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Constructing a rhenium complex supported on g-C₃N₄ for efficient visible-light-driven photoreduction of CO₂ to CO via a novel Z-scheme heterojunction†

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Visible-light-driven photocatalytic CO₂ reduction is a promising approach to addressing the problem of global warming and the energy crisis. A Z-scheme photocatalyst comprising a Re(I) complex and a polymeric semiconductor (bulk graphitic carbon nitride (g-C₃N₄)) converted CO₂ to CO even under the irradiation of low-intensity visible light. The electronic interaction between Re(I) and g-C₃N₄ units and the injection of electrons from g-C₃N₄ to the Re(I) complex improved the photocatalytic efficiency. The lower recombination of electron-hole pairs and the prolonged emission decay (the average emission lifetime $\tau = 5.8$ ms) contributed to the increased overall efficiency of the hybrid system. The maximum turnover number (TON) of CO formation reached 28.56 after 240 min with a high CO selectivity (99.8%). Compared to the homogeneous photocatalyst Re(I), the TON of CO formation was increased by 5.6 times and CO selectivity was higher. Density Functional Theory (DFT) was employed to investigate the impact of the substrate-supported Re complex (Re(bpy-COOH)/g-C₃N₄) on the CO₂ Reduction Reaction (CO₂RR) activity. The results indicate that Re(bpy-COOH)/g-C₃N₄ presents a lower energy barrier for *CO₂ to *COOH conversion, promoting *COOH formation more effectively than pure g-C₃N₄. Moreover, the energy barrier for *CO desorption is lower in Re(bpy-COOH)/g-C₃N₄ than in Re(bpy-COOH), suggesting a reduction in the strong binding of adsorbed CO intermediates, highlighting the intermediate ensemble effect at the active site. The improved CO₂RR activity in Re(bpy-COOH)/g-C₃N₄ can be attributed to the balance between the enhancement of reaction activity and the binding energy of intermediates at the active site. The study of photocatalytic CO₂ reduction (PCO₂R) under low-intensity-visible-light irradiation and DFT investigation has revealed an insight into the CO₂RR activity for CO₂ reduction under various irradiation conditions.

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1. Introduction

Carbon dioxide is known as a heat-trapping gas, which causes global heating. Heavy industries and human activities are the

main CO₂-emission sources that primarily impact global climate change and relate to severe natural events, including wildfires, floods, and droughts. Concerning climate change, several ways have been attempted to reduce CO₂ concentration, such as using sustainable energy sources instead of burning

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fossil fuels and utilizing CO₂ as a new chemical feedstock for producing energy-rich carbon compounds. Solar energy conversion of CO₂ into carbon compounds has been a promising research field that can solve global warming, shortage of fossil fuels, energy crisis, *etc.* To this end, numerous investigations have been carried out to develop many different kinds of visible-light-driven photocatalysts. Transition metal complexes (*e.g.*, Ru, Mn and Re) have been known to be potential homogeneous photocatalysts for CO₂ reduction with high selectivity and activity.^{1–3} They possess a long-lived excited state,^{4,5} tunable structure *via* changing the coordination ligand to the metal center,^{6,7} and intense emission properties.⁸ However, transition metal complexes, which have low quantum efficiency⁹ and strong absorption in the UV region,⁴ are high-cost and scarce, and could suffer from progressive structural degradation because of photochemical instability that may severely reduce catalytic performances. For those reasons, various hybrid photocatalytic materials including molecular/semiconductor hybrid materials^{10–15} and transition metal complex/nanoparticle¹⁶ hybrid materials have been introduced to overcome the drawbacks of homogeneous photocatalytic systems. [Re(2,2'-bipyridine-4,4'-bisphosphonic acid)(CO)₃(L)]⁷⁺ (ReP; L = 3-picoline or bromide) immobilized on TiO₂ nanoparticles¹⁷ was reported for a visible-light-driven hybrid displaying improvement in CO₂ reduction with the turnover number (TON) increasing 24 times in comparison with a ReP homogeneous photocatalyst (the TON of the ReP-TiO₂ hybrid was observed to be 48 mol_{CO} mol_{Re}⁻¹ in DMF). The metal-organic framework (MOFs supported Ru carbonyl complex¹⁸ for PCO₂R under visible light showed twofold enhanced catalytic activity compared to the pure Ru carbonyl complex.

To date, the incorporation of metal complexes with a semiconductor to achieve visible-light-driven photocatalysts¹⁹ has attracted attention, and the metal complexes/semiconductor hybrid system¹⁵ can utilize the advantages of both metal complexes and semiconductors, as well as reducing the usage of noble metals. To design a metal complexes/semiconductor system, the conduction band of semiconductors and the reduction potential of metal complexes need to be compatible to maximize electron transfer between the two components for efficient CO₂ photocatalysis conversion. The rational structure can be achieved by adsorption or by covalent links between metal complexes and semiconductors. Generally, semiconductors play the role of a light absorber and host oxidation reaction sites. Depending on the conduction-band (CB) potential of the semiconductor and the lowest occupied molecular orbital (LUMO) of the metal complexes, the system can be categorized into a hybrid system in which semiconductors function as photosensitizers and metal complexes catalyze CO₂ when the CB potential of semiconductors is more negative than the LUMO of metal complexes, and a Z-scheme system when the CB potential of semiconductors is less negative than the LUMO of metal complexes. In the Z-scheme system, both the semiconductor and metal complex undergo photo-excitation together, resulting in electron transfer and enhancement in the driving force of interfacial electron transfer.

Graphitic carbon nitride has been known as a polymeric semiconductor with high chemical stability and a narrow band gap (~2.7 eV, corresponding to an absorption edge of ≈460 nm), low cost, and ease of preparation.^{20,21} C₃N₄ has been applied for photocatalytic reactions, including water reduction/oxidation²² and environmental treatment.^{23–25} However, g-C₃N₄ still has common issues during a photocatalytic process such as insufficient visible-light absorption,²⁶ low quantum yield and fast recombination of photogenerated carriers^{27,28} that restrict the photocatalytic performance. Therefore, heterojunctions based on g-C₃N₄ with two or three semiconductor materials have been tailored to integrate their own advantages. The g-C₃N₄ based heterojunctions have been used for PCO₂R where the formed products were non-selective and abundant, containing long-chain hydrocarbons (CO, HCOOH, acetone, methanol, and acetaldehyde).^{29,30} g-C₃N₄ has a conduction band and valence band at -1.4 eV and 1.34 eV (*vs.* NHE, pH = 7),^{31,32} respectively, which are suitable for architecting a hybrid photocatalyst with metal complexes, and have thus been reported for the high selectivity for formed products. In a hybrid CO₂-reduction system, bulk g-C₃N₄ was explored as a semiconductor in conjunction with Ru complexes^{11,33,34} through carboxylic or phosphonic acid anchoring groups for converting CO₂ to formic acid (HCOOH) under visible light ($\lambda > 400$ nm). The combination of g-C₃N₄ and Ru complexes maximized the CO₂-reduction efficiency process and improved photocatalytic performance and reached the highest TON (>1000). A manganese (Mn) complex with phosphonic acid anchoring groups in conjunction with bulk g-C₃N₄ forming a Z-scheme system³⁵ was reported for efficient visible-light photoreduction of CO₂ to CO, where the TON of the hybrid system was increased two-fold in comparison with the base Mn complex. Other than Ru and Mn complexes, Ni and Co complexes have been used to combine with g-C₃N₄ to design hybrid materials for PCO₂R.^{14,36,37} Meanwhile, Re(CO)₃(N-N)Cl complexes have not been reported for catalytic CO₂ reduction in metal complexes/semiconductor hybrid systems. They are appropriate to incorporate with g-C₃N₄ to form an efficient visible-light-driven photocatalyst for CO₂ conversion, because Re(CO)₃(N-N)Cl complexes have efficient CO₂-capturing ability, better than that of Mn complexes in the lower CO₂ concentration in the presence of TEOA solvent.³⁸ Re(CO)₃(bpy-COOH)Cl with a dicarboxylic acid anchor and more negative LUMO potential than the CB of g-C₃N₄ will form a Z-scheme system, which can enhance efficient CO₂ reduction. The adsorption is likely *via* hydrogen bonding between NH₂ groups on g-C₃N₄ and -COOH anchors. Additionally, the hybrid system can efficiently convert CO₂ under low-intensity irradiation which is important for investigating photocatalytic systems working under various illumination.

