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Constructing a conjugated bridge for efficient electron transport at the interface of an inorganic–organic hetero-junction†

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The large barrier between the phase interfaces of heterojunction catalysts inhibits the electron transfer, resulting in a limited catalytic efficiency. Herein, amino-grafted carbon dots (CDs) were utilized as the building units for the preparation of a CD covalently doped porous polymer. Due to the formation of a conjugated bridge (C=N bond) with delocalized π -electrons, photo-generated electrons were quickly transferred from an organic semiconductor (N₃-COF) to an inorganic semiconductor (CDs). Correspondingly, the improvement percentage for the H₂ production rate of CD-N₃-COF was 560% and 290% compared to that of the physically doped and single bond linked COF systems, respectively. This work provides significant inspiration for consciously regulating the bridge structure at the atomic-level to facilitate the electron transport for the preparation of high-performance heterojunction catalysts.

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Introduction

Photocatalytic conversion as a sustainable, green, and efficient approach has become a hot issue worldwide to overcome the environmental pollution and energy shortage originating from the consumption of traditional fossil fuels.^{1–5} Because of adequate energy supply and no carbon emission, it has great significance in the fields of pollutant degradation,⁶ hydrocarbon production,^{7–9} and antibacterial sterilization.¹⁰ Generally, there are several steps during a photocatalytic reaction including light absorption, photogenerated electron–hole pairs, electron–hole migration, and redox reactions.^{11–14} Therein, the electron–hole migration procedure plays a crucial role in photocatalytic performance, but it is commonly repressed due to the excitonic effect originating from the powerful Coulomb attraction between photogenerated electrons and holes.^{15,16} The problem is particularly acute in semiconductor–semiconductor (S–S) heterojunction based photocatalysts. Because of the confined electronic conductivity, the interfacial transport of the photoinduced charge is critically inhibited, especially for inorganic–organic heterostructure-based semiconductors, resulting in low electron transport efficiency and limited catalytic activity (Fig. 1A).^{17–19} By now, several methods have been proposed to overcome this issue such as assembly of aligned arrays,^{20,21} adjustment of intra-band electronic states,^{22–25} and construction of conducting networks.^{26–30} Nevertheless, the effect of electron transport is not satisfactory, due to a relatively large internal energy dissipation as the electron crosses the homogeneous/heterogeneous boundary.^{31–33}

