

Overall Regulation of Exciton Dynamics by Defect Engineering in Polymeric Photocatalysts for Hydrogen Evolution

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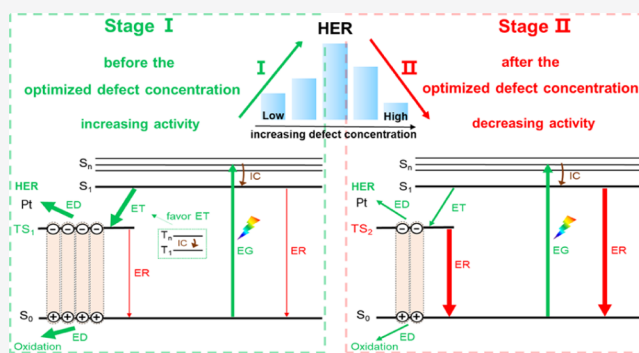
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ABSTRACT: For photocatalysts with a strong exciton effect, overall understanding and regulating exciton dynamics, which is central to optimizing performance, have been ignored. Herein, taking a carbon nitride derivative as the model system, we demonstrate the alteration of multiple band structures for regulating the overall exciton dynamics and accordingly the photocatalytic hydrogen evolution performance by introducing cyano defects. Both experimental and theoretical data show that with increasing defect concentration, the defect-mediated trap state (TS) increases the singlet exciton generation, facilitates the exciton transfer from the first singlet excited state to TS rather than to the triplet excited state, promotes exciton dissociation, and suppresses the singlet exciton recombination until reaching to the highest activity. However, excess defects will act as recombination centers, leading to severe exciton recombination and decreased activity. This work provides a new insight into an in-depth understanding of comprehensive regulation of exciton dynamics for high-efficiency solar energy conversion.



1. INTRODUCTION

Photocatalytic (PC) reactions such as hydrogen production from solar water splitting have attracted much attention owing to their great potential to reduce the energy shortage and environmental pollution issues.^{1–4} Among numerous studies, exciton (bound electron–hole pair) dynamics is particularly important to the performance of photocatalysts with a strong exciton effect, but less attention has been received.^{5–13} Unlike inorganic bulk photocatalysts, which generate free charge carriers or loosely bound excitons with binding energies (~ 0.01 eV) lower than the thermal energy at room temperature ($k_B T$, ~ 0.025 eV) that can easily dissociate into electrons and holes,^{14,15} organic photocatalysts and inorganic low-dimensional materials usually have strong Coulomb interactions between electrons and holes, leading to the formation of excitons with relatively high binding energies.^{8,14,16,17} Upon light irradiation, the singlet excitons generate and transfer to the defect site, or the interface with an electron or hole acceptor, where they dissociate into free electrons and holes. This exciton dissociation is caused by the higher charge separation energy, which is created by the built-in electric field between the defect site or the interface and the remaining electron or hole involved in the exciton, compared to the exciton binding energy. The dissociated free electrons and holes then transfer to the surface and eventually participate in the redox reactions.^{14,18} In addition, singlet excitons may

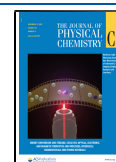
undergo intersystem crossing (ISC) and convert to triplet excitons, followed by dissociation of triplet excitons into free electrons and holes or triplet–triplet annihilation (TTA) back to singlet excitons.^{8,16} ISC and TTA processes can regulate the population of the singlet and triplet excitons. Both types of excitons are the sources of exciton dissociation, but the singlet exciton binding energy is theoretically lower than the triplet one, suggesting that singlet excitons are easier to dissociate into free electrons and holes than the triplet one.^{19–21} At the same time, the recombination of both types of excitons occur, having negative effects on the efficiency of exciton dissociation and thus PC reactions.^{16,22} Therefore, it is critical to understand and regulate the factors influencing the exciton dynamics to optimize the PC performance.^{8,16,17}

Some strategies have been applied to regulate the exciton dynamics; for instance, nanostructuring such as forming nanocrystals or quantum dots enhances the multiple exciton generation because of the quantum confinement effect,^{23,24} and surface plasmon resonance promotes the exciton