In this study, we report the straightforward synthetic process of a hybrid material Re(bpy-COOH)/g-C₃N₄. The characterization of chemical functional groups, chemical states, optical properties, and the morphology was performed by FTIR, XPS, UV-vis DRS, PL, and PL decay spectroscopy, and using SEM and TEM images. PCO₂R to CO of this hybrid material was studied in DMF/TEOA mixed solution under low-intensity visible light irradiation (21 mW cm⁻²) for the first time. Utilizing density

functional theory (DFT) calculations, we examined the influence of Re(bpy-COOH)/g-C₃N₄ on CO₂ Reduction Reaction (CO₂RR) activities, including factors such as activation energies and charge transfer between intermediates and substrates. Our findings indicate that CO₂RR in Re(bpy-COOH)/g-C₃N₄ is favorable, facilitated by an increase in reaction activity at the active site and a balanced binding energy of both *COOH and *CO intermediates. These results are critical in understanding the photocatalytic activity of this system under sunlight irradiation under various daytime conditions, providing a pathway for further research in this area.

2. Experimental section

Urea (NH₂CONH₂), pentacarbonylchlororhenium(i) [Re(CO)₅-Cl], 2,2'-bipyridine-4,4' dicarboxylic acid (bpy-COOH), and anhydrous *N,N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich. Triethanolamine (TEOA - (HOCH₂CH₂)₃-N), toluene, methanol, acetone, and hexane solvents were of HPLC grade and were obtained from Merck. All solvents were used without further purification. CO₂ and argon (Ar) gases used in all experiments were 99.999% purified.

Bulk g-C₃N₄ was prepared by calcining urea (20 g) under air at 550 °C for 2 hours at a temperature ramp rate of 2 °C min⁻¹ in a muffle furnace. The urea was placed in an alumina crucible with a cover. Then, the muffle furnace was cooled to room temperature, and the resulting light yellow powder was collected as bulk g-C₃N₄, which was ground finely. The Re(CO)₅(bpy-COOH)Cl complex was synthesized following a previous report.³⁹ The complex was synthesized by refluxing the mixture of [Re(CO)₅Cl] (200 mg, 0.55 mM) and 0.55 mM bpy-COOH ligand in 50 mL toluene for 6 hours under an Ar atmosphere to give a red-orange solution ([Re(CO)₅Cl(2,2'-bipyridine-4,4' dicarboxylic acid)] Re(bpy-COOH)). Re(bpy-COOH) was recrystallized from acetone-hexane. Yield: 70%. $\nu_{\text{CO}}/\text{cm}^{-1}$ (in MeCN): 2041, 1956, 1897, ¹H NMR (500 MHz, d₆-acetone, ppm) δ = 9.33 (2H, d, bpy H₆, H_{6'}), 9.18 (2H, s, H₃, H_{3'}), 8.24–8.26 (2H, m, H₅, H_{5'}). ESI-MS (in MeCN): *m/z*: (M⁺ for [C₁₅H₈N₂O₇Re]⁺), 512.9 (M³⁺ for [C₁₅H₈N₂O₇Re]³⁺). UV/Vis (in MeCN): 270–350 nm (ligand-to-ligand charge transfer (LLCT)), 350–475 nm (metal-to-ligand charge transfer (MLCT)) (ESI-MS and UV/Vis spectra are shown in Fig. S1b, S2, and S3†).

The hybrid photocatalyst Re(bpy-COOH)/g-C₃N₄ was prepared following a previously reported process.^{33,35} The synthesized g-C₃N₄ (50 mg) was added to NaOH (50 mL, 0.1 M), stirring the mixture for 10 minutes. Then, the mixture was ultrasonically cleaned with ionized water (100 mL) and separated by centrifugation. Re(bpy-COOH)/g-C₃N₄ with a mol ratio of 1:100 was prepared by dispersion of g-C₃N₄ (46 mg) in methanol (20 mL) and the suspension was ultrasonicated for 1 hour. Then, 2.75 mg of Re(bpy-COOH) was added to g-C₃N₄ suspension and the mixture was stirred for 24 hours in the dark and under room temperature. Re(bpy-COOH)/g-C₃N₄ was collected by filtration and washed with methanol.

After Re(bpy-COOH)/g-C₃N₄ was prepared and collected by filtration. The filtrate was kept in a closed vial and its volume was known. The adsorbed amount (Ads_A) of Re(bpy-COOH) on

g-C₃N₄ was calculated based on the UV/Vis absorption spectrum of the filtrate, using the following equation:

$$\text{Ads}_A \text{ (mol g}^{-1}\text{)} = \frac{A_1 - A_2}{A_1} \times \frac{C \text{ (mol L}^{-1}\text{)} \times 2 \times 10^{-2} \text{ (L)}}{46 \times 10^{-3} \text{ (g)}} \quad (1)$$

where A₁ and A₂ are the absorbance value of the Re(bpy-COOH) solution before and after the adsorption process, respectively, and C is the initial concentration of Re(bpy-COOH). The adsorbed amount of Re(bpy-COOH) on the surface of g-C₃N₄ in the prepared Re(bpy-COOH)/g-C₃N₄ was 31.5 μmol g⁻¹.

The crystalline structure of the prepared g-C₃N₄ was confirmed by using powder X-ray diffraction (XRD) patterns using the D8 Advance XRD with Cu K_α radiation (λ = 0.15418 nm), scanning from 10–70°. The chemical structure of the Re(bpy-COOH) complex was determined by using the proton nuclear magnetic resonance (¹H NMR) spectrum obtained using a Bruker Avance II (500 MHz) in acetone-D₆. Electrospray ionization mass spectrometry (EIS-MS) of Re(bpy-COOH) was performed in acetonitrile (CH₃CN) using an X500R QTOF. The chemical functional groups were determined by Fourier transform infrared (FTIR) spectroscopy in KBr pellets using a PerkinElmer MIR/NIR Frontier instrument in the range of 4000–800 cm⁻¹. The chemical states of the materials were tested using a Thermo Scientific X-ray photoelectron spectroscopy (XPS) instrument with Al K_α radiation. The morphology was observed by using a scanning electron microscope (SEM – Hitachi SM-4800) and transmission electron microscope (TEM-HRTEM, Tecnai G2 F20 S-Twin). The absorption of g-C₃N₄ and Re(bpy-COOH)/g-C₃N₄ was measured by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) performed on a UV-2600 (Shimadzu) in the wavelength range of 300–700 nm. The photoluminescence (PL) spectra were identified on a Cary Eclipse Fluorescence Spectrophotometer (Varian, USA) at 370 nm at room temperature. The emission decay profiles of Re(bpy-COOH)/g-C₃N₄ and g-C₃N₄ at 450 nm were recorded by using a 0.6 m grating monochromator (Jobin-Yvon HRD1) and detected with a fast photomultiplier (Hamamatsu model H733, with a rise time of 700 ps), using a 355 nm laser diode as the excitation source.

Photoelectrochemical experiments: Photocurrent transient response and electrochemical impedance spectroscopy (EIS) measurements were carried out on a potentiostat Biologic VSP-300 using a three-electrode system cell with a working electrode, a Ni mesh counter electrode, and an Ag/AgCl as the reference electrode in a 0.5 M Na₂SO₄ electrolyte. The working electrode was prepared by coating the as-prepared samples (g-C₃N₄ and Re(bpy-COOH)/g-C₃N₄) on fluorine-doped tin oxide (FTO) glass. The FTO glass with a size of 2.5 × 2.5 cm was washed in the following order with acetone, ethanol, and DI water under sonication, and then dried in a N₂ flow. Dispersing the mixture of a certain amount of sample and polyvinyl alcohol (PVA) in distilled water, the obtained slurry was coated on a FTO glass substrate (photoactive area of 1.2 × 1.2 cm) by the spin-coating technique, and dried at 70 °C in 30 min. Photocurrent transient response was recorded under an applied bias of 0.35 V and

irradiated with visible light (15 W energy-saving light bulb, center wavelength $\lambda = 408$ nm, and light intensity at a distance of 5 cm of 210 W m^{-2} , see Fig. S4†) with light chopping every 30 s. Electrochemical impedance spectroscopy (EIS) plots were obtained over the frequency range from 0.1 to 10^5 Hz in the dark.