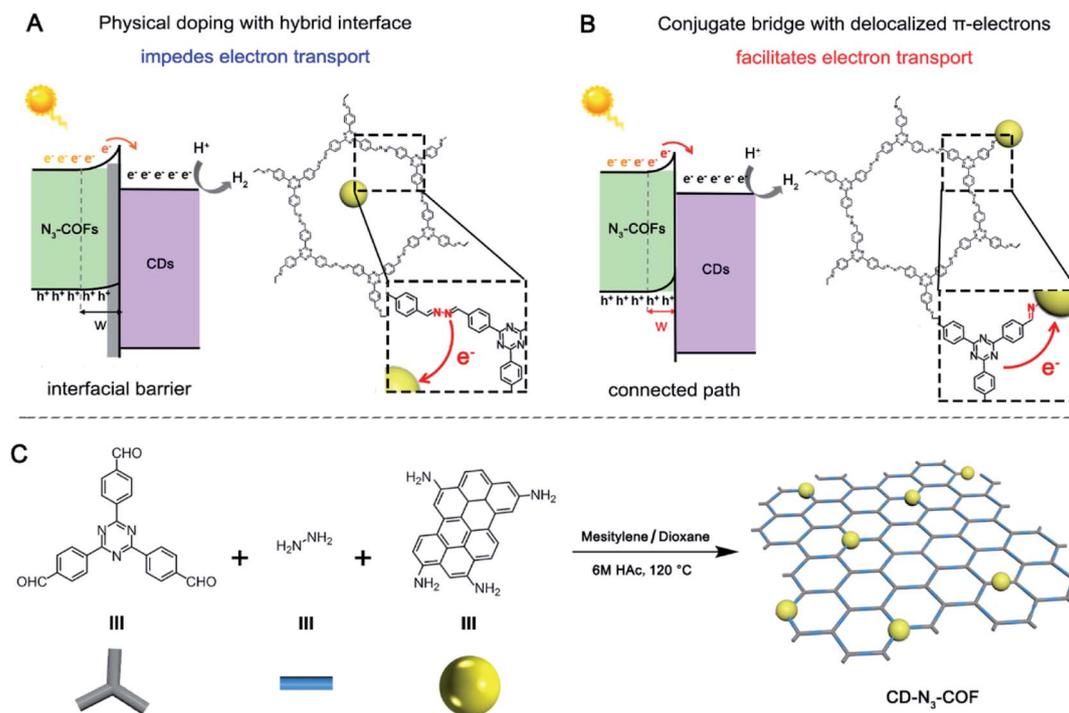


Fig. 1 Schematic illustration of electron transfer at the physically doped (A) and conjugated bridged (B) interfaces of the S-S heterojunction. The synthetic route for inorganic-organic heterostructure-based catalyst, CD-N₃-COFs (C).

Covalent organic frameworks featuring a reversible coupling pattern reveal some excellent characteristics of high crystallinity, large porosity, and tuneable composition. These solids could be equipped with a controllable band gap and wide visible light absorption to serve as novel photocatalysts.³⁴ Accordingly, previous reports focus on the introduction of photosensitive units into the porous networks, which is capable of improving light collection in the visible-light region and adjust the energy band structure.^{35–39} The open architecture could incorporate the guest semiconductor, and this sufficient contact facilitates the migration of electron-hole pairs between the inorganic-organic hetero-junction to some extent. Therefore, constructing a conjugated bridge with delocalized π -electrons between the inorganic-organic hetero-junction for electron transfer across the interface may become a promising strategy for enhanced photocatalytic activity, which is still a great challenge (Fig. 1B).

Herein, amino-grafted inorganic particles (carbon dots, CDs) with strong photoluminescence properties were utilized as the building units for copolymerization with 2,4,6-tris(4-formylphenyl)-1,3,5-triazine and hydrazine. Through a Schiff-base reaction, an imine bond (C=N) with delocalized π -electrons was then obtained to connect the CD particles and N₃-COF network, acting as a high-speed electron transport bridge. After comparison with physically doping and single bond linking (C-N) approaches, the photogenerated electrons of N₃-COF are effectively transferred to the CD acceptor, leading to obviously increased photocatalytic activity (Fig. 1B).

Results and discussion

According to a previous report, amino group-grafted CD nanoparticles (amino-CDs) are prepared from *p*-phenylenediamine in ethanol at 160 °C for 6 hours (Fig. S1†). CD covalently bonded COF frameworks are synthesized by copolymerization of amino-CDs with 2,4,6-tris(4-formylphenyl)-1,3,5-triazine and hydrazine catalyzed by 6 M acetic acid in a mesitylene/dioxane (1 : 1) mixture at 120 °C for 3 days. The synthesis method is consistent with that of N₃-COF (the synthetic diagram is depicted in Fig. 1C, and experimental details are provided in Fig. S2†). CD-N₃-COF solids with different doping contents are denoted as *x*CD-N₃-COF, where *x* represents the initial mass of amino-CDs involved in the reaction (*x* = 0.1, 0.2, 0.3, 0.5, and 1.0 mg). For comparison, both physically doping and single bond linking (C-N) approaches are adopted to prepare CD-based COF samples as the reference, denoted as CD@N₃-COF and CD/N₃-COF (Fig. S3†).

The powder X-ray diffraction (PXRD) analysis of CD-N₃-COFs shows a series of peaks at 6.0, 7.1, 9.5 and $\sim 26^\circ$ corresponding to the reflections of (110), (120), (200) and (001) planes, respectively. Notably, the intense 100 reflection gradually shifts with the increase of the CD mass involved in the reaction from 3.50° for the parent N₃-COF to 3.57° for 1.0CD@N₃-COF (Fig. 2A). As for the physically doped sample, there is no shift for the 100 plane observed (Fig. S4†). This result is caused by the introduction of CD particles during the co-polymerization step that changes the microscopic structure of the COF network,