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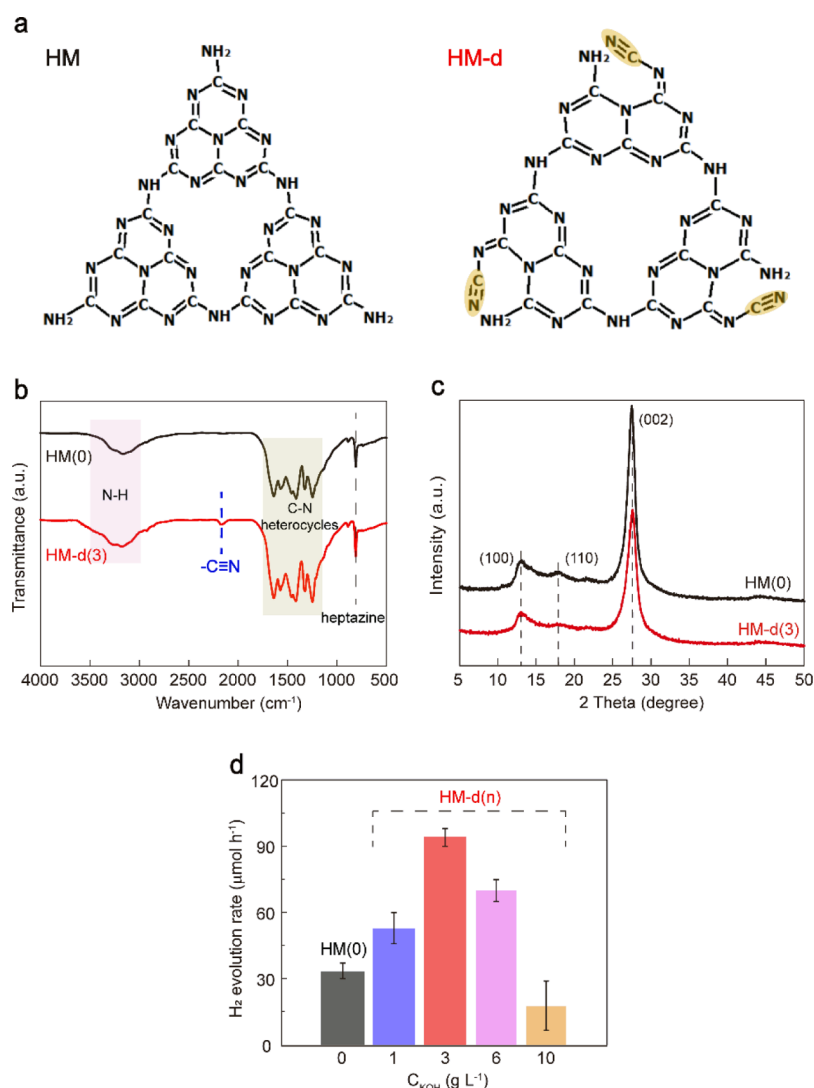


Figure 1. (a) Chemical formulas of HM and HM-d optimized by DFT, with the highlighted $-\text{C}\equiv\text{N}$ defects in HM-d. (b) FTIR spectra and (c) XRD patterns for HM(0) and HM-d(3). (d) PC H_2 production rate for HM-d(n) with different C_{KOH} -dependent $-\text{C}\equiv\text{N}$ defect concentrations in 10 vol % aqueous triethanolamine (TEOA) solution under visible-light irradiation ($\lambda > 420$ nm) with 1 wt % Pt, with HM(0) without adding any KOH for comparison.

generation by near-field enhancement and the exciton dissociation *via* exciton-plasmon coupling.²⁵ Among them, engineering defects (four main categories according to the dimensions, e.g., the point, line, planar, and volume)²⁶ has been considered as an effective, comprehensive, and facile way to enhance the performance of photocatalysts,^{27–32} such as increasing light absorption by narrowing the band gap, improving charge transfer and separation *via* temporarily trapping photogenerated electrons and holes, or maneuvering surface reactions through adsorption and activation of reactant molecules.^{26,33} In addition, the effect of defects on regulating the exciton dynamics is also explored.^{26,34} On the positive side, a proper amount of defects in photocatalysts can promote exciton dissociation.^{22,35–39} For example, the formation of ordered–disordered chains in the heptazine-based melon (HM) [which is also called polymeric carbon nitride (CN)], which has suitable band structures with the built-in electric field at the abundant ordered–disordered interfaces, can accelerate the exciton dissociation into free electrons and holes and thus effectively enhance the PC performance.¹⁶ Another study shows that the incorporation of oxygen

vacancies in the low-dimensional bismuth oxybromide (BiOBr) can promote exciton dissociation because the oxygen vacancies significantly distort the surrounding localization of band-edge states, leading to the instability of excitons.⁴⁰ On the negative side, excessive defects may act as exciton recombination centers, leading to poor PC performance.^{41,42} However, the related studies only limit to one or two steps of exciton dynamics, and their interpretations on exciton dynamics are usually controversial because of the incomplete experimental and theoretical characterizations and corresponding data analysis, restricting the understanding of the roles of defects in exciton regulation and thus hindering the development of photocatalysts with a strong exciton effect.