The photocatalytic CO_2 reaction was carried out in a reaction solution (0.75 mL) containing a photocatalyst (Re(bpy-COOH) (0.6 mM) and Re(bpy-COOH)/g- C_3N_4 (1 mg)) in DMF:TEOA mixed solvent (5:1 v/v). The reaction solution was placed in a visible-light-transparent vial (5 mL) and purged with Ar to remove all air, and then CO_2 gas was purged for 10 min. Then, the reaction vial was irradiated with a light-source system (15 W energy-saving light bulb, $\lambda = 408$ nm, and light intensity at a distance of 5 cm of 210 W m^{-2} , see Fig. S4†) in the photoreaction box. During irradiation, the solution was stirred slowly with a magnetic bar and the temperature of the solution was controlled at room temperature by using a constant temperature system. The gaseous reaction products were identified by using a gas chromatograph (GC Clarus 680- PerkinElmer), which was equipped with a TCD detector, molecular sieve column ($L \times \text{I.D.}$: 30.2 m \times 0.32 mm), and Ar carrier gas. The turnover number TON of CO and H_2 , and the selectivity of CO were calculated by using eqn (2)–(4), respectively.

$$\text{TON}_{\text{CO}} = \frac{\text{mol of CO formed}}{\text{mol of Re catalyst used}} \quad (2)$$

$$\text{TON}_{\text{H}_2} = \frac{\text{mol of H}_2 \text{ formed}}{\text{mol of Re catalyst used}} \quad (3)$$

$$\text{Selectivity} = \frac{\text{CO formed (mol)}}{\text{sum of reduction products (mol)}} \quad (4)$$

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP).^{40,41} The generalized gradient approximation (GGA) with parameterization by Perdew, Becke, and Ernzerhof (PBE)⁴² was employed to describe the exchange–correlation interactions. The interaction between core electrons and valence electrons was treated with the projector-augmented wave (PAW)⁴³ method. The DFT-D3 correction method in Grimme's scheme⁴⁴ was used to describe the long-range van der Waal interactions between atoms. A cutoff energy of 400 eV was chosen for wave function expansion. For Brillouin zone integration, only a Γ k -point with a Gaussian broadening of 0.05 eV was used. Crystal orbital Hamilton population (COHP) and charge transfer analyses were performed using the Lobster program.⁴⁵ To investigate the thermodynamics of CO_2RR , the Gibbs free energy (ΔG) was calculated using the equation proposed by Nørskov's group:⁴⁶

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}} \quad (5)$$

where ΔE is the total energy of reactions obtained from DFT calculation, and ΔE_{ZPE} and ΔS are the zero-point energy and entropic changes, respectively. T is the temperature, ΔG_{pH} is the

correction on the pH in the electrolyte and ΔG_{U} is the electrode potential. In this study, ΔG_{pH} and ΔG_{U} were set to zero.

In our simulation model, the Re(bpy-COOH) molecule was placed in a cubic unit cell with $a = 20$ Å, while g- C_3N_4 and Re(bpy-COOH)/g- C_3N_4 were constructed using a 2×2 hexagonal unit cell with an optimized lattice constant $a = 13.98$ Å. A vacuum spacing of 15 Å was selected to minimize the artificial interaction between the neighboring slabs. All atomic coordinates are fully relaxed with a force criterion of 1 meV Å^{-1} .

3. Results and discussion

The ^1H NMR and ESI-MS confirmed the high purity and the well-structured molecule of the Re(bpy-COOH) complex, as presented in Fig. S1 and S2.† The XRD pattern showed the characteristic diffraction peaks in the crystalline structure of g- C_3N_4 (Fig. S1(a)†). The two diffraction peaks centered at 13.10 and 27.32° correspond to the (100) and (002) crystal planes of graphite phase carbon nitride, respectively, which were in accordance with the planar structure stacking peak of aromatic systems and inter-layer structural packing.⁴⁷

The hybrid material Re(bpy-COOH)/g- C_3N_4 was optically characterized by FTIR, UV-vis DRS, PL spectroscopy, and TRPL measurement, as shown in Fig. 1. As seen in Fig. 1a, the FTIR spectra showed that the characteristic peaks of g- C_3N_4 in the range of $1650\text{--}800 \text{ cm}^{-1}$ did not change after combining with Re(bpy-COOH). The appearance of C=O stretching modes in the FTIR spectrum of the hybrid material, ranging from 2100 to 1800 cm^{-1} , confirmed the successful loading of the Re(bpy-COOH) complex on g- C_3N_4 .

The UV-vis DRS spectra and the calculated optical band gaps of the hybrid Re(bpy-COOH)/g- C_3N_4 and g- C_3N_4 are presented in Fig. 1(b and c). The g- C_3N_4 showed broad band absorption in the visible region with a bandgap edge of approximately 2.77 eV which was assigned to the $\pi\text{--}\pi^*$ transition of conjugated heptazine units. This result was consistent with previous reports.⁴⁸ The absorption edge of the hybrid material Re(bpy-COOH)/g- C_3N_4 exhibited an insignificant blue-shift from 2.77 to 2.83 eV ($\sim 447\text{--}4.38 \text{ nm}$), and the increase of the absorption from 250–315 nm could account for the strongest absorption of Re(bpy-COOH) in the UV region from 250–350 nm (Fig. S3†). Both of the hybrid Re(bpy-COOH)/g- C_3N_4 and g- C_3N_4 had the tailing absorption extended to 550 nm, which was ascribed to $n\text{--}\pi^*$ transitions involving lone pairs on the edge nitrogen atoms of the heptazine rings.⁴⁹

Fig. 1c presents the PL of the hybrid Re(bpy-COOH)/g- C_3N_4 and g- C_3N_4 , which had strong luminescence emission in the range of 420–550 nm. Anchoring Re(bpy-COOH) on g- C_3N_4 , the PL emission peak of the hybrid material was slightly narrow and showed two separated emission peaks at 435 and 455 nm. The PL intensity of Re(bpy-COOH)/g- C_3N_4 was lower than that of g- C_3N_4 , which indicated that Re(bpy-COOH)/g- C_3N_4 underwent less recombination of photo-induced electron–hole pairs than g- C_3N_4 did. The lower recombination rate would lead to the higher photocatalytic activity of Re(bpy-COOH)/g- C_3N_4 . The emission decay profiles of Re(bpy-COOH)/g- C_3N_4 and g- C_3N_4 under excitation of 355 nm, and emission of 450 nm without an

