in 30 mL of DMF and sonicated for 15 min to

obtain a homogeneous suspension. To this, a known amount of urea (GO: urea weight% ratio as 1:0, 1:0.05, 1:1, 1:3, and 1:5) was added to the dispersion and subsequently sonicated for 15 min to ensure thorough homogenization. The resulting solution was placed in a 100 mL Teflon-lined stainless-steel autoclave, which was securely sealed and subjected to heating in an air oven at 150 °C for 24 h. After 24 h, the autoclave was left to cool naturally to room temperature. The obtained sample was collected and washed thoroughly with methanol to eliminate any remaining organic impurities. The obtained samples were labelled as 0.05N-rGO, 1N-rGO, 1.5N-rGO, 3N-rGO, 5N-rGO, and 7N-rGO, respectively. For comparison, rGO was prepared via a similar procedure without urea addition.

2.2.2. Synthesis of SO_3H functionalised g- C_3N_4 /nitrogen doped rGO hybrid

A known weight (0.5 g) of sulfonated g- C_3N_4 was immersed in 25 mL of isopropanol, followed by sonication for 20 min to get a homogeneous dispersion. A calculated amount of nitrogen-doped rGO (1N-rGO, weight % sulfonated g- C_3N_4) was mixed to suspension and sonicated for 20 min to achieve homogenization. The sulfonated g- C_3N_4 /1N-rGO dispersion was heated at 80 °C for 1 h followed by natural cooling. Finally, the obtained dispersion was centrifuged and dried at 80 °C for 3 h in a vacuum oven. Here, 1N-rGO loading was adjusted to produce distinct sulfonated g- C_3N_4 /1N-rGO-x hybrid where x = 1, 5, 10, 15, 30, and 50 wt% of 1N-rGO.

2.3. Characterization

The structural characteristics of the synthesised samples were analyzed by X-ray diffraction (XRD) using Rigaku Ultima 2000 operated in 2 θ mode with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The measurements were carried out over a 10°–80° range with a scan rate of 0.5° min^{−1}. An attenuated total reflectance-infrared ATR-IR spectrometer (FT-IR, Thermo Fisher Scientific Inc.) was used to record spectra. The surface morphology and elemental composition of the prepared samples were examined with a field-emission scanning electron microscope (FE-SEM, Hitachi SU8600) equipped with a cold cathode field emission source and an energy-dispersive X-ray spectroscopy (EDX) detector (Oxford Instruments). Transmission electron microscopy (TEM) and high-resolution TEM/HRTEM (JEOL JEM-2200FS) with spherical aberration (Cs) correction and selected area electron diffraction (SAED) were used to evaluate crystal structure and lattice spacing. High-angle annular dark-field STEM (HAADF-STEM) imaging and STEM-EDS elemental mapping were carried out using a double aberration-corrected system (Spectra Ultra, Thermo Fisher Scientific, 300 kV). Data collection and analysis were conducted with Velox software (Thermo Scientific) at the KENTECH Center for Shared Research Equipment. UV–visible diffuse reflectance spectra (UV–Vis DRS) were performed with a Shimadzu UV-2600 spectrophotometer with an integrating sphere over a 200–800 nm wavelength range. Steady-state photoluminescence (PL) spectra were recorded at room temperature on a HORIBA FluoroMax-4 spectrofluorometer. Time-resolved photoluminescence (TR-PL) spectra and fluorescence lifetime imaging microscopy (FLIM) were obtained on a MicroTime-200 confocal platform (PicoQuant) operated in time-correlated single photon counting (TCSPC) mode. The samples were excited with a single-mode pulsed diode laser operating at 375 nm, with a pulse width of 30 ps and a power of approximately 5 μW . The detection path comprised a 150 μm pinhole, a 375 nm dichroic mirror (Z375RDC, AHF), a 405 nm long-pass emission filter (HQ405lp, AHF), and an avalanche photodiode detector (PDM series, Micro Photon Devices). Ultraviolet photoelectron spectroscopy (UPS) was performed on a Kratos Ultra DLD using a He discharge lamp. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo Scientific Nexsa G2 spectrometer equipped with a monochromatic Al K α radiation source. The analysis was conducted under high vacuum conditions to obtain high-resolution spectra for accurate identification of surface elemental composition and chemical states. Thermo Scientific Avantage and CASA

XPS were used for data analysis and fitting profile peaks.