To overcome these issues, a comprehensive consideration of the defect-regulated exciton dynamics as well as a consensus between theoretical calculations and various spectral interpretation, such as photoluminescence (PL) and transient absorption (TA), are urgently needed. To this end, polymeric photocatalysts are considered as suitable research objects of exciton dynamics because their low dielectric properties and the presence of significant electron–lattice interactions and

electron correlation effects endow them with potentially rich excitons.^{8,16,18} As a well-studied conjugated polymeric photocatalyst, the excitons in CN exhibit a relative strong Coulombic attraction (exciton binding energy) that is significantly higher than $k_B T$, which makes them difficult to dissociate into free charge carriers at room temperature, indicating a relative strong exciton effect in CN.^{8,39,43–46} In addition, this polymeric photocatalyst has been widely studied for PC water splitting owing to its excellent properties of lightweight, metal-free, low cost, ease of processing, visible-light activity, and so forth.^{45,47–50}

Taking HM, the most well-studied CN derivative in the PC field,^{17,47,48,51,52} as the model photocatalyst, our complementary experimental and theoretical results show that the alteration of multiple band structures for regulating the overall exciton dynamics (including generation, transfer, dissociation, and recombination of excitons) and accordingly the PC hydrogen evolution reaction (HER) activity can be realized by cyano defect ($-\text{C}\equiv\text{N}$) engineering. With increasing defect concentration, the defect-mediated trap state (TS) increases the singlet exciton generation by narrowing the band gap, facilitates the exciton transfer from the first singlet excited state (S_1) to exciton and defect-mediated TS (E&D TS) rather than to the triplet excited state (T_n) owing to the smaller transition energy, promotes exciton dissociation by forming the built-in electric field between $-\text{C}\equiv\text{N}$ and neighbored amine ($-\text{NH}-$) groups with different electronegativities, and suppresses the singlet exciton recombination by trapping the electrons involved in excitons until reaching to the highest HER activity. However, excess defects will act as recombination centers, leading to severe exciton recombination and resulting in decreased HER activity. Our comprehensive understanding and regulating exciton dynamics in HM will open up a new way to tune the catalytic performance.

2. MATERIALS AND METHODS

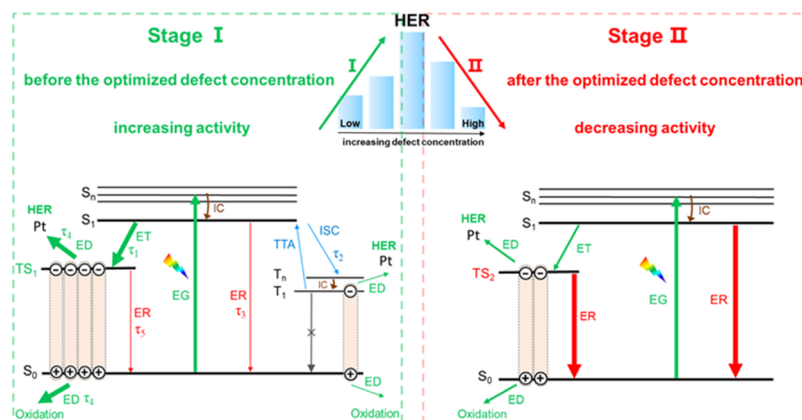
In this study, HM experimental samples with and without the presence of $-\text{C}\equiv\text{N}$ defects, which are denoted as HM-d(n) (d, $-\text{C}\equiv\text{N}$ defect) and HM(0), respectively, were prepared by a thermal condensation method, and the number in the bracket represents the corresponding KOH concentration (C_{KOH}) in g L^{-1} (see details in the Supporting Information).⁵³ In addition, the theoretical models with and without the presence of $-\text{C}\equiv\text{N}$ defects are denoted as HM-d and HM, respectively (Figure 1a). Note that the theoretical models cannot be exactly the same as the experimental samples, so the calculation results are qualitative.

After the preparation of photocatalyst, some physical characterizations, including scanning electron microscope (SEM), X-ray diffraction (XRD) patterns, Fourier transform infrared (FTIR) spectrometer, X-ray photoelectron (XPS) spectroscopy, ultra violet–visible (UV–vis) absorption spectra, N_2 adsorption–desorption isotherms, prompt fluorescence (PF) spectra and ultrafast TA spectroscopy were used to analyze the structure and photophysical properties (see the Supporting Information for details). In addition, the PC H_2 evolution and photoelectrochemical (PEC) measurements as well as density functional theory (DFT) calculations are exhibited in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Structure Characterization. The FTIR measurements were first performed to confirm the chemical bonds and functional groups of the representative samples HM-d(3) and HM(0). Both samples have characteristic peaks (Figure 1b) of HM located at 804 (black dashed line), 1150–1740 (yellow region), and 3000–3500 cm^{-1} (pink region), attributing to the out-of-plane bending vibration of heptazine units, the stretching vibration of aromatic C–N heterocycles, and the N–H stretching, respectively,⁵⁴ thus confirming the formation of the basic heptazine structure of HM. In addition, a new peak at 2188 cm^{-1} (blue dashed line) appears in the spectrum of HM-d(3) can be assigned to an asymmetric stretching vibration of the $-\text{C}\equiv\text{N}$,⁵³ indicating the formation of $-\text{C}\equiv\text{N}$ groups in HM-d(3). The XPS data further give detailed information on the chemical structure of these two samples (Figure S1). According to the calculation of the C/N ratio and the percentage of the $-\text{C}\equiv\text{N}$ group in the chemical structure (Table S1, see details in the Supporting Information) from XPS C1s and N1s spectra (Figure S1b), two main points can be concluded. First, the C/N ratio of HM-d(3) sample (~ 0.60) is smaller than that of HM(0) (~ 0.68), indicating a further decrease of condensation degree due to the increase of $-\text{C}\equiv\text{N}$ defects relative to the theoretical value of 0.75 in $\text{g-C}_3\text{N}_4$.⁵⁵ Besides, the peak representing $-\text{C}\equiv\text{N}$ group appears in the C1s curve-fitting of HM-d(3). Furthermore, combining the FTIR data (3000–3500 cm^{-1}) and the XPS N1s data (401.2 eV), as well as the reported solid-state ^{13}C magic angle spinning nuclear magnetic resonance measurement,⁵³ it can be confirmed that the amount of $-\text{NH}-$ groups in HM-d(3) is the same as that in HM(0). The SEM images (Figure S2) and N_2 physisorption measurements (Figure S3) suggest similar sheet-like morphology and specific surface area for both samples. The XRD patterns of both samples (Figure 1c) show two characteristic peaks at 13.0 and 27.5°, which can be assigned to the (100) and (002) crystal planes of HM, representing in-plane packing and interfacial stacking of HM sheets, respectively.⁵³ However, both peaks broaden and weaken in the spectrum of HM-d(3) compared to those of HM(0), suggesting that the formation of $-\text{C}\equiv\text{N}$ groups in HM-d(3) causes the loss of ordered structures within the framework. Another small peak at around 18.0° can be assigned to the (110) crystal plane of HM.⁵⁶ Therefore, we can safely conclude that both HM-d(3) and HM(0) experimental samples with and without the $-\text{C}\equiv\text{N}$ defects were successfully synthesized.