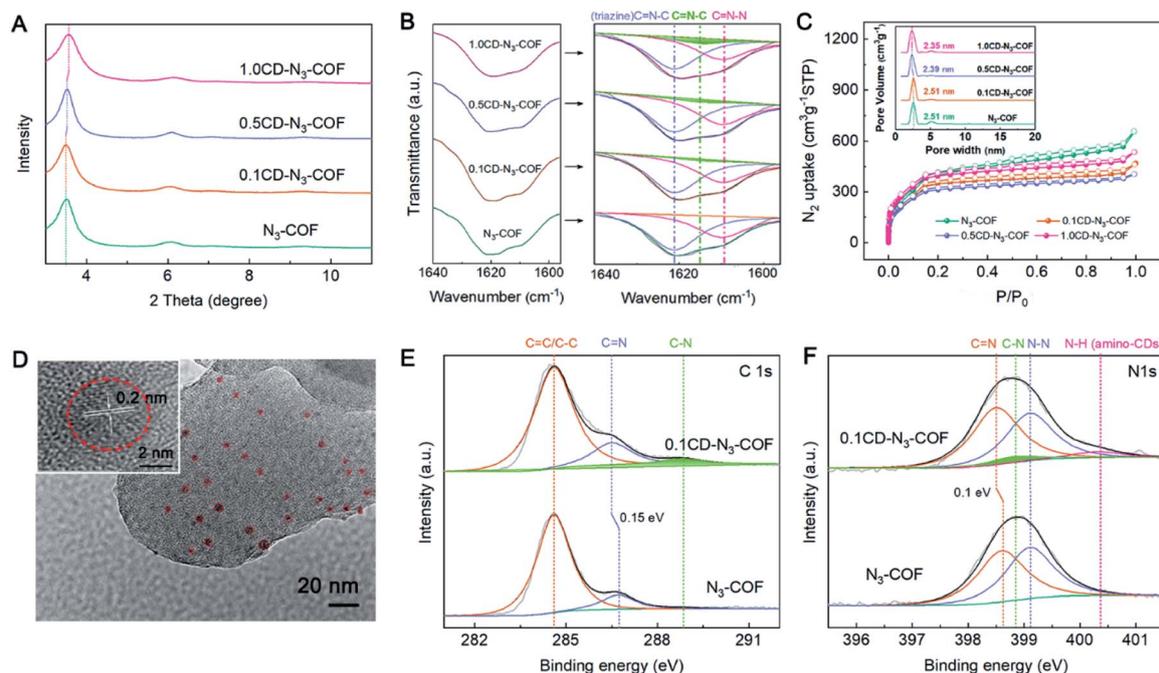


Fig. 2 (A) PXRD patterns for N_3 -COF and CD- N_3 -COFs. (B) C=N band in the FT-IR spectra of N_3 -COF and CD- N_3 -COFs from 1640 to 1590 cm^{-1} . (C) N_2 sorption isotherms and pore size distributions of N_3 -COF and CD- N_3 -COFs. (D) TEM image of 0.1CD- N_3 -COF. Carbon dot nanoparticles are highlighted by a red circle. C_{1s} (E) and N_{1s} (F) XPS spectra for 0.1CD- N_3 -COF and N_3 -COF, respectively.

proving the successful integration of CD particles into the COF architecture.

According to Fourier transform infrared (FT-IR) spectral analysis, the characteristic peaks of amino-CDs are observed at 2848–2958 cm^{-1} corresponding to the stretching vibration of the $-\text{CH}_2-$ group. The retention of the $-\text{NH}_2$ peak at 3373–3200 cm^{-1} demonstrates the presence of amino groups on the CD particles (Fig. S5[†]).⁴⁰ After the coupling reaction, the FTIR spectra of CD- N_3 -COFs showed an azine C=N stretching band at around 1640–1590 cm^{-1} which could be subdivided into three peaks of C=N–N at 1609 cm^{-1} , C=N–C (triazine) at 1621 cm^{-1} , and C=N–C (CD connected Schiff base bond) at 1615 cm^{-1} (Fig. 2B). The C–C stretching vibrations ascribed to the $-\text{CH}_2-$ group of amino-CDs (emerged at 2848–2958 cm^{-1}) indicated that the CD particles were connected to the COF frameworks through C=N bonds (Fig. S6[†]).