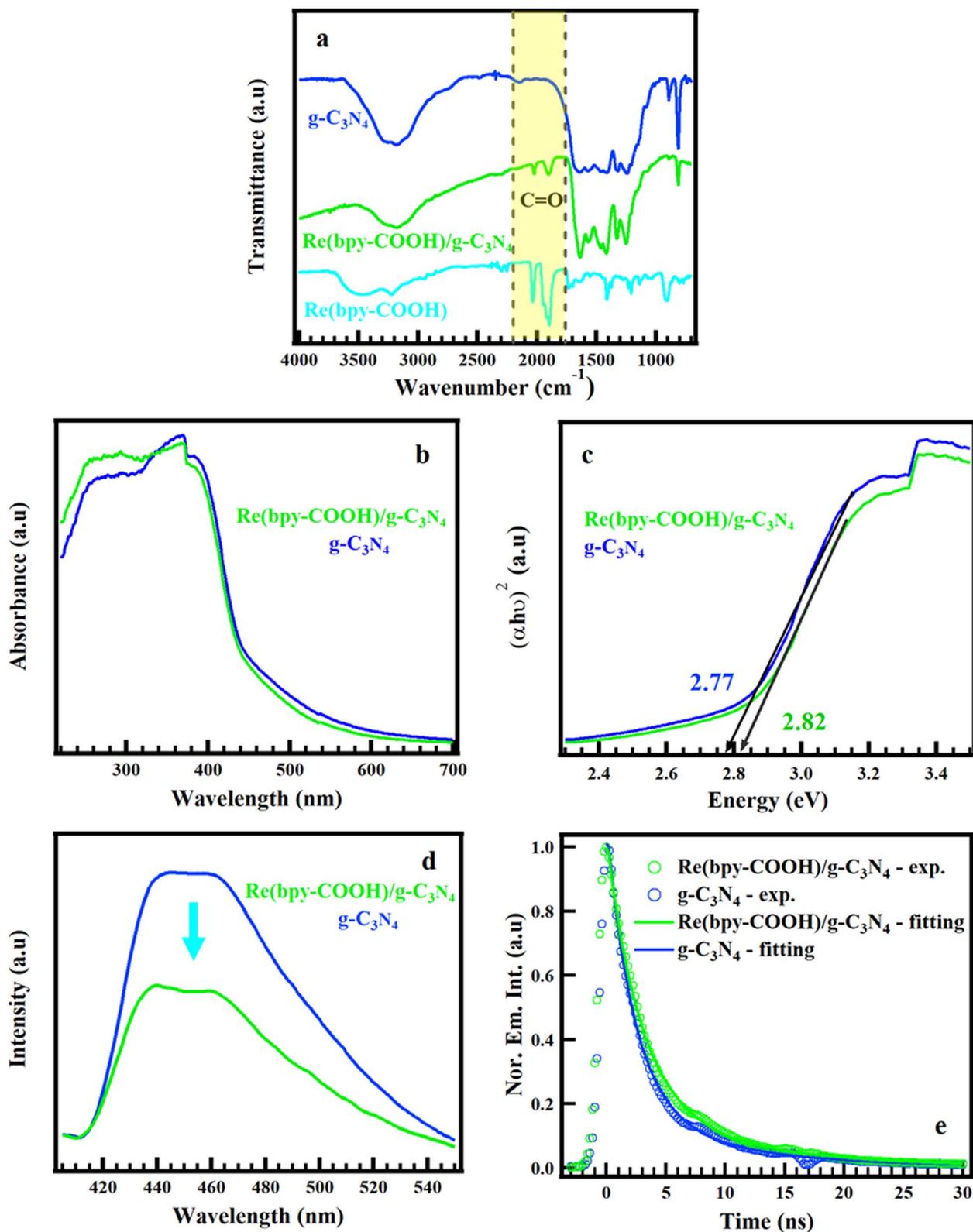


Fig. 1 Fourier transform infrared spectra (a), UV-vis diffuse reflectance spectra (b), band gap energy of the corresponding UV-vis DRS determined from the Tauc plot (c), photoluminescence spectra under 365 nm of irradiation (d), and emission decay profiles of Re(bpy-COOH)/g-C₃N₄ and g-C₃N₄ (e) at $\lambda_{\text{ex}} = 355$ nm and $\lambda_{\text{em}} = 450$ nm without the quenching factor.

electron donor source (TEOA), and the fitting curve are shown in Fig. 1e. The emission decay of (bpy-COOH)/g-C₃N₄ and g-C₃N₄ had the timescale of nanoseconds, which agreed with a previous report from Zhidong Wei.^{49,50} The complex [Re(CO)₃(N-N)Cl] (N-N: polypyridine) displayed its emission lifetime on the

nanosecond timescale (as shown in Fig. S7 in the ESI†).⁵¹ The emission lifetime of the hybrid and g-C₃N₄ was fitted to a triple exponential function and the fitting data are summarized in Table S1.† The lifetime of the hybrid was prolonged (average emission lifetime $\tau = 4.34$ ns) compared to g-C₃N₄ ($\tau = 3.47$ ns).

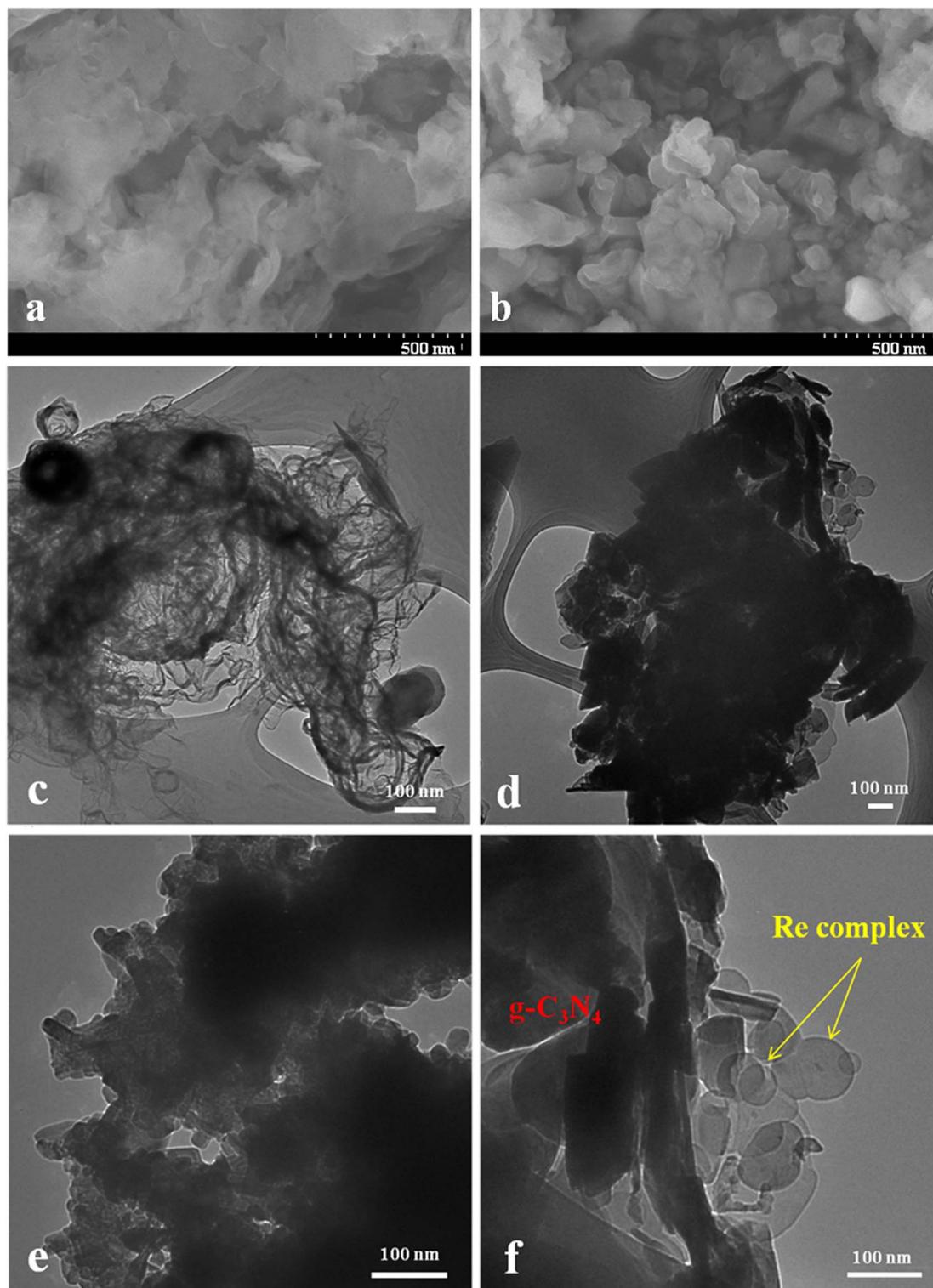


Fig. 2 SEM images of g-C₃N₄ (a) and Re(bpy-COOH) (b), and TEM images of g-C₃N₄ (c), Re(bpy-COOH)/g-C₃N₄ (d and f), and Re(bpy-COOH) (e).

Under 355 nm excitation, $g\text{-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})$ underwent dual-photoexcitation, resulting in interfacial electron transfer from the conduction band of $g\text{-C}_3\text{N}_4$ to the HOMO of $\text{Re}(\text{bpy-COOH})$, minimizing recombination with holes in the valence band. It is noted that the COOH anchor was reported as intrinsically superb in terms of electron transfer due to the greater degree of nonadiabatic coupling,¹² which was important for the overall efficiency of the hybrid system. These migrated electrons localized on the HOMO and prevented the combination of photo-induced electrons of $\text{Re}(\text{bpy-COOH})$ with holes. That could account for the prolong decay time and the decrease of emission intensity of the PL spectrum. The longer emission lifetime was favorable for promoting PCO2R.

