

An All-Organic D-A System for Visible-Light-Driven Overall Water Splitting

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Direct water splitting over photocatalysts is a prospective strategy to convert solar energy into hydrogen energy. Nevertheless, because of the undesirable electron accumulation at the surface, the overall water-splitting efficiency is seriously restricted by the poor charge separation/transfer ability. Here, an all-organic donor-acceptor (D-A) system through crafting carbon rings units-conjugated tubular graphitic carbon nitride (C-TCN) is proposed. Through a range of characterizations and theoretical calculations, the incorporation of carbon rings units via continuous π -conjugated bond builds a D-A system, which can drive intramolecular charge transfer to realize highly efficient charge separation. More importantly, the tubular structure and the incorporated carbon rings units cause a significant downshift of the valence band, of which the potential is beneficial to the activation for O₂ evolution. When serving as photocatalyst for overall water splitting, C-TCN displays considerable performance with H₂ and O₂ production rates of 204.6 and 100.8 μ mol g⁻¹ h⁻¹, respectively. The corresponding external quantum efficiency reaches 2.6% at 405 nm, and still remains 1.7% at 420 nm. This work demonstrates that the all-organic D-A system conceptualized from organic solar cell can offer promotional effect for overall water splitting by addressing the charge accumulation problem rooted in the hydrogen evolution reaction.

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1. Introduction

Hydrogen production by means of photocatalytic water splitting represents a green way to convert solar energy into the renewable and clean hydrogen energy.^[1-5] For this reason, photocatalytic water splitting holds great promise in addressing the long-standing environmental and energy issues, which has attracted extensive attention of researchers from different scientific and engineering domains.^[5-9] Despite the intriguing prospect of photocatalytic water splitting, recent photocatalytic systems are still far from meeting the requirements of industrial standard for water splitting reaction, especially the challenges associated with the low solarto-hydrogen (STH) conversion efficiency (the targeted STH conversion efficiency for commercial application threshold is 10%).^[10-12] The unfavorable STH conversion efficiency can be explained from three different aspects, which are photoabsorption performance, charge separation/transfer efficiency, and surface reactions.^[13] Therefore, in order to

enhance the STH conversion efficiency, the selection of suitable photocatalytic materials and the design of efficient photocatalytic systems appear to be especially important.^[14]

Among various photocatalytic materials, graphitic carbon nitride (g-C₃N₄) has taken tremendous interest in photocatalytic overall water splitting because of its suitable electronic structure ($E_{\rm g}$: 2.7 eV, $E_{\rm VB}$: +1.6 V, and $E_{\rm CB}$: -1.1 V, which are the prerequisite for photocatalytic overall water splitting).^[15-17] However, bulk g-C₃N₄ (Bulk CN) is also facing the abovementioned obstacles.^[18] From this perspective, numerous strategies, including nanostructuring, cocatalyst loading, elemental doping, heterojunction construction, and so on, have been developed to enhance the photocatalytic activity of Bulk CN through optimizing one or more of the above three aspects.^[16,19-21] Despite tremendous effort devoted to optimizing the three aspects mentioned above, the photocatalytic enhancement is insufficient to reach parity with those metal-based photocatalysts, let alone satisfying the requirements of industrial standard.^[2,16] Hence, further insight into how material design affect the performance of g-C₃N₄ is essential to provide basic guideline for achieving enhancement in photocatalytic activity. Considering that the



Figure 1. a) Schematic representation, b) SEM image, c) TEM image, and d) HRTEM image of C-TCN (The circular area represents carbon rings units and the rectangular area is g-C₃N₄); Chemical element mapping images of C-TCN: e) C and f) N.

high adjustability and compatibility of g-C₃N₄ due to its intrinsic polymeric feature and tunable chemical composition, rational molecular design is an efficient strategy that can be used to optimize the photocatalytic performance of g-C₃N₄.^[18,22–24] Molecular design strategy can deliberately introduce some appointed elements, functional groups, or molecules into the basal plane of g-C₃N₄, which intrinsically optimizes the band structure and textual property of g-C₃N₄, thus achieving outstanding photocatalytic efficiency.^[25,26] Even so, the conventional molecular design strategy still suffers from unfavorable charge separation/transfer efficiency, thereby limiting the photocatalytic performance and stability.