Upon evaluation by the N_2 adsorption–desorption experiment at 77 K, CD- N_3 -COFs showed high porosity, consistent with that of N_3 -COF (Fig. 2C). The Brunauer–Emmett–Teller (BET) surface areas of N_3 -COF, 0.1CD- N_3 -COF, 0.5CD- N_3 -COF, and 1.0CD- N_3 -COF were calculated to be 1100, 974, 955, and 1197 $\text{m}^2 \text{g}^{-1}$, respectively. The pore size distributions were located at around 2.51, 2.51, 2.39, and 2.35 nm for N_3 -COF, 0.1CD- N_3 -COF, 0.5CD- N_3 -COF, and 1.0CD- N_3 -COF, respectively (Fig. 2C). The result was in concert with that of PXRD analysis that the pore size became narrow with the increase of the CD content.

Scanning electron microscope (SEM) images exhibited rod-like morphology for N_3 -COF and CD- N_3 -COFs (Fig. S7 and S8[†]). The high-resolution transmission electron microscope (HRTEM) image demonstrated that a lot of carbon dots of size

~5 nm were decorated on the skeleton of CD- N_3 -COFs. A 0.2 nm lattice fringe in the dotted line area is attributed to amino-CDs (Fig. 2D). CD- N_3 -COFs exhibited a relatively high thermal stability up to 380 °C, analyzed by using thermogravimetric analysis (TGA) under an air atmosphere (Fig. S9[†]). After soaking 0.1CD- N_3 -COF in water for 24 hours, 0.1CD- N_3 -COF maintained the ordered structure, facilitating the photocatalytic reduction of water into H_2 molecules (Fig. S10[†]).

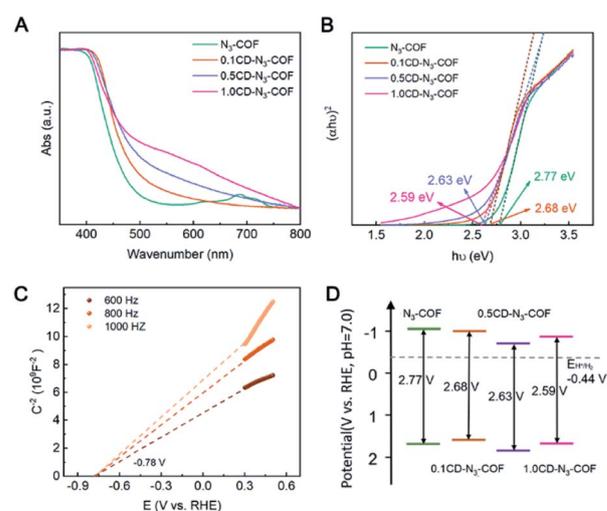


Fig. 3 (A) Solid-state UV/Vis absorption spectra and (B) band gap energies of N_3 -COF and CD- N_3 -COFs. (C) Mott–Schottky plots of 0.1CD- N_3 -COF, and (D) proposed band structures of N_3 -COF and CD- N_3 -COFs.

The chemical state and intimate interaction of CD-N₃-COF were studied by X-ray photoelectron spectroscopy (XPS) (Fig. S11†). Using 0.1CD-N₃-COF as an object, the high-resolution C_{1s} spectra illustrated three conspicuous peaks corresponding to C=C/C-C, C=N, and C-N groups. As displayed in Fig. 2E, the peak centered at 286.5 eV assigned to the C=N signal of CD-N₃-COF shifted to the lower-energy side by 0.15 eV compared with that of N₃-COF, because electron-rich CD particles offered their electrons to the surrounding skeleton, increasing the electron cloud density.^{41–43} As for the high-resolution N_{1s} spectra, they could be divided into four peaks, including 398.5 eV for C=N, 398.8 eV for C-N, 399.1 eV for N-N, and 400.4 eV for N-H (Fig. 2F). Compared to N₃-COF, there was a slight shift with a binding energy of 0.1 eV for the C=N peak in 0.1CD-N₃-COF.⁴¹ This result was in good agreement with the high-resolution C_{1s} XPS spectra indicating that the electron cloud density of N atoms (C=N) was affected by CD particles. To sum up, these results confirmed that amino-CDs were successfully spliced into the COF network through C=N covalent bonds.