3.2. HER Activity. Then we assessed the photoactivity of HM-d(n) samples with different $-\text{C}\equiv\text{N}$ defect concentrations toward visible-light driven water splitting for H_2 generation in the presence of TEOA as a sacrificial agent and platinum (Pt) as a co-catalyst (see details in the Supporting Information), to investigate the influence of various $-\text{C}\equiv\text{N}$ defect concentrations, which is tuned by adding KOH with different C_{KOH} ,⁵³ as well as HM(0) without adding any KOH for comparison. As shown in Figure 1d, the HER activity increases with increasing defect concentration (at C_{KOH} from 1 to 3 g L^{-1}) until reaching the highest value (at $C_{\text{KOH}} = 3 \text{ g L}^{-1}$). However, excessive defects (at C_{KOH} from 6 to 10 g L^{-1}) lead to poor PC performance. As a result, the defect concentration-dependent HER activity is obtained for further exploration. Among them, the representative samples HM-d(3) and HM(0) show no significant photoactivity loss (remaining about 90% of the

Scheme 1. Schematic Illustration of the Defect Concentration-Dependent Exciton Dynamics Involved in the PC HER^a

^aIC: internal conversion; ISC: intersystem crossing; TTA: triplet-triplet annihilation; EG: exciton generation; ET: exciton transfer; ED: exciton dissociation; ER: exciton recombination; TS: trap state (TS₁: exciton and low concentration defect-mediated TS; TS₂: exciton and high concentration defect-mediated TS); the cross in gray: no phosphorescence

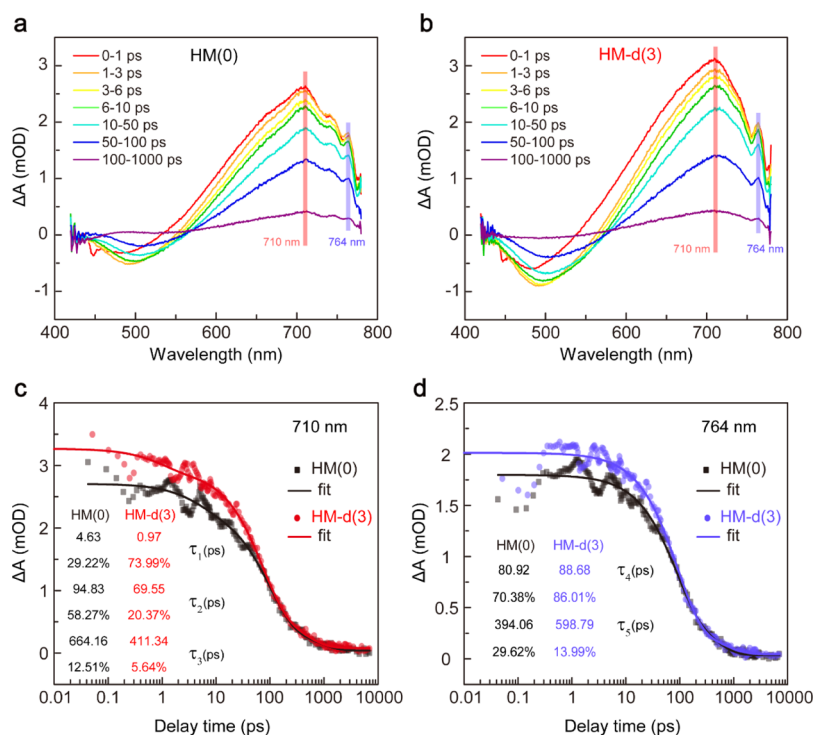


Figure 2. TA spectra. Average TA spectra at different delay time windows of (a) HM(0) and (b) HM-d(3). TA kinetic traces probed at (c) 710 and (d) 764 nm for both samples. The solid lines in Figure 2c,d show the fitting of the decay kinetics using a tri-exponential and bi-exponential function, respectively. The TA signal is given in mOD, where OD stands for optical density.

activity) after 4 cycles up to 12 h (Figure S4), and the apparent quantum efficiency of HM-d(3) at 420 nm is 3.10% (see details in the Supporting Information).