In the past few years, the feasibility of donor-acceptor (D-A) system has been demonstrated in organic solar cells. which can effectively overcome the limit of charge diffusion length of polymer and promote the charge separation via intramolecular charge transfer.^[27-30] Inspired by the high performance of D-A system in organic solar cells in addition to the high malleability of g-C₃N₄, we therefore believe that the D-A system also can duplicate its success in the photocatalysis field. With this in mind, molecular design strategy is utilized to build a g-C₃N₄-based D-A system by precisely embedding suitable small organic molecules into the basal plane of g-C₃N₄. Recently, Wang and co-workers developed an efficient D-A system by cocondensation of urea with oxamide in molten salt, where the corresponding apparent quantum efficiency reached up to 57% at $\lambda = 420 \text{ nm.}^{[24]}$ Wang and coworkers also built another D-A system by preparing a selenium and cyanamide-functionalized heptazine-based melon to accelerate the charge transfer, which further proved the feasibility of D-A system.^[30] In particular, carbon rings units can be seamlessly grafted into the basal plane of g-C₃N₄ via continuous π -conjugated bond due to their similar aromatic structures.^[31-35] Theoretically, the electron-withdrawing property of carbon rings units is stronger than that of g-C₃N₄, so carbon rings units and the basal plane of g-C₃N₄ can serve as the electron acceptor and donor, respectively. Once the g-C₃N₄-based D-A polymer is photoexcited, the excited electron is rapidly extracted from the basal plane of $g-C_3N_4$ (the electron donor) to carbon rings units (the electron acceptor), which can reduce the potential for charge accumulation by accelerating the charge separation, resulting in the optimization of photocatalytic performance and even the realization of overall water splitting.

As a proof-of-concept, we constructed an all-organic D-A system by grafting carbon rings units on the basal plane of $g-C_3N_4$. In addition, melamine and glucose served as the precursor of $g-C_3N_4$ units and carbon rings units, meanwhile supramolecular self-assembly strategy was employed for the assembly of 1D tubular structure. On one hand, carbon rings-conjugated tubular $g-C_3N_4$ (C-TCN) has stronger oxidation ability than the Bulk CN, which is more likely to enable the O_2 evolution reaction that is inaccessible by the Bulk CN. On the other hand, the incorporation of carbon rings units can also extend the light absorption and promotes the charge separation due to the intramolecular charge transfer, as verified by density functional theory (DFT) calculations. Consequently, the C-TCN exhibits excellent and stable photocatalytic overall water splitting activity.

2. Results and Discussions

2.1. Synthesis and Structure of C-TCN

As illustrated in **Figure 1**a, we report a template-free preassembly strategy to prepare C-TCN. In the first step, melamine and glucose are used as the precursors for the synthesis of supramolecular intermediate via molecular self-assembly. It is postulated that the self-assembly process starts with the reaction between melamine and H_2O to produce cyanuric acid at 200 °C for 12 h before the cyanuric acid assembles with the unreacted melamine into the supramolecular intermediate through hydrogen bonding.^[36] Thanks to the abundant hydroxyl groups of glucose, such unique feature ensures that glucose is perfectly combined into the supramolecular intermediate through hydrogen bonding. The supramolecular assembly process has a significant effect on the synthesis of final photocatalyst. On the one hand, the supramolecular intermediate is employed as a self-template to control the formation of TCN. In the second step, the as-prepared supramolecular intermediate is further polymerized under a N₂ atmosphere at 550 °C for 4 h. Due to the similar aromatic structures, carbon rings units can be in situ incorporated into the conjugated network of TCN via continuous π -conjugated bond, and named C-TCN.^[31–33,35]