The morphological surface of the materials was observed by using SEM and TEM images, as shown in Fig. 2. The SEM images of $g\text{-C}_3\text{N}_4$ showed the planar structure stacking while $\text{Re}(\text{bpy-COOH})$ exhibited a crystal-like morphology with sizes varied from a few dozen to a hundred nanometers, as presented in Fig. 2(a) and (b). The TEM image (Fig. 2(c) and (e)) showed

that $\text{Re}(\text{bpy-COOH})$ had a particle shape with the size of a few hundred nm and $g\text{-C}_3\text{N}_4$ possessed a sheet-like morphology. Fig. 2(d) and (f) show the morphological images of the hybrid with $\text{Re}(\text{bpy-COOH})$ successfully loaded on the surface of $g\text{-C}_3\text{N}_4$.

XPS spectra determined the surface chemical state of $g\text{-C}_3\text{N}_4$, $\text{Re}(\text{bpy-COOH})$, and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ and the interaction or bonding between $\text{Re}(\text{bpy-COOH})$ and $g\text{-C}_3\text{N}_4$ (Fig. 3). Fig. 3a shows the full scan of $g\text{-C}_3\text{N}_4$, $\text{Re}(\text{bpy-COOH})$, and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$. The XPS survey spectrum of $g\text{-C}_3\text{N}_4$ showed the typical structure of graphitic carbon nitride which showed the existence of the elements C, N, and O on the surface. Element O can be the impurity species absorbed on the surface of $g\text{-C}_3\text{N}_4$. The full scan of $\text{Re}(\text{bpy-COOH})$ consisted of the peaks of Re (Re 4f and Re 4d), C, N, Cl and O, clearly from the structure of the Re complex, and the obtained spectrum reached an agreement with a previous report of this complex.⁵² The surface state of $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ was composed of peaks of Re (Re 4f and Re 4d), C, N, and O. The high-resolution scan of the Re 4f

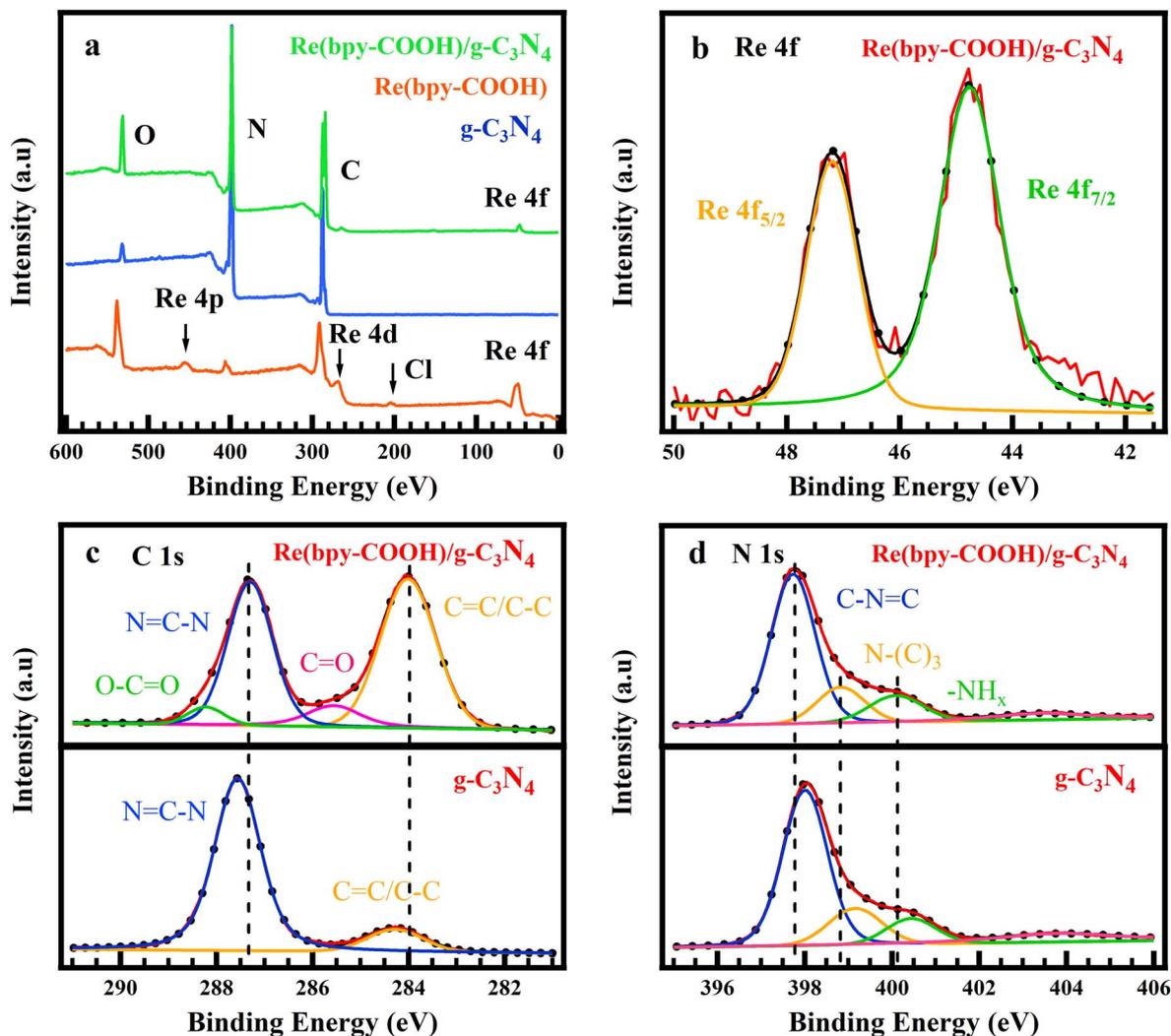


Fig. 3 XPS survey scan of $g\text{-C}_3\text{N}_4$, $\text{Re}(\text{bpy-COOH})$, and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ (a), high resolution scan of Re 4f of $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ (b), C 1s (c), and N 1s (d) of $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ (top) and $g\text{-C}_3\text{N}_4$ (bottom).

spectrum of the hybrid material $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$ included $\text{Re } 4f_{5/2}$ and $4f_{7/2}$ peaking at 44.78 eV and 47.18 eV, respectively; meanwhile the $\text{Re } 4f$ spectrum of $\text{Re}(\text{bpy-COOH})$ showed those $4f$ peaks at 45.23 eV and 48.05 eV (Fig. S5(a)†). The peak displacement of $\text{Re } 4f_{5/2}$ and $4f_{7/2}$ indicated the interaction between Re with the surrounding elements.

Fig. 3c presents the high-resolution XPS spectra for $\text{C } 1s$ of $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4$. The $\text{C } 1s$ spectrum of $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$ showed the peak changes in the position and intensity, and new peaks appeared at binding energies 285.6 and 288.2 eV assigned to $\text{C}=\text{O}$ and $\text{O}-\text{C}=\text{O}$, respectively. $\text{C}=\text{O}$ and $\text{O}-\text{C}=\text{O}$ were the featured groups characterized for $\text{Re}(\text{bpy-COOH})$, and hence their appearance on the $\text{C } 1s$ spectrum of $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$ indicated the successful linking between $\text{Re}(\text{bpy-COOH})$ and $\text{g-C}_3\text{N}_4$. The blue-shift of $\text{O}-\text{C}=\text{O}$ at 285.6 eV in $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$ from 286.0 to 285.6 eV (compared to $\text{O}-\text{C}=\text{O}$ in $\text{Re}(\text{bpy-COOH})$, see Fig. S5(b)†) determined the chemical bonding of the anchor group $-\text{OOC}$ of $\text{Re}(\text{bpy-COOH})$ on $\text{g-C}_3\text{N}_4$. The binding energy at 287.6 and 284.3 eV corresponded to typical sp^2 bonded-carbon $\text{N}=\text{C}-\text{N}$ and $\text{C}=\text{C}/\text{C}-\text{C}$ of $\text{g-C}_3\text{N}_4$, respectively, which reached agreement with previous reports.⁵³

The $\text{N } 1s$ spectra were deconvoluted into three peaks at 398.0, 399.2, and 400.5 eV, which were assigned to sp^2 -hybridized pyridine N ($\text{C}-\text{N}=\text{C}$), tertiary pyrrolic N ($\text{N}(\text{C})_3$), and graphitic N , respectively^{54,55} (Fig. 3d). The binding energy of the corresponding peaks obtained in $\text{N } 1s$ of $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$ (397.8, 398.9, and 400.1 eV) were shifted by 0.2, 0.3, and 0.4 eV, respectively. The peak shifts revealed the interfacial interaction between $\text{Re}(\text{bpy-COOH})$ and $\text{g-C}_3\text{N}_4$.