2.4. Photo/electrochemical measurements

The photo/electrochemical studies were performed on a standard three-electrode configuration using a VSP-3 multi-channel potentiostat (Biologic Ltd.). A fluorine-doped tin oxide (FTO) substrate coated with a catalyst was used as the working electrode, a platinum foil served as the counter electrode, and an Ag/AgCl electrode saturated with KCl as the reference electrode. The aqueous solution of KHCO_3 (0.5 M) was used as electrolyte. For electrode preparation, pre-cleaned FTO glass substrates were employed. Catalyst inks were made by dispersing 0.01 g of each catalyst in 2 mL of ethanol, followed by 30 min sonication. Then, 20 μL Nafion solution was added, with further sonication for 20 min. A 200 μL portion of uniform suspension was drop-cast onto an FTO substrate, resulting in an effective loading area of 0.25 cm². Electrochemical impedance spectroscopy (EIS, a Biologic VSP-3 multi-channel potentiostat) measurements were recorded in a frequency range of 200 kHz to 20 mHz with an AC perturbation amplitude of 10 mV.

2.5. Quantification of the SO_3H group by the titration method

An acid-base titration was performed to determine the $-\text{SO}_3\text{H}$ group content in sulfonated g- C_3N_4 [22]. Precisely weigh 0.05 g of sulfonated g- C_3N_4 samples and place them in separate beakers. Add 20 mL of deionized water to each, followed by ultrasonication for 30 min and stirring for 24 h. The suspensions are then titrated with a standardised NaOH solution (0.001 M) with phenolphthalein indicator until a stable pale pink endpoint is observed. For comparison, pristine g- C_3N_4 was also titrated against standardised NaOH solution (0.001 M) following the above procedure.

2.6. Photocatalytic CO_2RR performance and product identification

The photocatalytic CO_2RR performance of as prepared catalysts was performed in 0.5 M KHCO_3 solution without a sacrificial reagent [6,19]. The light source utilised in photocatalytic CO_2 reduction studies was a 300 W Xenon lamp in an Asahi Solar Simulator (HAL-320). The solar simulator used in the experiments possesses an AM 1.5G filter, and the light intensity was set to 100 mW cm^{−2}. About 0.05 g of photocatalyst was dispersed in 50 mL of a 0.5 M KHCO_3 solution (1 mg/mL). To prepare a CO_2 saturated electrolyte, the solution was purged with CO_2 gas for 30 min after dispersing the photocatalyst by sonication. At a rate of 20 sccm, the CO_2 reduction process was conducted while the CO_2 gas was bubbled in the solution. To verify that the CO_2 reduction reaction is initiated by photogenerated electrons and CO_2 gas, control experiments were performed for the same duration under no light (dark) conditions in a CO_2 atmosphere and in an Ar atmosphere under illumination of light, respectively. The light illumination was carried out for 2 h under continuous CO_2 purging throughout the experiment to ensure a consistent CO_2 rich environment. After the reaction, the photocatalyst was separated from the reaction mixture through vacuum filtration employing a 0.22 μm PTFE membrane. The CO_2 reduction liquid-phase products were analyzed in a reaction aliquot (5 mL) and quantified via gas chromatography–mass spectrometry (GC–MS) and high-performance liquid chromatography (HPLC) analysis. To confirm the carbon source of the reduction products, isotopic labelling experiments were conducted using ¹³ CO_2 . Prior to the reaction, deionized water was purged with argon to eliminate dissolved gases and subsequently used to prepare a bicarbonate electrolyte enriched with ¹³C. The catalyst was then dispersed in the electrolyte, and ¹³ CO_2 was continuously introduced under light irradiation to drive the photocatalytic reaction. After completion, the catalyst was separated by centrifugation, and the liquid phase was analyzed by GC–MS.

2.6.1. High-performance liquid chromatography (HPLC) analysis

Formaldehyde was quantified using HPLC following derivatization with 2,4-dinitrophenylhydrazine (DNPH). The analysis employed a reversed-phase EC-C18 column (4 μm , 4.6 $\times$ 150 mm; serial no. USHKB29720; lot no. B22399; USA). For derivatization, 700 μL of sample, 700 μL of acetonitrile, and DNPH solution were mixed directly in an HPLC vial and reacted at room temperature. The resulting mixture was injected without further treatment. Acetonitrile enhanced solubility and chromatographic resolution, and in-vial derivatization minimized sample loss while maintaining analytical accuracy.