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The significance of supramolecular assembly process can be further illustrated from scanning electron microscope (SEM) and transmission electron microscopy (TEM) images. As illustrated in Figure S1a (Supporting Information), the melamine is random-shaped particles with a wide size distribution. In contrast, the supramolecular intermediate exhibits uniform hexagonal rod morphology after hydrothermal reaction (Figure S1b, Supporting Information). The X-ray diffraction (XRD) patterns (Figure S3a, Supporting Information) and Fourier transform infrared (FTIR) spectra (Figure S3b, Supporting Information) also confirm that the melamine has turned into the supramolecular intermediate via molecular self-assembly.^[36,37] As shown in Figure S3a (Supporting Information), the characteristic diffraction peaks of supramolecular intermediate accord well with the structure in previous report, the strongest peak at 28.1° assigns to the graphite-like stacking of sheet-like structure, and the other peaks at about 11.8°, 17.7°, and 21.9° are attributed to the in-planar packing in (100), (110), and (200) planes, respectively.^[38,39] The above result is further substantiated by FTIR spectra (Figure S3b, Supporting Information), the peaks located at 763, 1442, and 1528 cm⁻¹ are attributed to the breathing mode of triazine units, the stretching of CN-heterocycles, and the stretching mode of the triazine units, respectively. The peaks at 1727 and 1778 cm⁻¹ are assigned to the stretching modes of the carbonyl group, and the bands observed at 3200–3400 cm⁻¹ are attributed to the stretching vibration band of the amino group.^[40] In order to further investigate the important role of the supramolecular intermediate in determining the morphology of the final product, SEM and TEM analyses on the C-TCN were carried out (Figure 1b,c and Figure S1c,d, Supporting Information). The Bulk CN derived from melamine is composed of macrosized particles with irregular blocky structure (Figure S1c, Supporting Information). In contrast, as shown in Figure 1b,c and Figure S1d (Supporting Information), the C-TCN exhibits uniform hexagonal tubular morphology (diameter: 1-3 µm, length: 10-30 µm), demonstrating that the C-TCN retains the original 1D structure of the supramolecular intermediate well. Additionally, as can be seen from the magnified TEM image of the C-TCN in Figure S2a (Supporting Information), the C-TCN also possesses plentiful nanoscale pores on the tubular structure, which might result in larger specific surface area than the Bulk CN. Such a presumption is verified by the N₂ adsorption-desorption experiments (Figure S2c, Supporting Information), in which the specific surface area of the C-TCN (116.8 $m^2 g^{-1}$) is clearly larger than that of the Bulk CN (8.6 m² g⁻¹). The high-resolution TEM (HRTEM) image in Figure 1d exhibits that the C-TCN consists of amorphous and crystalline regions. The amorphous region belongs to the disordered triazine units of the g-C₃N₄, which is the same as the HRTEM image of the Bulk CN (Figure S2b, Supporting

Information). On the other hand, the crystalline region that features a lattice space of 0.35 nm can be assigned to the (002) plane of the carbon rings.^[32] The energy-dispersive X-ray (EDX) elemental mapping images of the C-TCN exhibit the homogeneous distribution of C and N elements over the entire nanotube (Figure 1e,f).