Fig. 4 represents the (EIS) results in the form of Nyquist, Bode, and transient photocurrent response of $\text{g-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$. The reduction of the arc diameter as shown in Fig. 4a suggests a decrease of film and charge transfer resistance, indicating an enhanced charge transfer of $\text{g-C}_3\text{N}_4$ by $\text{Re}(\text{bpy-COOH})$ addition. Fig. 4b indicates the local surface defects that are detected at the high-frequency data, the pore and substrate/film interface can be detected at the medium and low-frequency data, respectively. It also indicates a significant reduction in the impedance aperture and phase angles when $\text{Re}(\text{bpy-COOH})$ was doped in $\text{g-C}_3\text{N}_4$. The data indicate two phase constants in an equivalent circuit inserted in Fig. 4a. This equivalent circuit was combined with the ZSimpWin program to determine the optimized charge transfer resistance values of

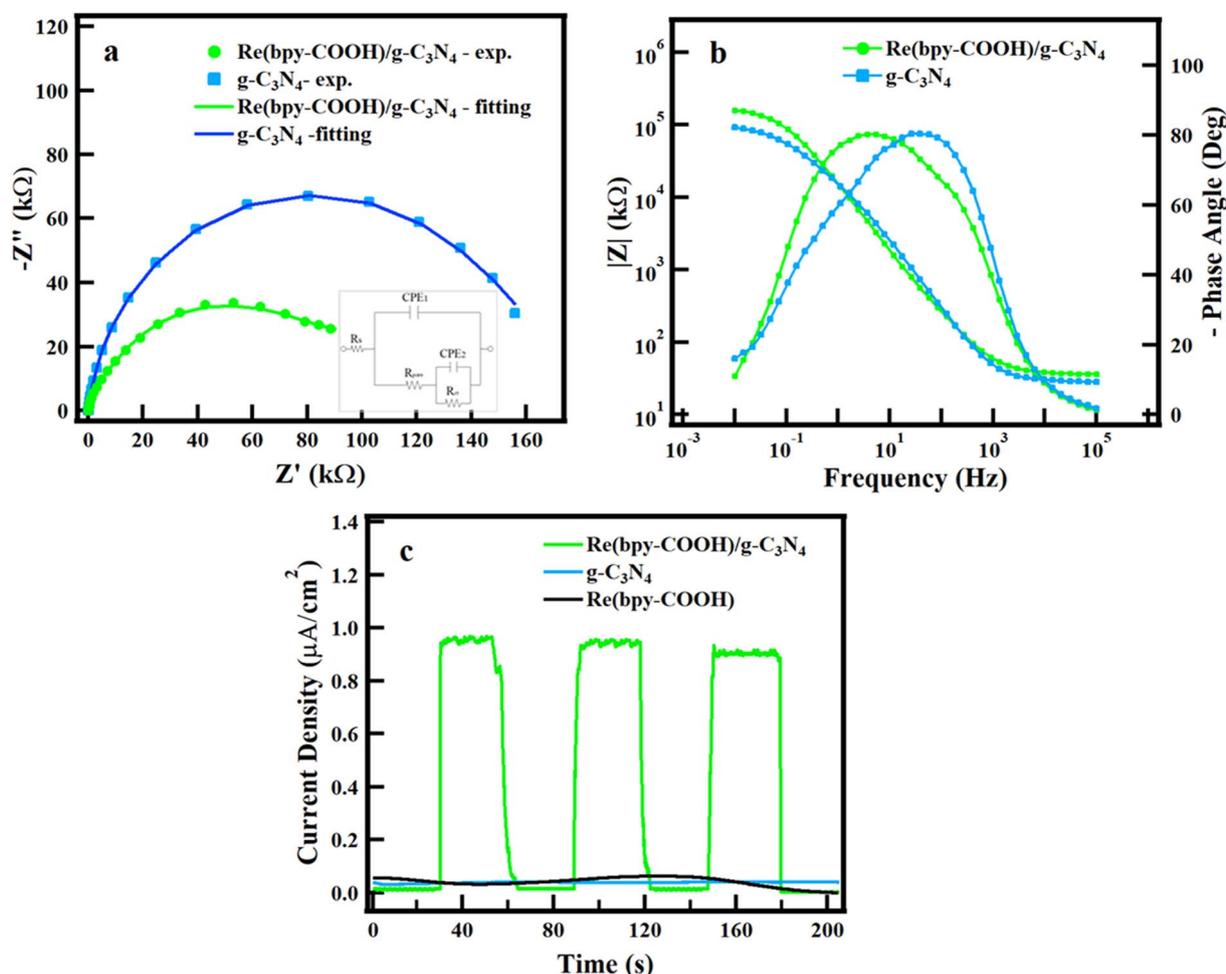


Fig. 4 Electrochemical impedance spectroscopy (EIS) results in the form of Nyquist (insert equivalent circuit) (a) and Bode plots (b), and photocurrent under visible light in Na_2SO_4 of $\text{g-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})/\text{g-C}_3\text{N}_4$ (c).

the investigated specimens. The fitting results indicated that the charge transfer resistance values reached 1.645×10^5 and 1.182×10^5 for $g\text{-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ specimens, respectively. The significant reduction in charge transfer resistance values suggested that $\text{Re}(\text{bpy-COOH})$ doping increases the resistivity of $g\text{-C}_3\text{N}_4$. The current response upon light irradiation of $g\text{-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})$ was undetermined, whereas that of $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ showed a large (approximately $1 \mu\text{A cm}^{-2}$) and fast rising of the current (Fig. 4c). The slightly attenuation of the current density was observed after the second cycle. As expected, linking $\text{Re}(\text{bpy-COOH})$ and $g\text{-C}_3\text{N}_4$ enhanced electronic communication and reduced the recombination of photo-induced carriers.

PCO2R of $g\text{-C}_3\text{N}_4$, $\text{Re}(\text{bpy-COOH})$ and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ was conducted in DMF:TEOA mixed solution under low-intensity visible irradiation. Generally, photocatalytic activity was tested under standard test conditions of AM 1.5G, 100 mW cm^{-2} .⁵⁶ This investigation studied the photocatalytic CO_2 conversion and the selectivity of the hybrid system under low-light intensity. DMF solvent was the best choice for the highest selectivity of CO formation. TEOA was used as an effective

sacrificial electron donor that scavenges holes generated in the valence band of $g\text{-C}_3\text{N}_4$. As shown in Fig. 5a and b, for the photocatalytic system with $g\text{-C}_3\text{N}_4$ as the photocatalyst, there was no CO and H_2 formation found, which met agreement with a previous report.⁵⁷ The CO generation of the hybrid system reached the highest TON = 28.56 at 240 min and then reached saturation, while the highest TON of $\text{Re}(\text{bpy-COOH})$ was 5.6 at 120 min before saturation, as shown in Fig. 5a. Ono *et al.* reported the total amount of CO production of $\text{Re}(\text{bpy-COOH})$ reached $\text{TON}_{\text{CO}} = 6.59$ for 2 h.⁵⁸ In our experiment, the TON_{CO} of $\text{Re}(\text{bpy-COOH})$ obtained was lower than that in the Ono report, which can be explained by the low-intensity irradiation used. The amount of CO formation increased significantly when $\text{Re}(\text{bpy-COOH})$ was anchored to $g\text{-C}_3\text{N}_4$ (increased by 5.6 times at 240 min of irradiation), indicating that $\text{Re}(\text{bpy-COOH})$ and $g\text{-C}_3\text{N}_4$ combination enhanced the efficiency of the PCO2R.