2.6.2. Gas chromatography-mass spectrometry (GC-MS) analysis

GC-MS measurements were carried out using an Agilent 8860 gas chromatograph equipped with an HP-INNOWAX capillary column (60 m $\times$ 0.25 mm, 0.50 μm film thickness, Agilent J&W) coupled to an Agilent 5977B mass selective detector (Agilent Technologies, Santa Clara, CA, USA). High-purity helium (99.999%) served as the carrier gas, maintained at a steady flow rate of 1.0 mL/min. Samples of 5 mL liquid were placed into a 20 mL headspace vial, which was then securely sealed with a PTFE-lined septum cap, and introduced using an Agilent 7697A headspace sampler for analysis. The vial was equilibrated at 80 $^{\circ}\text{C}$ for 10 min to allow partitioning of volatile compounds into the gas phase. The headspace vapour was automatically sampled and directly injected into the GC-MS system for analysis. The mass spectrometer was operated in SIM mode (selected ion monitoring) to improve detection sensitivity and specificity by targeting specific ions characteristic of the target analyte, ethanol.

2.7. In-situ ATR-IR analysis for intermediates monitor

In-situ ATR-FTIR spectra were collected on a Nicolet iS50 spectrometer (Thermo Fisher Scientific) equipped with a deuterated triglycine sulfate (DTGS) detector to monitor carbon-containing intermediates formed during the CO_2 reduction process. A multi-bounce germanium (Ge) horizontal ATR crystal (4 mm thickness, 7 $\times$ 0.9 cm^2 ; Pike Technologies) was used as the optical element. The reaction was performed in a custom-fabricated Teflon reactor in CO_2 -saturated 0.5 M KHCO_3 solution, continuously purged with CO_2 for 30 min before and during measurement. *In-situ* ATR-IR spectra were recorded for 60 min under simulated solar illumination (1 sun, AM 1.5G) using an Asahi solar simulator.

2.8. Density functional theory (DFT)

All periodic DFT calculations were performed using CASTEP 2023 (BIOVIA Materials Studio). Exchange-correlation interactions were described using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. Long-range dispersion interactions were accounted for using Grimme's DFT-D G06 correction ($s_6 = 0.75$, $d = 20.0$). A plane-wave cutoff energy of 520 eV was applied throughout. The supercell had dimensions $a = b = 14.760 \text{ \AA}$, $c = 20.000 \text{ \AA}$ ($\gamma = 120^{\circ}$, hexagonal), with a 20 $\text{\AA}$ vacuum layer along z to eliminate periodic image interactions. Brillouin-zone sampling used a $2 \times 2 \times 1$ Monkhorst-Pack k -point grid. Geometry optimizations employed the LBFGS algorithm with energy convergence of 1.333×10^{-5} eV/atom, force convergence of 0.01 eV/ $\text{\AA}$, and displacement convergence of 5×10^{-4} $\text{\AA}$. All calculations were spin-polarized (collinear). The free energy profile was constructed using the computational hydrogen electrode (CHE) framework.

3. Result and discussion

3.1. Effect of $-\text{SO}_3\text{H}$ group functionalization on $\text{g-C}_3\text{N}_4$

The crystalline structure and phase composition of pristine $\text{g-C}_3\text{N}_4$ and SO_3H -functionalized $\text{g-C}_3\text{N}_4$ samples ($\text{xxS-g-C}_3\text{N}_4$) were examined