XRD, FTIR, synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy, Raman, solid-state ¹³C NMR spectra, and X-ray photoelectron spectroscopy (XPS) analyses were used to characterize the chemical composition of the C-TCN. The XRD patterns are shown in Figure 2a, the C-TCN exhibits two typical diffraction peaks, which is consistent with that of the Bulk CN, indicating the C-TCN retains the crystal structure of g-C₃N₄. More specifically, the (100) diffraction peak at around 13.1° originates from the in-plane repeated units of tri-s-triazine,^[41] while the (002) diffraction peak at 27.3° is attributed to the interlayer stacking of g-C3N4.[42] Compared with the Bulk CN, the intensities of (002) peak in TCN and C-TCN become weaker, which is ascribed to the evident size-dependent properties of tubular structure.^[36] The intensity of the (002) peak in C-TCN tends to be weaker than that of TCN, indicating the introduction of glucose in calcination process may cause weaker crystallinity.^[31,43] Furthermore, the structural information about the C-TCN is further characterized by FTIR analysis shown in Figure S4a (Supporting Information). No significant difference is observed between the FTIR absorption peaks of the C-TCN and Bulk CN, and all the peaks can be assigned to the basic crystal structure of g-C₃N₄.^[44] Relevant structural characteristics of C-TCN are further performed by C and N K-edge XANES measurement (Figure 2b,c). In the C K-edge XANES spectra (Figure 2b), both samples display a typical structure of g-C₃N₄, which can be indexed to $\sigma^*(C-N-C/C-N)$, $\pi^*(C-N-C)$, and $\pi^*(C-C/C=C)$.^[31,45] Interestingly, C-TCN exhibits higher peak intensity of $\pi^*(C-C/C=C)$ than that of Bulk CN and TCN, which may be derived from the introduction of carbon rings units. In consideration of the higher electronwithdrawing property of carbon rings than g-C₃N₄, the electron migration from the basal plane of g-C₃N₄ to carbon rings units could be expected in C-TCN. The peak intensity of $\pi^*(C-N-C)$ increases a lot after the incorporation of carbon rings units into the conjugated network of TCN, indicating a stronger interfacial interaction between carbon rings units and the basal plane of g-C₃N₄.^[46] Such stronger interfacial interaction can create a conductive path across the layers to accelerate the electron transport in C-TCN, which brings efficient charge separation/ transfer and then promotes the photocatalytic performance.^[47] In addition, the N K-edge XANES spectra (Figure 2c), for Bulk CN, TCN, and C-TCN show four typical features at 399.7, 401.4, 402.5, and >405 eV, which can be assigned to $\pi^*(C-N-C)$, $\pi^*(N-3C)$, $\pi^*(N-3C)$ bridging), and $\sigma^*(C-N-C/C-N)$.^[45] The enhancement of $\pi^*(C-N-C)$ feature for C-TCN suggests a strengthen interfacial interaction between carbon rings units and the basal plane of g-C3N4, which is consistent with the result of C K-edge XANES spectra. This newly formed carbon rings units can be further verified by the solid-state ¹³C NMR spectra (Figure 2d). For Bulk CN, TCN, and C-TCN, two typical peaks at the chemical shifts of 162.5 and 154.4 ppm are observed, which are assigned to the basic crystal structure of g-C₃N₄.^[48] Different from Bulk CN and TCN, two new peaks





Figure 2. a) XRD patterns, b) C K-edge XANES spectra, c) N K-edge XANES spectra, and d) solid-state ¹³C MAS NMR spectra of C-TCN.

assigned to the incorporated carbon rings units are clearly found at the chemical shifts of 128.1 and 118.7 ppm, which confirms the successful incorporation of carbon rings units into the basal plane of g-C₃N₄.^[49] Raman spectra in Figure S4b (Supporting Information) are carried out to further prove the presence of carbon rings units in the C-TCN. Typically, Bulk CN and TCN show no characteristic absorption bands. In comparison, two characteristic peaks corresponding to characteristic features of crystalline graphite are observed at 1350 and 1574 cm⁻¹ in the C-TCN, confirming that crystalline graphite unit indeed exists in the C-TCN.^[32,50] Furthermore, XPS was conducted to examine the presence of crystalline graphite unit in the basal plane of the g-C₃N₄. XPS survey spectra (Figure S4c, Supporting Information) and elemental composition (Table S1, Supporting Information) indicate that C-TCN has the higher C content than Bulk CN. In order to further determine the origin of increased C content, the high-resolution C 1s spectra in Figure S4d (Supporting Information) are deconvoluted into three areas at 284.8, 286.3, and 288.2 eV, which are assigned to N-C=N, C-NH_x, and C-C/C=C, respectively.^[51] Note that C-TCN shows higher content of C-C/C=C bonds than Bulk CN (Table S2, Supporting Information). The sp² hybridization of C-C/C=C bonds is ascribed to crystalline graphite, demonstrating the formation of carbon rings units in the C-TCN. Meanwhile, the high-resolution N 1s spectrum (Figure S4e, Supporting Information) can be deconvoluted into four areas, including 398.7 eV for sp²-hybridized nitrogen (C=N-C), 400.1 eV for the tertiary N bonding to carbon atoms $N-(C)_3$ or $H-N-(C)_2$, 401.1 eV for terminal amino functions (C-N-H), and 404.4 eV

for π -excitations of the C=N conjugated structure.^[52] The above analysis results evidence the successful incorporation of carbon rings units into the conjugated network of TCN via continuous π -conjugated bond during pyrolysis.