Hydrogen formation of the three materials is presented in Fig. 5b. Namely, the TON of H_2 formation reached 0.1 and 0.05 for $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})$ at 240 min, respectively. The comparison of CO and H_2 formation of $\text{Re}(\text{bpy-}$

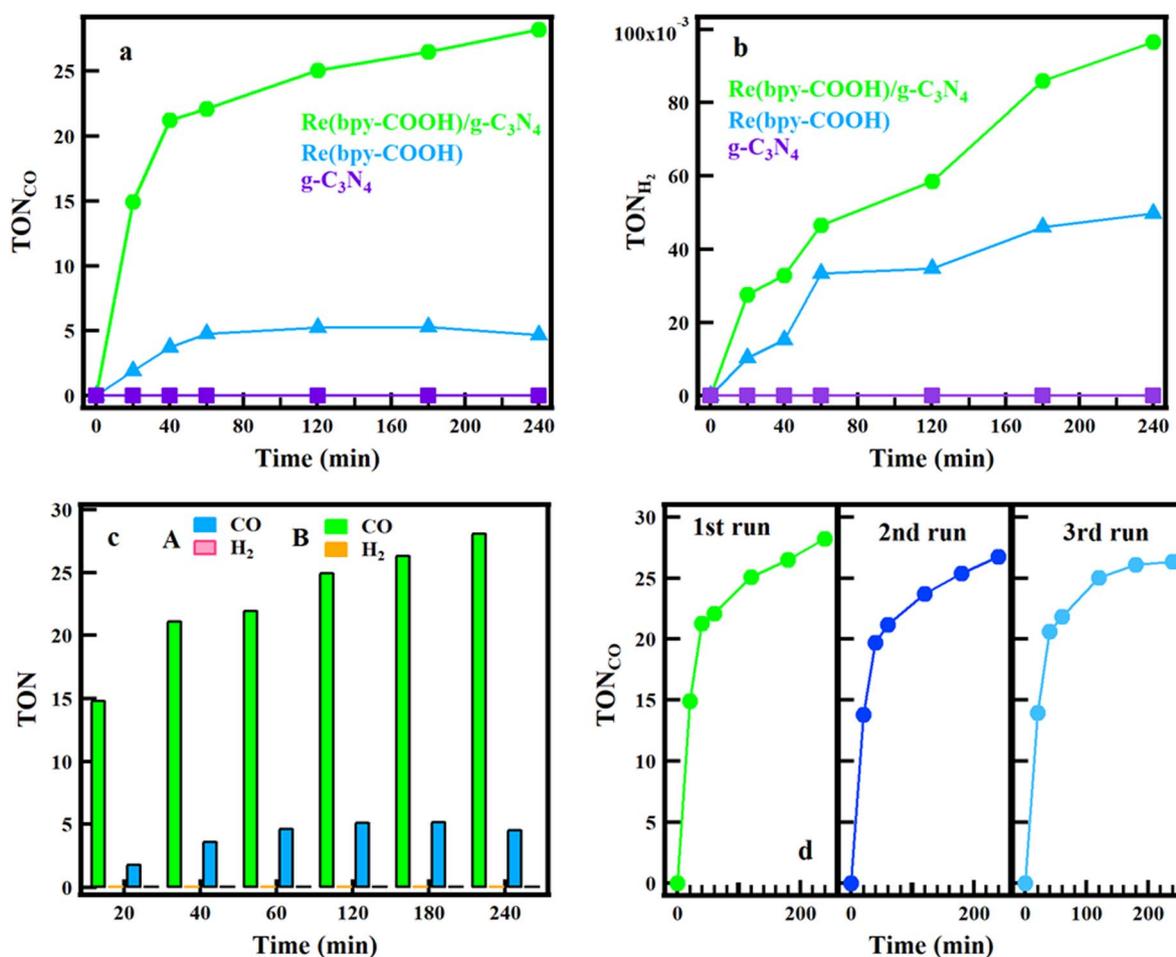


Fig. 5 The formation of Co (a) and H_2 (b) during photocatalytic reduction by time of $g\text{-C}_3\text{N}_4$, $\text{Re}(\text{bpy-COOH})$, and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$, the comparison of Co and H_2 formation of $\text{Re}(\text{bpy-COOH})$ (a – Co: turquoise blue and H_2 : pink), and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ (Co: green and H_2 : orange) (c), and three consecutive 240 min irradiation cycles using the same hybrid material (d).

Table 1 Photocatalytic activities of $g\text{-C}_3\text{N}_4$, $\text{Re}(\text{bpy-COOH})$, and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ for CO_2 reduction under visible light ($\lambda > 400$ nm)

Photocatalyst	TON_{CO}	TON_{H_2}	CO selectivity (%)
$g\text{-C}_3\text{N}_4$	—	—	—
$\text{Re}(\text{bpy-COOH})$	5.14	0.03	99.4
$\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$	22.44	0.05	99.8

$\text{COOH})/g\text{-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})$ is shown in Fig. 5c, in which the amount of CO was dominant. Table 1 shows the TON of CO and H_2 formation, and the selectivity of CO of $\text{Re}(\text{bpy-COOH})$ and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ at 60 min. The selectivity of CO formation was determined to be 99.4 and 99.8% for $\text{Re}(\text{bpy-COOH})$ and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$, respectively (as shown in Table 1). $[\text{Re}(\text{CO})_3(\text{N-N})\text{Cl}]$ complexes presented high CO selectivity (greater than 90%), and the CO selectivity of $\text{Re}(\text{bpy-COOH})$ under low-intensity irradiation was evaluated to be 99.4% that agreed with previous studies.⁵⁸ The CO selectivity of the hybrid system was greater than that of the homogeneous catalyst, and thus combining $\text{Re}(\text{bpy-COOH})$ with $g\text{-C}_3\text{N}_4$ improved the photocatalytic performance and the selectivity of CO.

To study the stability, the PCO₂R of the same hybrid material was re-employed for three successive cycles. After each cycle, the hybrid material was washed with acetonitrile and then dried at 70 °C. After that, the hybrid material was dispersed into DMF : TEOA solution as the preparation process for PCO₂R measurement in the experimental section and then started the new cycle. The results (Fig. 5d) showed the stability of CO production in the three cycles. The CO formation rate and generation remained stable in three cycles; however, in the second and third cycles, a slightly insignificant reduction of CO yield was observed. That could be explained by the photo-degradation of $\text{Re}(\text{bpy-COOH})$ under irradiation and the loss of the catalyst due to collecting and washing the catalyst after each cycle run.

This hybrid system and a similar hybrid system $\text{Mn}(\text{i})/g\text{-C}_3\text{N}_4$ ($\text{Mn}(\text{i}) : \text{Mn}(\text{bipyridineCOOH})(\text{CO})_3\text{Br}$) possessed similar photocatalytic properties such as photoreduction CO_2 products (PCO₂P) (CO and H_2) and photocatalytic structure (Z-scheme model and $g\text{-C}_3\text{N}_4$ surface with the $-\text{COOH}$ anchor). The comparison of the two systems showed that the enhancement of PCO₂P of the $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ hybrid was lower than that of the $\text{Mn}(\text{i})/g\text{-C}_3\text{N}_4$ system.⁵⁷ Namely, TON_{CO} was increased approximately 10 times, whereas TON_{CO} in this study was increased 5.6 times. It should be noted that $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ worked under the low-intensity visible light, and meanwhile $\text{Mn}(\text{i})/g\text{-C}_3\text{N}_4$ was studied under a 300 W Xe lamp (100 mW cm^{-2}). The different light-irradiation intensities in the two research conditions might affect the CO generation. Referring to the PCO₂P, the hybrid was evaluated to be more dominant in the number of products formed. PCO₂P of Ru complex/ C_3N_4 included HCOOH (80% selectively), CO, and H_2 ,¹¹ whereas that of $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ generated only two products CO (more than 90% selectively) and H_2 .



Scheme 1 The illustration of the photocatalytic CO_2 reduction process.

To clarify the mechanism of PCO₂R of the hybrid system, the reduction potential of $\text{Re}(\text{bpy-COOH})$ and the energy level of $g\text{-C}_3\text{N}_4$ need to be mentioned. $\text{Re}(\text{bpy-COOH})$ is a good electrocatalyst for CO_2 reduction, with LUMO potential³⁹ at -1.94 vs. NHE (or one-electron reduction potential, $E_{\text{red}} = -1.69$ V vs. Ag/AgNO_3) and the HOMO potential for absorbing visible light is approximately 0.75 eV vs. NHE (MLCT band, see the UV/Vis absorbance spectrum of $\text{Re}(\text{bpy-COOH})$ in Fig. S3†). Bulk $g\text{-C}_3\text{N}_4$ has a conduction band and valence band at -1.4 and 1.34 eV (vs. NHE, pH = 7),^{31,32} respectively, which is sufficiently negative for the injection of one electron from the CB to the HOMO of $\text{Re}(\text{bpy-COOH})$. The energy structure of $\text{Re}(\text{bpy-COOH})$ and $g\text{-C}_3\text{N}_4$ forms a Z-scheme hybrid system^{59–61} as illustrated in Scheme 1.