Solid-state UV-Vis absorption spectra were recorded to investigate the band structure of the COF samples. The bandgap value (E_g) was estimated from the transformational Tauc plots obtained from the Kubelka-Munk function.⁴³ As shown in Fig. 3A, the absorption region of CD-N₃-COFs increased obviously in the UV-Vis absorption spectra, illustrating that the introduction of CD particles influenced the band structure of the COF network. The E_g values of N₃-COF and CD-N₃-COFs were calculated to be 2.77, 2.68, 2.63, and 2.59 eV, respectively (Fig. 3B). The obvious red shift of the absorption edge visible for the UV-Vis spectra of CD-N₃-COFs suggests a decreased band gap. A narrow E_g value is beneficial to the absorption of visible light and the generation of optical carriers to improve the photocatalytic performance.⁴⁴ Mott-Schottky plots proved that the flat band (E_{fb}) potentials of N₃-COF and CD-N₃-COFs were -0.82, -0.78, -0.53, and -0.74 V (vs. RHE), respectively (Fig. 3C and S12†).⁴⁵

Besides, the positive slopes of M-S plots prove that N₃-COF and CD-N₃-COFs are n-type semiconductors. As previously reported, the conduction band potential (E_{CB}) of an n-type semiconductor is about 0.2 eV negative compared with the E_{fb} ,⁴³ and the E_{CB} values of N₃-COF and CD-N₃-COFs are calculated to be -1.02, -0.98, -0.73, and -0.96 V (vs. RHE), respectively. The valence band (E_{VB}) potentials of N₃-COF and CD-N₃-COFs are 1.75, 1.70, 1.95, and 1.85 V (vs. RHE), respectively, which are calculated by using the equation $E_{VB} = E_{CB} + E_g$ (Fig. 3D).⁴⁵ The reduction potential of hydrogen is known to be at -0.44 V (vs. RHE), so N₃-COF and CD-N₃-COFs thermodynamically favor photocatalytic water splitting. In addition, the more positive valence band position of CD-N₃-COFs reduces the barrier height of the photocatalyst-Pt (cocatalyst), thus the electron transfer of thermionic emission through the interface becomes easier to boost the capability for photocatalysis.⁴⁶

The photocatalytic activity of COF solids for visible light-induced hydrogen evolution was investigated under light irradiation with a $\lambda \geq 420$ nm. The hydrogen evolution experiments were conducted using Pt as a co-catalyst with the addition of

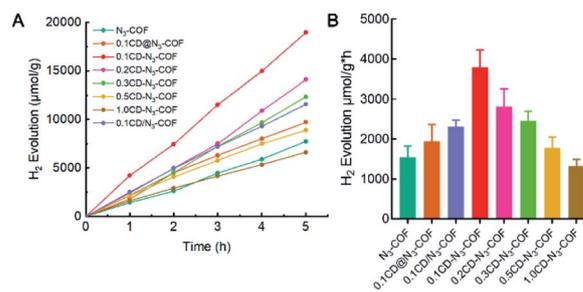


Fig. 4 (A) Photocatalytic performance for H₂ evolution per unit mass. (B) Comparisons of H₂ evolution amounts for the COF samples.

triethanolamine (TEOA) as a sacrificial electron donor in PBS at pH 7. Notably, the H₂ release rate is determined by a standard curve drawn from the integral area of the H₂ peak (Fig. S13†). After 5 hours of irradiation, the H₂ evolution amount of 18939.4 μmol per unit mass by the 0.1CD-N₃-COF photocatalyst remarkably increased from that (7720 μmol g⁻¹) of N₃-COF (Fig. 4A). Correspondingly, the H₂ evolution rate of the 0.1CD-N₃-COF photocatalyst was calculated to be 3787 μmol g⁻¹ h⁻¹, which was enhanced up to 245% and 195% compared with that of pure N₃-COF and physically doped N₃-COF, respectively (Fig. 4B). As shown in Fig. 4B, the H₂ evolution rates of COF photocatalysts decreased along with the increased doping content of CD particles. This phenomenon is due to the excessive surface defects caused by the high doping amount that leads to easy electron-hole recombination and inhibits the transfer of electrons.⁴⁷ As revealed in Fig. S14,† 0.1CD@N₃-COF exhibited excellent photocatalytic H₂ evolution durability after four recycles. The experimental results showed that the photocatalytic performance of covalently bonded heterostructures was superior to that of traditional physically doped heterojunctions.