The incorporation of carbon rings units into the basal plane of g-C₃N₄ can dramatically influence the optical property, which is measured by UV-vis absorption spectra in Figure 3a. Specifically, an obvious blueshift is observed in the absorption edge of the TCN with respect to the Bulk CN, which is usually ascribed to the strong quantum confinement effect arises from the ultrathin and porous structure of the TCN.^[53] Interestingly, for C-TCN, a redshift emerges in the absorption edge with regard to the TCN, due to the efficient incorporation of carbon rings units. Meanwhile, the incorporation of carbon rings units in the basal plane of g-C₃N₄ causes the absorption profile further stretches into the visible range, making the full range of visible light usable for photocatalysis. Correspondingly, the bandgaps of Bulk CN, TCN, and C-TCN are calculated to be 2.78, 2.86, and 2.81 eV by Kubelka-Munk function (Figure 3b). The valence band (VB) positions of the Bulk CN and C-TCN are measured by VB XPS spectra (Figure 3c), which are about 1.74, 2.01, and 2.05 V, respectively. Obviously, the C-TCN possesses the strongest oxidation ability due to the deepest VB level, which is beneficial for O₂ evolution reaction. The outstanding oxidation ability of the C-TCN is verified by the electron spin resonance (ESR) shown in Figure S5 (Supporting Information). As expected, for Bulk CN, only ESR signals of DMPO-'O2⁻ but no ESR signal of DMPO-'OH are observed because the VB potential of the Bulk CN is higher than the potential of







Figure 3. a) UV-vis absorption spectra, b) the estimated bandgaps, c) VB XPS spectra, and d) band alignment of C-TCN.

OH[−]/•OH (1.99 V).^[54] Interestingly, the characteristic signals of DMPO-OH are detected in the C-TCN, and the VB potential of the C-TCN is sufficiently positive for the oxidation of OH[−] to generate •OH. Therefore, the above analysis indicates that the C-TCN has better oxidation ability superior to Bulk CN, inferring that O₂ evolution reaction is more likely to happen in the C-TCN. According to the combined analysis of bandgaps and VB edges, the CB potentials of the Bulk CN, TCN, and C-TCN are calculated to be −1.04, −0.85, and −0.76 V, respectively. Although the CB potential of the C-TCN reveals a positive shift with regard to the Bulk CN, it is still more negative than the reduction potential of H⁺/H₂ (−0.41 V vs NHE, pH = 7). The corresponding band alignments of the Bulk CN and C-TCN are schematically depicted in Figure 3d.

2.2. Photocatalytic Overall Water Splitting

In view of the excellent photoelectric properties, the C-TCN is expected to be a promising photocatalyst. First, the photocatalytic performance of the C-TCN was evaluated by examining the efficiency of photocatalytic overall water splitting using Pt (3%) as the cocatalyst at $\lambda > 400$ nm irradiation in pure water, the photocatalytic water splitting equipment is an on-line photocatalytic analysis system (Lbsolar-IIIAG, PerfectLight, Beijing). As revealed in **Figure 4**a, the C-TCN exhibits excellent photocatalytic activity (2.69 µmol h⁻¹ H₂ and 1.30 µmol h⁻¹ O₂) with a H₂/O₂ ratio of 2:1. Meanwhile, no noticeable attenuation of the photocatalytic performance is observed in a 25 h reaction, demonstrating that the C-TCN has a promising photostability. As expected, when CoO_x (1%) is further deposited on C-TCN, the

photocatalytic performance of C-TCN is significantly improved in comparison with only using Pt (3%) as the cocatalyst, and the average H_2 and O_2 evolution rates are estimated to be 10.23 and 5.04 µmol h⁻¹, respectively (Figure 4b). To our knowledge, the photocatalytic activity is superior to most of the previous reported g-C₃N₄-based photocatalysts (Table S3, Supporting Information). Moreover, no obvious decay is observed in a 25 h reaction, which further implies the remarkable photostability of the C-TCN. The control experiment of photocatalytic overall water splitting is further performed, and no gases are detected when using no cocatalytst or CoO_r (1%) as the cocatalytst (Figure S6a, Supporting Information). The influence of the weight ratio between carbon rings units and TCN was further evaluated in Figure 4c. After the incorporation of carbon rings units, the photocatalytic activity is dramatically improved, and the optimized amount of carbon rings units in our system is when the addition of glucose reaches 0.01 g. In order to further prove that the morphological effect endowed by the 1D tubular structure and D-A system play critical roles in the enhancement of photocatalytic activity, the control experiments were conducted. Figure S6b (Supporting Information) shows that no gases are detected for the Bulk CN or TCN photocatalyst, while C(0.02)/Bulk CN, C(0.02)/TCN, and C-TCN are photocatalytically active toward overall water splitting, indicating that the introduction of carbon rings units makes the above process more favorable. Furthermore, the C-TCN shows the highest overall water splitting performance among the three photocatalysts, followed by the C(0.02)/TCN and C(0.02)/Bulk CN, which also implies that the in-plane incorporation of carbon rings units and 1D tubular structure have a real impact on the water splitting performance. Furthermore, the external quantum