Under visible-light irradiation, both $g\text{-C}_3\text{N}_4$ and $\text{Re}(\text{bpy-COOH})$ undergo photoexcitation that generates electron-hole pairs. Due to the high potential difference between the CB of $g\text{-C}_3\text{N}_4$ and the HOMO of $\text{Re}(\text{bpy-COOH})$ interfacial photo-induced electron transfer occurred, which reduces electron-hole pair recombination on $\text{Re}(\text{bpy-COOH})$. The photo-induced electrons generated on the LUMO on the catalyst side reduce CO_2 molecules while the holes in the VB of $g\text{-C}_3\text{N}_4$ are scavenged by TEOA. The efficient interfacial electron transfer and the decrease in electron-hole pair recombination manifest *via* photoluminescent decay and PL spectra sufficiently boost the photocatalytic performance of the system.

To enhance our understanding of the ensemble effect within the $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ catalyst and its implications for the critical intermediate adsorption in CO₂RR, we performed Density Functional Theory (DFT) calculations. Fig. 6 depicts the computed Gibbs free energy (ΔG) progression for CO₂RR across $g\text{-C}_3\text{N}_4$, $\text{Re}(\text{bpy-COOH})$, and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$. This includes a focus on four fundamental steps: (1) CO_2 adsorption onto the N atom of $g\text{-C}_3\text{N}_4$ or the Re atom of $\text{Re}(\text{bpy-COOH})$; (2) formation of COOH through hydrogenation; (3) creation of CO *via* disproportionation; (4) CO desorption. Our computations reveal that the ΔG of both $\text{Re}(\text{bpy-COOH})$ and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$ is less than that of $g\text{-C}_3\text{N}_4$, suggesting a more favorable environment for CO₂RR processes in the former materials. Remarkably, in $\text{Re}(\text{bpy-COOH})$ and $\text{Re}(\text{bpy-COOH})/g\text{-C}_3\text{N}_4$, the

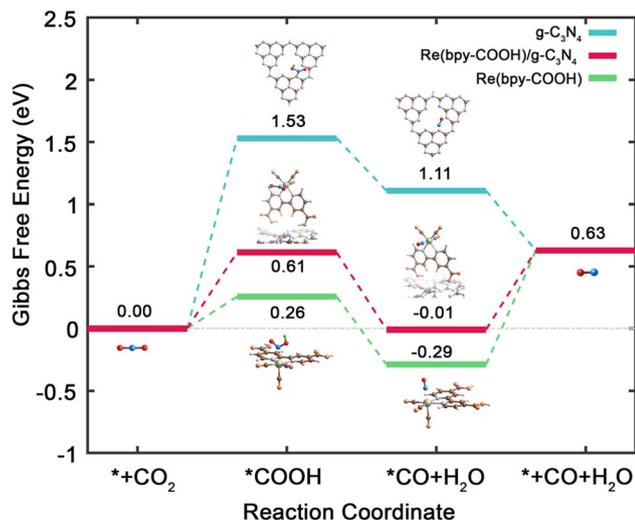


Fig. 6 Calculated Gibbs free energy diagram of CO₂RR processes with the corresponding intermediates for g-C₃N₄ (blue), Re(bpy-COOH) (green), and Re(bpy-COOH)/g-C₃N₄ (red). The asterisk (*) denotes the adsorption site.

conversion of *CO₂ to *COOH *via* hydrogenation overcomes the Gibbs energy barrier with just 0.26 and 0.61 eV, respectively, a significant reduction compared to the 1.53 eV needed in g-C₃N₄. Additionally, *CO formation is energetically exothermic at -0.55 eV for Re(bpy-COOH) and -0.62 eV for Re(bpy-COOH)/g-C₃N₄, compared to -0.42 eV for g-C₃N₄. Interestingly, the Gibbs energy barrier for CO desorption is only 0.64 eV in the hybrid material, lower than the 0.92 eV required in the Re(bpy-COOH) system. Our findings suggest that, despite a slightly higher Gibbs energy barrier for *COOH, the CO₂RR processes favoring CO formation in the Re(bpy-COOH)/g-C₃N₄ system are more likely, aligning with our experimental results.

For a deeper understanding of the CO₂RR catalytic activity, we delved into the charge transfer analysis between *COOH, *CO, and g-C₃N₄, Re(bpy-COOH), and Re(bpy-COOH)/g-C₃N₄, respectively. The Mulliken charge and corresponding charge transfer for each atom involved in the *COOH and *CO intermediates are detailed in Table S2 (see the ESI†). Positive and negative charge transfer values denote electron loss and gain, respectively. Remarkably, the charge transfers in both Re(bpy-COOH) and Re(bpy-COOH)/g-C₃N₄ scenarios register negative values (-0.51 and -0.48 for *COOH, and -0.15 and -0.13 for *CO, respectively). This contrasts with the negligible charge transfers observed in the case of g-C₃N₄. These findings suggest that the chemical interactions between CO and COOH with Re(bpy-COOH) and Re(bpy-COOH)/g-C₃N₄ are more potent compared to those with g-C₃N₄. It's noteworthy that the charge transfer of Re(bpy-COOH)/g-C₃N₄ is slightly less than that of Re(bpy-COOH) alone, indicating that g-C₃N₄ reduces the charge transfer between Re(bpy-COOH) and the intermediates, thus moderating their bond strength. This observation provides an explanation for the reduced Gibbs energy barrier for CO desorption observed in Re(bpy-COOH)/g-C₃N₄, as depicted in Fig. 6.

Additionally, we employed COHP analysis to unravel the interactions between the orbital pairs of intermediates and substrates. This strategy facilitates an understanding of the bonding and antibonding states emanating from each atomic orbital. In Fig. S6 (in the ESI†), we show the energy-resolved COHP between the 2p-orbitals of adsorbed C and a surface N 2p-orbital of g-C₃N₄, or a Re d-orbital of Re(bpy-COOH) and Re(bpy-COOH)/g-C₃N₄ for *COOH and *CO intermediates, respectively. Our analysis indicates weak C-N interactions in g-C₃N₄, as nearly zero COHP is observed around the Fermi level (E_F). In contrast, the C-Re interactions display a peak of the bonding state at E_F in the case of Re(bpy-COOH) and Re(bpy-COOH)/g-C₃N₄, signifying substantial interaction. These strong chemical interactions between C-Re atoms contribute to the favorable CO₂RR observed in Re(bpy-COOH) and Re(bpy-COOH)/g-C₃N₄. Our DFT calculations affirm that Re(bpy-COOH)/g-C₃N₄ acts as a more efficient catalyst for CO₂RR to CO conversion compared to Re(bpy-COOH) and g-C₃N₄. In line with this, our composite catalysts achieve a peak TON (Turnover Number) of CO formation and CO faradaic efficiency of 22.44 and 99.8%, respectively.

4. Conclusions

The hybrid photocatalytic material comprising the molecular catalyst Re(bpy-COOH) and the graphitic carbon nitride g-C₃N₄ is among the first examples of PCO₂R under low-intensity visible-light irradiation. Re(bpy-COOH)/g-C₃N₄ is highly selective for CO production and has a high TON of CO formation. The combination of Re(bpy-COOH) and g-C₃N₄ formed a Z-scheme structure that improves the quantum efficiency and interfacial electron transfer, and decreases electron-hole pair recombination, hence boosting the photocatalytic efficiency. Utilizing DFT calculations, it was found that the Re(bpy-COOH)/g-C₃N₄ hybrid system exhibits efficient charge transfer and demonstrates lower energy barriers for *CO₂ to *COOH conversion, as well as an increased propensity for *COOH formation compared to pure g-C₃N₄. Furthermore, the desorption activation energy of the *CO intermediate is also lower in the Re(bpy-COOH)/g-C₃N₄ system than in pure Re(bpy-COOH), indicating that the hybrid system achieves a balance between two rate-limiting steps for CO₂RR. The unique combination of the two components contributes to the development and tailoring of highly active photocatalysts for low-intensity visible-light irradiation.

Conflicts of interest

The authors declare no competing financial interests.

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