After a simple calculation, it can be seen that the highest H₂ evolution rate of HM-d(3) (94.16 $\mu\text{mol h}^{-1}$) is about three times as fast as that of HM(0) (33.24 $\mu\text{mol h}^{-1}$). Obviously, such a great increase cannot be easily interpreted by a little increased surface area from 7 to 10 $\text{m}^2 \text{g}^{-1}$ (Figure S3) or a little reduced band gap from 2.71 to 2.65 eV (Figure S5). In addition, the HER tests for all of the samples have the same amount of the cocatalyst Pt and the sacrificial agent TEOA, and the fundamental HM structure and morphology are similar for both HM(0) and HM-d(3). Because the HM material has a

relatively strong exciton effect, we assume that the enhancement of the HER activity for HM-d(3) compared to HM(0) is mainly caused by the $-\text{C}\equiv\text{N}$ defect-induced exciton dynamics optimization, and then explore it by various experimental characterizations and DFT calculation later.

3.3. Exciton Dynamics. To gain an in-depth understanding on the impact of $-\text{C}\equiv\text{N}$ defect on exciton dynamics, a combination of femtosecond time-resolved TA spectroscopy, PF spectra as well as DFT calculation (see details in the Supporting Information) is quite necessary because they can give a comprehensive information about ultrafast exciton dynamics involved in photophysical processes.¹⁷ Upon light irradiation, electrons can be first excited from the ground state

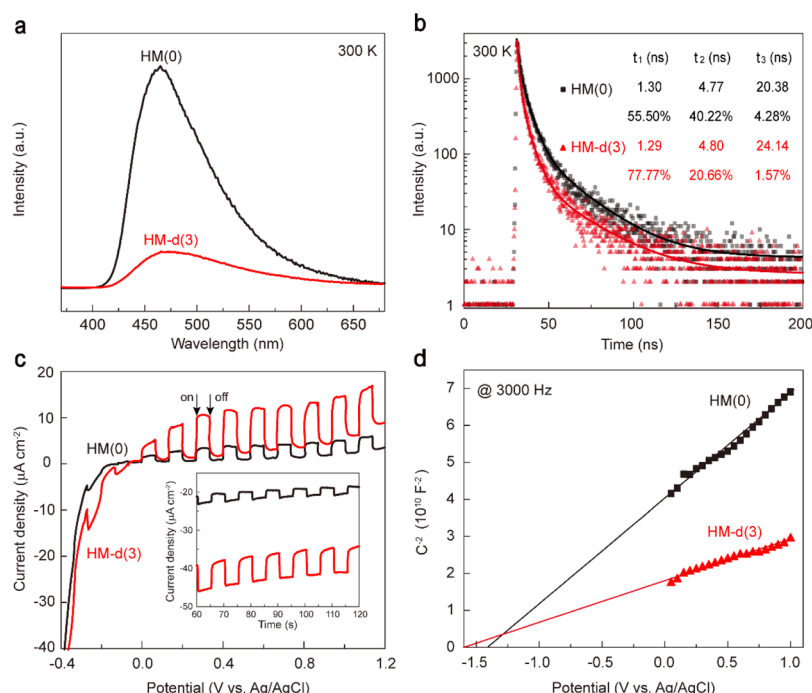


Figure 3. (a) Steady-state and (b) time-resolved PF spectra of HM(0) and HM-d(3) obtained at 300 K under 350 nm excitation. (c) Potential-dependent photocurrent measurements (inset: photocurrent transient response at -0.4 V vs Ag/AgCl, pH 5.86) for HM(0) and HM-d(3). (d) Mott-Schottky (MS) plots of HM(0) and HM-d(3) at a frequency of 3000 Hz.