Figure 4. The overall water splitting performance of C-TCN under visible light irradiation: a) using Pt (3%) as a cocatalytst, and b) using Pt (3%) and CoO_x (1%) as the cocatalytsts; c) The overall water splitting performance of C-TCN with different compositions; d) Wavelength dependence of EQE for photocatalytic overall water splitting using Pt (3%) and CoO_x (1%) as the cocatalytsts.

efficiency (EQE) of the C-TCN for photocatalytic overall water splitting using Pt (3%) and CoO_r (1%) as the cocatalytsts was further measured (Figure 4d). The trend of EQE curve fits nicely with the UV-vis absorption spectra, suggesting that the light absorption behavior significantly affects the photocatalytic performance of the C-TCN. Specifically, C-TCN exhibits a quite high EQE up to 2.6% at 405 nm, and even the EQE values can also reach 1.7%, 0.8%, and 0.2% at longer visible light wavelength of 420, 435, and 450 nm, respectively. To confirm the source of the generated O_2 , the $H_2^{18}O$ isotopic labeling experiment is performed in a ratio $H_2^{16}O/H_2^{18}O$ of 4:1. As shown in Figure S6c (Supporting Information), the peaks at m/z = 32, m/z = 34, and m/z = 36 in the mass spectra can be assigned to 16-16O2 (81.7%), 16-18O2 (16.3%), and 18-18O2 (2.0%), respectively. The two types of O_2 species (¹⁶⁻¹⁸ O_2 and ¹⁸⁻¹⁸ O_2) further affirm that the oxygen source of O₂ is indeed derived from H₂O caused by photocatalytic overall water splitting.^[55,56]

The photocatalytic performance of the C-TCN was further evaluated by H₂ evolution half-reaction. First, the photocatalytic H₂ evolution was further evaluated without any cocatalysts with just the presence of triethanolamine (TEOA) that acts as the hole sacrificial reagent at $\lambda > 400$ nm. As shown in Figure S7a (Supporting Information), the Bulk CN displays a negligible H₂ evolution rate of 0.01 µmol h⁻¹. Thanks to the morphological effect conferred by the 1D tubular structure, the TCN exhibits much higher H₂ evolution rate of 1.66 µmol h⁻¹. After grafting carbon rings units into the basal plane of g-C₃N₄, the H₂ evolution rate of the C-TCN can be enhanced significantly. The H₂ evolution rate of the C-TCN can even reach 5.65 µmol h⁻¹, which is 3.4 times as much as that of the

value of the TCN. The improved water splitting performance stems from the electron-withdrawing effect imposed by the carbon rings units, which swiftly extract electrons from the basal plane of the g-C₃N₄ to participate in H₂ evolution reaction after being photoexcited. In order to further illustrate the role of carbon rings units, 3 wt% Pt is selected as the cocatalyst. As revealed in Figure S7b (Supporting Information), the TCN displays superior photocatalytic performance of 105.18 μ mol h⁻¹, which is \approx 11.35 times higher than that of the Bulk CN (9.27 μ mol h⁻¹). The improved water splitting performance mainly attributes to the 1D tubular structure, large surface area, and excellent charge separation/transfer efficiency. After the incorporation of carbon rings units, the photocatalytic activity of the C-TCN is further improved. The H_2 evolution rate increases up to 221.80 µmol h⁻¹, which is about 23.93 and 2.11 times as much as that of the Bulk CN and TCN, respectively. This phenomenon implies that the implantation of carbon rings units into the basal plane of g-C₃N₄ can facilitate the photocatalytic H₂ evolution. When the addition of glucose is higher than 0.02 g, the photocatalytic H₂ evolution rate declines. The possible reason is that the presence of excess carbon rings units reduces the visible light utilization of the sample and disrupts the crystal structure of g-C₃N₄. Moreover, the photocatalytic stability test of the C-TCN is shown in Figure S7c,d (Supporting Information) and no obvious decay is observed after five cycles in 25 h, which implies the remarkable photostability of C-TCN. In addition, the EQE values of C-TCN for H₂ evolution half-reaction at 420, 435, 450, and 550 nm are calculated to be 9.3%, 4.8%, 3.2%, and 0%, respectively (Figure S8a, Supporting Information).