using powder XRD, as shown in Fig. 1(a). The XRD spectra of pristine $\text{g-C}_3\text{N}_4$ display two different diffraction peaks at 12.9° and 27.6° , which are attributed to (100) and (002) planes, respectively (ICDD Card No. 00-066-0813). The peak at 27.6° corresponds to the (002) plane, representing interlayer stacking of conjugated aromatic melon units, while the peak at 12.9° , indexed to the (100) plane, arises from in-plane structural ordering of tri- s -triazine units, confirming the successful formation of the graphitic carbon nitride phase. Additional minor peaks at 17.6° and 21.7° , assigned to the (110) and (210) planes, indicate a well-ordered heptazine framework [23,24]. Upon sulfonation, notable changes appear in the XRD patterns. A distinct broadening of the (002) diffraction peak is evident, with the full width at half maximum (FWHM) increasing from 1.28 for pristine $\text{g-C}_3\text{N}_4$ to 1.79, 2.43, 2.39, and 2.35 for 0.5S- $\text{g-C}_3\text{N}_4$, 1S- $\text{g-C}_3\text{N}_4$, 1.5S- $\text{g-C}_3\text{N}_4$, and 2S- $\text{g-C}_3\text{N}_4$, respectively, as the concentration of chlorosulfonic acid increases. This progressive peak broadening reflects a reduction in crystallite size and increased interlayer stacking disorder within the layered graphitic framework [25,26]. Concurrently, the intensity of the (002) peak decreases with increasing sulfonate content, confirming disruption of the regular interlayer π - π stacking interactions between adjacent heptazine layers caused by SO_3H functionalization [27,28]. Together, the peak broadening and intensity reduction indicate an expansion of interlayer spacing accompanied by a decline in overall crystallinity [29]. The amount of SO_3H groups was quantified by employing an acid-base titration [22]. The measured SO_3H contents for various sulfonated $\text{g-C}_3\text{N}_4$, as 0.5S- $\text{g-C}_3\text{N}_4$, 1S- $\text{g-C}_3\text{N}_4$, 1.5S- $\text{g-C}_3\text{N}_4$, 2S- $\text{g-C}_3\text{N}_4$, and 2.5S- $\text{g-C}_3\text{N}_4$, were found to be 0.116, 0.126, 0.136, 0.156, and 0.166 mmol/g, respectively, as listed in Table S1.

ATR-IR analysis provides additional information on structural changes occurring from sulfonate group incorporation (Fig. 1(b)). In pristine $\text{g-C}_3\text{N}_4$, a prominent absorption band appearing at $\sim 809 \text{ cm}^{-1}$ corresponds to the distinctive breathing vibration of the tri- s -triazine units [30,31]. This band remains at an identical position after sulfonation in 2S- $\text{g-C}_3\text{N}_4$, confirming that the heptazine framework remains intact [27,32]. A weak absorption band appearing at $\sim 890 \text{ cm}^{-1}$ in the 2S- $\text{g-C}_3\text{N}_4$ sample corresponds to the N-H deformation vibration, which is less prominent compared to pristine $\text{g-C}_3\text{N}_4$ [33]. At lower wavenumbers, a band appearing near $\sim 584 \text{ cm}^{-1}$ is assigned to the S=O bending vibration of sulfonic acid ($-\text{SO}_3\text{H}$) groups [34,35]. The multiple absorption bands appearing between 1080 and 1650 cm^{-1} are associated with the stretching vibration modes of tri- s -triazine units, present in both pristine $\text{g-C}_3\text{N}_4$ and 2S- $\text{g-C}_3\text{N}_4$ [36]. Within this region, the bands at $\sim 1629 \text{ cm}^{-1}$ and $\sim 1536 \text{ cm}^{-1}$ correspond to the stretching vibrations of sp^2 -hybridized C=N bonds and C-N linkages within the heptazine (heterocyclic) framework, respectively [36,37]. Additionally, C-N bonds associated with aromatic secondary and tertiary amine groups give rise to absorption bands at ~ 1401 , ~ 1313 , and $\sim 1235 \text{ cm}^{-1}$ in both pristine $\text{g-C}_3\text{N}_4$ and 2S- $\text{g-C}_3\text{N}_4$, attributed to C-N(C)-C and C-NH-C linkages [38]. Upon sulfonation, the band at $\sim 1401 \text{ cm}^{-1}$ appears broadened due to overlapping SO_2 vibrations of the sulfonic groups, while subtle shifts are also observed in the $\sim 1313 \text{ cm}^{-1}$ and $\sim 1235 \text{ cm}^{-1}$ bands, consistent with the incorporation of $-\text{SO}_3\text{H}$ groups [39]. A distinct new absorption band appears at $\sim 1058 \text{ cm}^{-1}$ in 2S- $\text{g-C}_3\text{N}_4$, which is absent in pristine $\text{g-C}_3\text{N}_4$. This band is attributed to the S=O stretching vibration of sulfonic acid ($-\text{SO}_3\text{H}$) groups, confirming successful integration of sulfonate functionalities into $\text{g-C}_3\text{N}_4$ [40]. Finally, the broad absorption band observed near $\sim 3200 \text{ cm}^{-1}$ corresponds to the O-H stretching vibration, likely arising from the hydroxyl group of the incorporated sulfonic acid moieties [30,41]. This feature indicates enhanced surface hydroxylation and hydrogen bonding, which are essential for improved proton conductivity and increased surface hydrophilicity.