(S_0) to different singlet excited states (S_n , $n = 1, 2, 3...$), leaving holes in the S_0 . The excited electrons at higher S_n ($n = 2, 3...$) can then go back to the first singlet excited state (S_1) in picosecond *via* the internal conversion (IC) and form singlet excitons (Scheme 1).⁵⁷ As seen from the TA spectra of HM(0) and HM-d(3) (Figure 2a,b and S6), the negative signal between 450 and 550 nm represents the ground state bleach;⁵⁸ while the positive signal between 550 and 800 nm represents the excited state absorption,⁸ and has a higher intensity in the spectrum of HM-d(3) at the initiate delay time (0–1 ps). Because excitons are produced upon light absorption, the increased TA absorption intensity for HM-d(3) indicates that the singlet exciton concentration of HM-d(3) is approximately 1.2 times as high as that of HM(0) under the same irradiation condition, which is consistent with the increased UV–vis absorption by narrowing the band gap (Figure S5) for HM-d(3) relative to those of HM(0) and increased oscillator strength between the S_0 and a S_n ($n = 1, 2, 3...$) calculated from the DFT (Tables S2 and S3) based on optimized S_0 geometries (Figure S7) for HM-d relative to those of HM. The promoted singlet exciton generation in HM-d(3) provides more singlet excitons for subsequent exciton dissociation process. Furthermore, as the $-C\equiv N$ defect concentration further increases (at C_{KOH} from 6 to 10 g L⁻¹), the absorption edge has a progressive redshift (Figure S8), resulting in enhanced light absorption for increased exciton generation.

As shown in Figure 2a,b, there is no significant change in the shape of the TA with time, suggesting only one photoinduced species is contributing to the TA signal for both HM(0) and HM-d(3).⁵⁹ Because (i) the HM material has a strong exciton effect;^{7,8,45} (ii) PF spectra (radiative decay of singlet excitons)^{7,17} has been characterized for both samples to confirm the existence of singlet excitons (Figure 3a); (iii) no phosphorescence (radiative decay of triplet excitons)^{7,17} was detected at very long delay times (Figure S9), we assign the

main photoinduced species and the positive TA peak centered at 710 nm to the singlet excitons and S_1 , respectively.⁸ In addition, another positive TA peak at 764 nm may represent the intermediate TS: because of a strong exciton effect in HM(0), the formed excitonic state can act as an intermediate TS, that is, an exciton-mediated TS (E-TS);⁴⁰ after introduction of $-C\equiv N$ defects, both exciton and E&D-TSs exist in HM-d(3).⁶⁰ Note that the peak assigned at 764 nm is based on the following two points: (1) Gaussian fit of PF emission spectra (Figure S10a) shows that the energy difference between S_1 and TS for both samples (40–50 nm) is in good agreement with the energy difference of two peaks (54 nm) obtained from TA spectra; (2) the trends of the TA dynamics at 710 (decay) and 764 nm (growth) for both samples are opposite in the initial time (Figure S11a,b) and then become consistent (decay) (Figure S11c,d), suggesting some singlet excitons in S_1 may be trapped in TS at the beginning, and then the trend of both states becomes consistent owing to exciton transfer, trapping, dissociation and recombination and so forth (Scheme 1).

After singlet exciton generation, three relaxation pathways of singlet excitons in the S_1 can be confirmed on the basis of the tri-exponential function curve-fitting and corresponding time constants (τ) of the TA kinetics at 710 nm (Figure 2c, Table S4):^{8,40} (i) a fast relaxation (τ_1 , a few picoseconds) of excitons from S_1 to TS. (ii) An ISC process (τ_2 , a few tens of picoseconds) of excitons converted from the S_1 to the first triplet state (T_1) with a change of spin-multiplicity; (iii) the formed excitons in the S_1 decay back to S_0 on a nanosecond time scale (τ_3) (Scheme 1). In addition, two discrete relaxation pathways of excitons on the TS can be confirmed according to the bi-exponential fitting results and corresponding time constants (τ) of the TA kinetics at 764 nm (Figure 2d, Table S4): (iv) singlet excitons dissociate into free charge carriers (τ_4 , a few tens of picoseconds); (v) singlet excitons

decay back to S_0 on a nanosecond time scale (τ_s). Noted that there will be a TS which can participate in exciton dynamics if the defect exists,^{40,60} so single relaxation pathway is not applicable in this work.

Among these pathways, paths (i) and (iv) are closely related to the singlet exciton dissociation process. In path (i), the HM-d(3) has a shorter τ_1 ($0.97 < 4.63$ ps) and a larger proportion of τ_1 in the overall decay components ($73.99\% > 29.22\%$) compared to those of the HM(0) according to the TA fitting results (Figure 2c, Table S4), indicating that a higher singlet exciton concentration can be reached at the E&D-TS in a much shorter time owing to the introduction of $-C\equiv N$ defects, which offers an adequate amount of singlet excitons for the dissociation. Although the τ_4 in path (iv) for HM-d(3) and HM(0) is similar, the proportion of τ_4 for HM-d(3) (86.01%) is larger than that of HM(0) (70.38%) according to the TA fitting results (Figure 2d, Table S4), suggesting that singlet excitons in HM-d(3) are more prone to dissociate than those in HM(0). This result is consistent with the qualitative prediction: because the electronegativity of $-C\equiv N$ is different from that of the adjacent $-NH-$, a built-in electric field may be formed between $-C\equiv N$ and neighbored $-NH-$ groups in HM-d(n) owing to their relative great electrostatic potential difference (Figure S12), resulting in exciton dissociation.^{61–64}