Figure 5. a) Room-temperature PL spectra, b) time-resolved PL spectra, c) Mott–Schottky plots, d) transient photocurrent response, e) EIS Nyquist plots, and f) the calculated free-energy diagram for hydrogen evolution reaction of C-TCN.

2.3. Possible Photocatalytic Mechanism

Apart from the bandgap structure, the incorporation of carbon rings units in the basal plane of the g-C₃N₄ also promotes the charge separation/transfer efficiency, which is mainly driven by the intramolecular charge transfer in a D-A system. The charge carrier behavior can be measured by photoluminescence (PL) spectra, time-resolved PL spectra, Mott-Schottky plots, photocurrent measurement, and electrochemical impedance spectroscopy (EIS).^[57] As shown in Figure 5a, the emission peak of the TCN exhibits a slight blueshift with respect to the Bulk CN, and a gradual redshift is observed in the C-TCN with the incorporation of carbon rings units, which is in accordance with the result of UV-vis absorption spectra. Furthermore, the PL intensities of the TCN and C-TCN are lower than that of the Bulk CN, confirming that the recombination rate of the photogenerated charge carriers can be efficiently suppressed by the 1D tubular structure and the introduction of carbon rings units.^[58] The time-resolved PL spectra are also conducted in Figure 5b. The C-TCN shows longer lifetime (7.84 ns) compared with Bulk CN (3.29 ns) and TCN (5.07 ns), suggesting the improved charge transfer efficiency. To further verify the improved charge transfer efficiency, the Mott-Schottky plots are measured, as shown in Figure 5c. The carrier density $(N_{\rm D})$ is obtained by the Mott-Schottky equation

$$N_{\rm D} = 2e_0^{-1} \varepsilon^{-1} \varepsilon_0^{-1} \left| d\left(C^{-2} \right) / dV \right|^{-1} \tag{1}$$

where e_0 is the elemental charge value ($e_0 = 1.60 \times 10^{-19}$ C), ε is the relative permittivity of CN ($\varepsilon = 5.5$), and ε_0 is the permittivity of vacuum ($\varepsilon_0 = 8.85 \times 10^{-14}$).^[59] The $N_{\rm D}$ values of the

Bulk CN, TCN, and C-TCN are 2.38×10^{31} , 2.13×10^{31} , and 5.96×10^{31} cm⁻³, respectively. The higher $N_{\rm D}$ value signifies the enhanced transfer efficiency of photogenerated carriers, which further confirm that carbon rings units can effectively promote charge transfer because carbon rings units can effectively avoid electron accumulation via withdrawing photogenerate electron from the basal plane of g-C₃N₄. A similar trend is observed in photocurrent and EIS measurements, which contributes to more in-depth understanding on the charge transfer process. As shown in Figure 5d, all the samples exhibit stable photoelectrochemical responses under intermittent light irradiation. The photocurrent intensities of the TCN and C-TCN are all higher than that of the Bulk CN, and C-TCN has the highest photocurrent intensity, which further demonstrates that C-TCN possesses the best charge separation/transfer efficiency. From the EIS measurement shown in Figure 5e, the arc radius of the C-TCN is smallest among all the samples, indicating its lowest charge transfer resistance and further confirming that the improved charge transport ability conferred by the in-plane incorporated carbon rings units.^[60,61] The optoelectronic performance of the C-TCN is further investigated through DFT calculations (Figure S9, Supporting Information), which is fitting to the experimental results. It is found that C-TCN exhibits better refractive index and photoconductivity, which means C-TCN possesses the better optoelectronic performance and thus improving the photocatalytic performance.^[62] Therefore, combining the characterization and DFT calculations of photoelectricity property shown above, it is concluded that the improved water splitting performance arises from the charge separation/ transfer capability of the C-TCN after the carbon rings units are incorporated.