As for physically doping and single bond linking (C-N) approaches, the H₂ evolution rates of CD@N₃-COF and CD/N₃-COF were calculated to be 1940 and 2312 μmol g⁻¹ h⁻¹, which were enhanced up to 26% and 50% compared with that of pure N₃-COF. But these values were much lower than that of CD-N₃-COF with the conjugated bridge (3787 μmol g⁻¹ h⁻¹) under the same experimental conditions (Fig. 4B). It could be calculated that the hydrogen production performance improvement rate of CD-N₃-COF is 5.6 times and 2.9 times that of CD@COF and CD/N₃-COF, respectively. This phenomenon is attributed to the imine bond (C=N) with delocalized π-electrons being effective to transport the photo-generated electrons from the N₃-COF network to CD particles. Notably, the performance of CD-N₃-COF surpasses that of many remarkable COF solids, such as TP-BDDA-COF (3240 μmol g⁻¹ h⁻¹), TpDTz-COF (941 μmol g⁻¹ h⁻¹), and a porphyrin-based COF (413 μmol g⁻¹ h⁻¹) (Table S1†).

Further effort was made to determine the working mechanism of the conjugated bridge of CD-N₃-COF photocatalysts. The photoluminescence (PL) spectra of CD@N₃-COF (physically doping), CD/N₃-COF (single bond linking), and CD-N₃-COF (conjugated bridging) displayed a prominent emission peak centered at 600 nm after the 420 nm excitation (Fig. 5A). Under the same conditions, CD-N₃-COF revealed the strongest PL

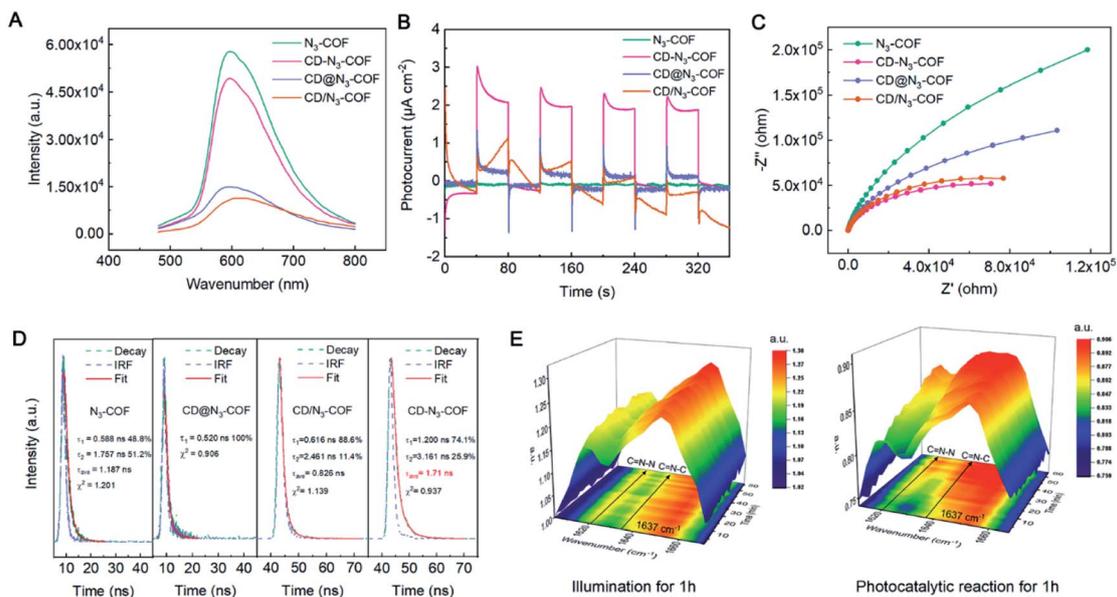


Fig. 5 (A) PL spectra, (B) transient photocurrent response, (C) electrochemical impedance spectra, and (D) time-resolved transient PL decay for N_3 -COF, $CD@N_3$ -COF, CD/N_3 -COF and $CD-N_3$ -COF, respectively. (E) *In situ* FT-IR spectra of 0.1 $CD-N_3$ -COF under photocatalytic conditions and illumination for 1 h.