FE-SEM analyses were conducted on pristine $\text{g-C}_3\text{N}_4$ and sulfonated $\text{g-C}_3\text{N}_4$, namely 0.5S- $\text{g-C}_3\text{N}_4$, 1S- $\text{g-C}_3\text{N}_4$, 1.5S- $\text{g-C}_3\text{N}_4$, and 2S- $\text{g-C}_3\text{N}_4$, to examine their surface morphology and microstructure, as shown in Fig. S1. The FE-SEM image of pristine $\text{g-C}_3\text{N}_4$ (Fig. S1(a)) reveals an irregular morphology composed of curled sheets aggregated into

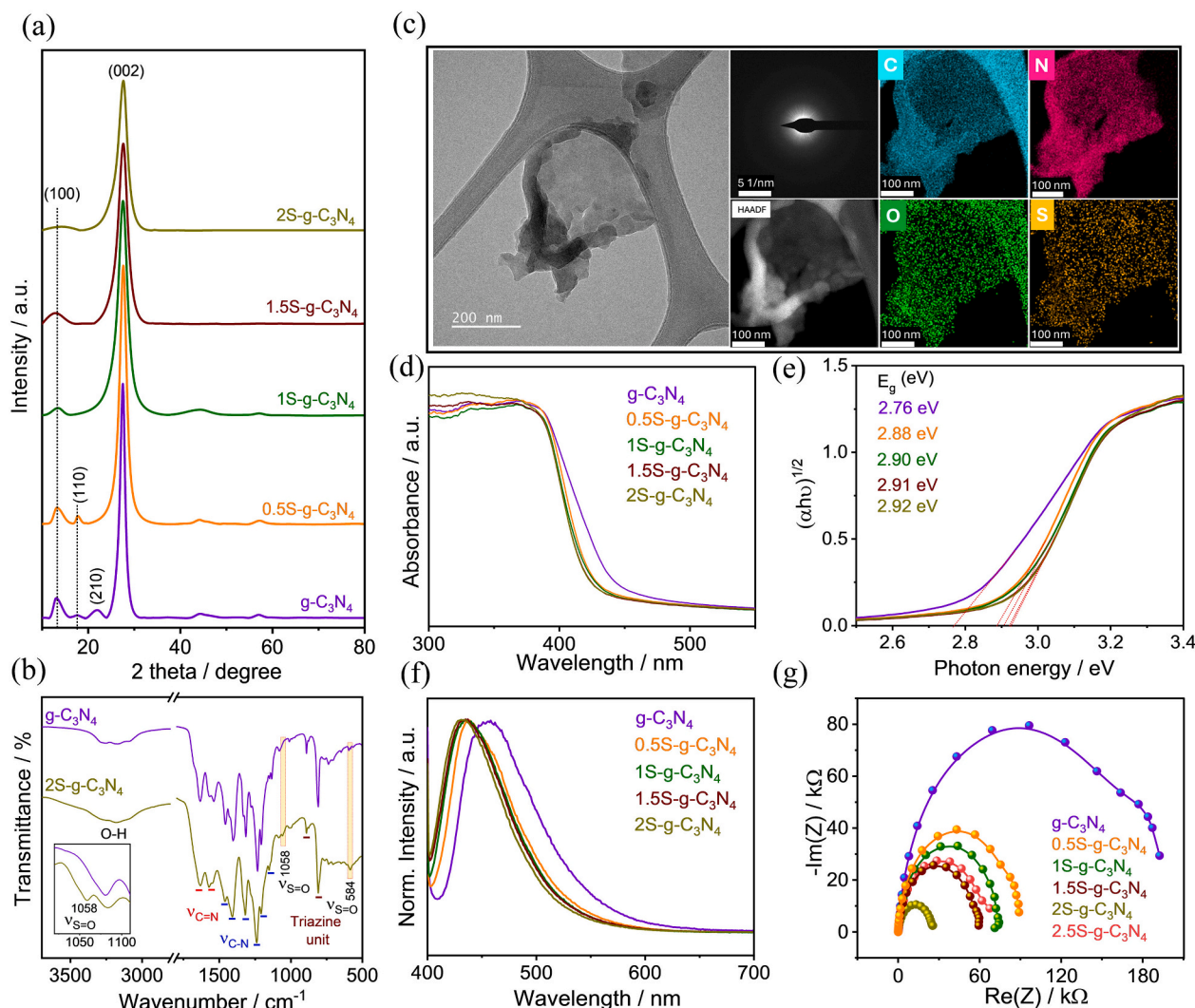


Fig. 1. (a) XRD spectra of pristine g-C₃N₄ and sulfonated g-C₃N₄ photocatalysts designated as 0.5S-, 1S-, 1.5S-, and 2S-g-C₃N₄; (b) ATR-IR spectra of g-C₃N₄ and 2S-g-C₃N₄; (c) TEM image, SAED pattern, High-angle annular dark-field (HAADF) image, and elemental mapping of 2S-g-C₃N₄ catalysts; (d) UV-Vis DRS; (e) corresponding Kubelka-Munk transformed (Tauc) plots of pristine and sulfonated g-C₃N₄; (f) normalized PL spectra of g-C₃N₄ and sulfonated g-C₃N₄; and (g) EIS Nyquist plot of pristine g-C₃N₄ and 0.5S-, 1S-, 1.5S-, 2S-, and 2.5S-g-C₃N₄ catalysts, recorded at 0.5 V vs. Ag/AgCl in 0.5 M KHCO₃ electrolyte under 1 sun illumination (100 mW/cm²).

cylindrical formations, characteristic of g-C₃N₄ obtained through thermal polycondensation. After sulfonation, these curled sheets exhibit partial delamination, resulting in a notable decrease in particle size across the sulfonated g-C₃N₄ samples (Fig. S1(b-e)). To further corroborate the accuracy of the titration-derived -SO₃H quantification, FESEM-EDS elemental mapping was conducted on pristine g-C₃N₄, 0.5S-g-C₃N₄, 1S-g-C₃N₄, 1.5S-g-C₃N₄, and 2S-g-C₃N₄ samples. As presented in Fig. S2 and summarized in Table S2, the sulfur distribution across all functionalized samples was spatially homogeneous, and the EDS-derived sulfur content increased progressively and uniformly with increasing chlorosulfonic acid loading, consistent with the trends observed from acid-base titration. TEM analysis was performed to gain further insight into the morphology and structural characteristics. The