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Figure 6. Differential charge density map of C-TCN: a) the Bader charge between the basal plane of $g_{-C_3N_4}$ and carbon rings units, b) the Bader charge of two adjacent tubes (Δq is the Bader charge change of the TCN, the yellow and blue regions indicate electron accumulation and depletion, respectively); c) Schematic illustration of the proposed mechanism for photocatalytic overall water splitting about the all-organic D-A system.

Furthermore, Gibbs free energy change of H* adsorption $(\Delta G_{\rm H}^{*})$ is considered to be an important descriptor to evaluate the H₂ evolution performance, which is calculated by DFT calculations.^[63–65] As shown in Figure 5f and Table S4 (Supporting Information), for Bulk CN and TCN, the calculated $\Delta G_{\rm H}{}^{\star}$ values are -0.41 and -0.45 eV. Dramatically, after grafting carbon rings units into the basal plane of TCN, the $\Delta G_{\rm H}^*$ value of C-TCN is reduced to -0.25 eV, which is very close to that of Pt (-0.09 eV), indicating that the H₂ evolution reaction activity of C-TCN is greatly promoted. In order to explain the existence of intramolecular charge transfer between the basal plane of g-C₃N₄ and carbon rings units, the Bader charge of C-TCN is conducted by DFT calculations. For clarity, Figure 6a shows the Bader charge between the basal plane of g-C₃N₄ and carbon rings units in the structure of C-TCN, the negative value of the calculated Bader charge change means that the electrons can transfer from the basal plane of g-C₃N₄ to the carbon rings units, signifying the existence of intramolecular charge transfer between them. On the other hand, the Bader charge of two adjacent tubes is close to zero (Figure 6b), indicating that there is almost no charge transfer.

Based on above analysis and discussion, a possible photocatalytic mechanism to elucidate the overall water splitting process on the C-TCN is proposed in Figure 6c. First, a D-A system is formed via the effective incorporation of carbon rings units in the basal plane of the g-C₃N₄, which is the major driving force for intramolecular charge transfer. Meanwhile, the energy bands of the C-TCN match well with the requirements of photocatalytic overall water splitting. Once the C-TCN is exposed to the light, the photogenerated electron–hole pairs in the basal plane of the g-C₃N₄ are separated. Due to the strong electron-withdrawing property, carbon rings units can serve as the electron acceptor to allow a smooth transfer of the excited electrons in the CB from the basal plane of $g-C_3N_4$ to the carbon rings units. Such an intramolecular charge transfer can effectively suppress the recombination of the photogenerated electron–hole pairs. Afterward, the electrons that are being transferred to the carbon ring reduce H_2O to H_2 while the photogenerated holes react with H_2O to produce O_2 . In this process, carbon rings units that act as the electron acceptor are responsible for inhibiting rapid recombination of the photogenerated electron–hole pairs, thus optimizing the water splitting performance.

3. Conclusions

In summary, we have successfully built an all-organic D-A system to optimize the photocatalytic overall water splitting activity through the implantation of carbon rings units into the basal plane of g-C₃N₄ via continuous π -conjugated bond. Owing to the effective intramolecular charge transfer of the D-A system, the C-TCN exhibits enhanced charge separation capability, which contributes to its remarkable photocatalytic performance (EQE = 1.7% at 420 nm). Moreover, the VB position can be effectively downshifted due to the tubular structure and the incorporation of carbon rings units, which can bypass the limit of water oxidation reaction. Therefore, the all-organic D-A system can efficiently execute water splitting reaction without any sacrificial reagents. This work successfully extends the concept of D-A system usually employed in organic solar cells to photocatalysis field.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Z.M. and J.D. contributed equally to this work. Z.M., J.D., H.X., and Q.Y. designed the experiments; Z.M., P.Y., C.L., D.L., and X.Z. carried out the experiments; Y.S., C.L., Q.Y., H.L., and Y.L. analyzed the experimental results; Z.M. wrote the manuscript.

Keywords

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