emission, proving that the conjugated bridge (C=N bond) with delocalized p-electrons facilitated the separation of photo-generated carriers.⁴⁸

Utterly, the kinetic transfer of carriers is determined from time-resolved transient PL (TRPL) spectra (Fig. 5D). The decay curves of $CD-N_3$ -COF and N_3 -COF were automatically calculated by the double exponential kinetic function fitting. As depicted in Fig. 5D, the short lifetime (τ_1) increased from 0.588 (N_3 -COF) to 1.200 ns ($CD-N_3$ -COF). Similarly, the long lifetime (τ_2) of N_3 -COF (1.757 ns) was also shorter than that of $CD-N_3$ -COF (3.161 ns); as reflected by the nonradiative energy transfer process, self-trapped excitons in $CD-N_3$ -COF were hard to form by captured electrons.⁴⁹ The TRPL spectrum of $CD@N_3$ -COF was fitted by a single-exponential term with a fluorescence lifetime of ~ 0.520 ns, implying a poor capability of $CD@N_3$ -COF for carrier separation (Fig. 5D).⁵⁰ All these results indicated that the existence of the conjugated bridge decreased the electronic transmission resistance, which improved the photocarrier transport rate and inhibited the recombination of free electrons and holes obviously.^{43,45,49}

Measured from transient photocurrent responses ($I-t$), the photocurrent density of $CD-N_3$ -COF was revealed to be 48, 7.3 and 6.1 times higher than that of N_3 -COF, $CD@N_3$ -COF, and CD/N_3 -COF (Fig. 5B). Correspondingly, the calculated photoelectron diffusion length (L_n) of $CD-N_3$ -COF was significantly increased by 1.72 times relative to that of $CD@N_3$ -COF, confirming the accelerated photoelectron movement (Fig. S15[†]).⁴⁵ The electrochemical impedance spectroscopy (EIS) results for all COF powders are revealed in Fig. 5C. The semicircle of $CD-N_3$ -COF was the smallest, compared to that of N_3 -COF, CD/N_3 -COF, and $CD@N_3$ -COF. The conjugated bridge (C=N bond) with delocalized p-electrons between CD nanoparticles and the

COF network reduced the interfacial charge transfer resistance for the acceleration of electron transfer.

The key role of the conjugated bridge (C=N bond) for electron transfer was monitored by *in situ* FT-IR spectroscopy. Within 1 hour of light exposure of 0.1 $CD-N_3$ -COF, the peak intensity of C=N-C (CD connected Schiff base bond) and C=N-N stretching vibrations remained unchanged (Fig. 5E and S16[†]). As for the photocatalytic H_2 production, the C=N-N stretching vibration located at 1621 cm^{-1} was gradually enhanced. This is ascribed to the double bonded N-N groups in N_3 -COF being the active centers for the hydrogen reduction reaction. They will generate electrons under visible light radiation and increase the electron cloud density, leading to the enlarged vibration frequency of the C=N (C=N-N) band. For the C=N-C groups, they are determined to have little ability to generate electrons.^{41,51} After the irradiation, the C=N stretching vibration at 1637 cm^{-1} was also significantly enhanced along with the catalytic reaction (Fig. 5E and S16[†]). It is proved that the conjugate bridge (C=N bond) is effective for electron transfer from the COF network to CD particles.

Conclusions

In summary, we described that carbon dots were covalently bonded to N_3 -COF matrices in the heterojunction $CD-N_3$ -COF through the C=N bond. The conjugated bridge with delocalized p-electrons was effective in overcoming the transfer barrier to increase the electron transfer rate. Based on this unique structure, effective electron transfer was achieved, and then an efficient photocatalytic water splitting system was obtained. The corresponding evolution rate for hydrogen production was obviously enlarged compared with that of physically doped N_3 -COF. This work provides an effective strategy for the connection

of the interface of the S–S heterojunction, which will attract a broad audience from material synthesis and design and application for heterogeneous catalysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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