TEM image of pristine g-C₃N₄ shown in Fig. S3 reveals a typical two-dimensional lamellar morphology with a sheet-like texture. The HRTEM image (Fig. S3(b)) and SAED pattern (Fig. S3(c)) indicate the amorphous nature of pristine g-C₃N₄. Elemental mapping (Fig. S3(d-e)) confirms the uniform distribution of carbon (C) and nitrogen (N) without any detectable impurities. In contrast, the 2S-g-C₃N₄ sample exhibits partial exfoliation accompanied by aggregation of the layered structure, as displayed in Fig. 1(c). The SAED analyses further verify the amorphous

structure of 2S-g-C₃N₄. Elemental mapping demonstrates the homogeneous distribution of carbon (C), nitrogen (N), oxygen (O), and sulfur (S) elements across the sample, indicating the absence of any impurities.

To examine the influence of sulfonation on the optical properties of g-C₃N₄, UV-Vis DRS spectra were acquired, as shown in Fig. 1(d). Pristine g-C₃N₄ reveals strong visible light absorption with an absorption edge at ~460 nm. The distinct absorption features at ~280 nm and ~390 nm are associated with π - π^* and n - π^* electronic transitions of the conjugated aromatic heptazine framework [42]. A large portion of the visible spectrum remains unutilized, as pristine g-C₃N₄ primarily absorbs light at wavelengths shorter than ~460 nm. After sulfonation, incorporation of -SO₃H functional groups at terminal sites results in a progressive blue shift of the absorption edge (λ_{max}) to the range of ~423–448 nm with increasing sulfonic acid content, accompanied by a modest band gap increase of about 0.2 eV, as shown in Fig. 1(e). The incorporation of bulky -SO₃H groups into the g-C₃N₄ framework disrupts its planar conjugated structure, thereby weakening the π -electron delocalization within the heptazine units. This structural distortion leads to partial localization of electronic density, resulting in band gap widening and a corresponding blue shift of the optical absorption edge [43]. Moreover, functionalization with -SO₃H groups induces structural