To compare the degree of singlet exciton dissociation between two samples more intuitively and quantitatively, the efficiencies of singlet exciton dissociation for HM(0) and HM-d(3) are estimated as 20.6 and 76.4%, respectively, when considering that the absorption intensity of HM-d(3) is 1.2 times that of HM(0) under the same irradiation condition and the proportion of τ_1 and τ_4 in the two paths are related to the singlet exciton dissociation process (Table S4, see details in the Supporting Information), and the exciton transfer from S_1 to TS [path (i)] is the main factor for the significantly improved singlet exciton dissociation efficiency of HM-d(3). On the basis of singlet exciton dissociation efficiencies for HM(0) and HM-d(3), the contribution of D-TS in HM-d(3) is 2.7 times as much as that of E-TS for singlet exciton dissociation ($D-TS/E-TS = (76.4 - 20.6\%)/20.6\% = 2.7$), indicating that D-TS by the introduction of $-C\equiv N$ defects plays a dominant role in promoting singlet exciton dissociation in HM-d(3). Further DFT calculation based on optimized S_0 geometries of HM and HM-d (Figure S7) confirms that the singlet exciton binding energy of HM-d (~ 0.62 eV) is much smaller than that of the HM (~ 0.79 eV) owing to the incorporation of $-C\equiv N$ defects, indicating that the dissociation of singlet excitons into free charge carriers is easier in HM-d (Table S5, see details in the Supporting Information).^{65–67} Steady-state PF spectroscopy is another effective method to evaluate the exciton dissociation degree.¹⁶ The steady-state PF spectra of HM(0) and HM-d(3) show a maximum emission peak near 465 nm (Figure 3a); however, a significantly decrease in the PF intensity was observed in the spectrum of HM-d(3) compared to that of the HM(0), which in turn verifies a higher degree of singlet exciton dissociation of HM-d(3). In order to further explore the role of $-C\equiv N$ defects of HM-d(3) in exciton dissociation, we compared the PF intensity of HM(0) added with a hole sacrificial agent (i.e., TEOA) with that of HM-d(3) without TEOA.⁹ It was found that the PF spectrum of the HM(0) suspension with a 1.87 M TEOA was similar to that of the HM-d(3) without TEOA (Figure S13), suggesting that the $-C\equiv N$ defects in HM-d(3) can promote exciton dissociation same as the function of TEOA.

In addition, paths (iii) and (v) describe the radiative decay or recombination process of singlet excitons in HM(0) and HM-d(3).¹⁶ The steady-state PF spectra (Figure 3a) of both samples can be fitted into two components, which include peaks at around 2.70 and 2.45 eV representing the PF emissions from the S_1 and the TS, respectively (Figure S10a). The remarkable intensity differences for both S_1 and TS peaks between two samples (Figures 3a and S10a) reveal that singlet excitons in HM(0) prefer to go through radiative decay paths (iii) and (v) back to S_0 , leading to a higher degree of exciton recombination compared to HM-d(3). Time-resolved PF spectra of both samples were then acquired to monitor the exciton recombination process (Figure 3b). Three components, which represent the direct radiative decay from S_1 to S_0 (t_1), the radiative decay from S_1 to TS and then to S_0 (t_2), as well as the radiative decay from S_1 to S_0 experienced the ISC and TTA processes (t_3), were fitted for both samples (Table S6, see details in the Supporting Information). The average radiative decay lifetimes calculated from the PF data for HM-d(3) (2.37 ns) is shorter than that of HM(0) (3.51 ns) as shown in Table S6, which is consistent with the average radiative decay lifetimes derived from the TA result (Table S7, see details in the Supporting Information), indicating that both PF and TA characterizations corroborate each other. Furthermore, the PF quantum yields (ϕ_F) of HM(0) and HM-d(3) were measured to be 2.34 and 0.81%, respectively, and the PF rate constant (k_F) of HM(0) is twice as much as that of the HM-d(3) (Table S6, see details in the Supporting Information), both of which confirming that the introduction of $-C\equiv N$ defects in HM-d(n) can suppress more singlet exciton recombination by introducing the D-TS to trap the electrons involved in excitons as compared to the HM(0), until reaching to the largest amount in HM-d(3) (Figure S14). However, excess defects will act as recombination centers, leading to severe exciton recombination (Figure S14).

Another important part involved in the exciton dynamics is the exciton ISC transfer process [path (ii)] of singlet excitons, where the major ISC channel should be confirmed first. Considering the identical transition orbital compositions between S_1 and T_n , the effective energy levels of T_n (within the range of $E_{S_1} \pm 0.4$ eV) as well as the El-Sayed rule,^{68–72} which are the conditions for selecting the major ISC channel, the DFT calculation verifies that the major ISC channels for HM (Table S8, Figure S15) and HM-d (Table S9, Figure S16) are $S_1 \rightarrow T_2$ and $S_1 \rightarrow T_3$, respectively (Table S10, see details in the Supporting Information). The ISC efficiency was then evaluated by using the energy difference between S_1 and T_n ($\Delta E_{S_1T_n}$) and the spin–orbit coupling (SOC) matrix element (Table S11).^{7,73} The DFT calculation results show that the HM exhibits a smaller $\Delta E_{S_1T_2}$ (0.17 eV) but a larger SOC matrix element value (1.20 cm^{-1}) compared to those of the HM-d ($\Delta E_{S_1T_3} = 0.35$ eV, SOC = 0.41 cm^{-1}), which are both beneficial for achieving a higher ISC efficiency.^{70,73} The result was also confirmed by the TA results (Figure 2c, Table S4), in which the proportion of path (ii) in HM(0) (58.27%) is nearly twice higher than in HM-d(3) (20.37%). Because “the smaller the energy difference, the better the exciton transition”,^{70,74} on the basis of the DFT calculation results, the exciton transfer competition between path (i) and path (ii) for HM and HM-d can be explained by comparing the $\Delta E_{S_1T_n}$ (HM: $\Delta E_{S_1T_2} = 0.17$ eV; HM-d: $\Delta E_{S_1T_3} = 0.35$ eV) and the energy difference

between the S_1 and the TS (ΔE_{S_1TS} ; HM: 0.27 eV; HM-d: 0.28 eV), which was obtained from the curve-fitting result of the calculated PF spectra (Figure S10b). The comparison between ΔE_{S_1TS} and $\Delta E_{S_1T_1}$ in the same sample suggests that the HM has a lower $\Delta E_{S_1T_1}$ value ($0.17 < 0.27$ eV) while HM-d has a lower ΔE_{S_1TS} value ($0.28 < 0.35$ eV), further proving that the singlet excitons in HM prefer to go through path (ii) converting into triplet excitons rather than undergo path (i) to the E-TS, while singlet excitons in HM-d have an opposite choice and prefer to go to the E&D-TS. As a result, by suppressing the ISC process, HM-d can not only enlarge the population of singlet excitons, which have a lower exciton binding energy than that of triplet excitons (Table S5), but also prolong the singlet exciton lifetimes as well as their diffusion length making them easier to transfer to the $-C\equiv N$ defects to some extent,⁷⁵ both of which can facilitate the singlet exciton dissociation and thus contribute to the higher HER efficiency.

The triplet excitons generated after the ISC process in HM(0) and HM-d(3) first decay to T_1 in picosecond via IC process,⁵⁷ and then may either go back to S_1 through TTA, dissociate into free charge carriers or recombine. No phosphorescence was detected at very long delay times, suggesting almost no triplet excitons could decay from T_1 to S_0 in both samples (Figure S9). Furthermore, because $\Delta E_{S_1T_1}$ of HM-d (0.39 eV) is much larger than that of HM (0.17 eV), triplet excitons in HM prefer to go through TTA process. Focusing on the triplet exciton dissociation, the triplet exciton binding energies of HM and HM-d are calculated as 0.9634 and 1.0059 eV, respectively (Table S5), indicating both samples have a similar ability for triplet exciton dissociation.

3.4. PEC Measurements. In view of the promoted singlet exciton dissociation, the free charge carrier behavior in HM-d(3) is thereby distinct from that in HM(0), which is confirmed by the following PEC measurements (see details in the Supporting Information). The photocurrent–voltage curves (Figure 3c) suggest an enhanced photocurrent response from HM(0) to HM-d(3) under both negative and positive bias, confirming an enhanced photogeneration of free electrons and holes in HM-d(3), which was further verified by the promotion of photocurrent transient response under a negative bias voltage (-0.4 V vs Ag/AgCl, pH 5.86) compared with HM(0) (Figure 3c inset). In addition, the slopes of MS curves for HM(0) and HM-d(n) with different $-C\equiv N$ defect concentrations are positive with the smallest slope in the HM-d(3) (Figures 3d and S17), demonstrating that all of the samples belong to n-type semiconductors and HM-d(3) has the maximum electron concentration.¹⁶ On the basis of MS equation,⁷⁶ the electron concentration of HM-d(3) is about 2.5 times as much as that of HM(0). However, excess defects will act as recombination centers, leading to reduced exciton dissociation and decreased electron concentration (Figures S14 and S17).

Furthermore, combining the MS curves (Figure 3d) as well as the band gaps obtained from Figure S5 can estimate the energy levels for the highest-performance HM-d(3) with HM(0) as a contrast,^{77,78} shown in Figure S18. It can be seen that the introduction of $-C\equiv N$ defects in HM-d(3) could result in the up-shift of both conduction band (CB) and valence band levels. Specifically, the up-shift CB level of HM-d(3) is believed to be favorable for the generation of free electrons with more powerful reducing-ability after exciton

dissociation, which benefits for the HER. In addition, HM-d(3) has a higher electron mobility than HM(0) because it has smaller electron effective mass (Figure S19, see details in the Supporting Information), lower PL intensity (Figure 3a) as well as higher photocurrent (Figure 3c).^{79–82} It indicates that the introduction of $-C\equiv N$ defects in HM-d(3) creates partial structural distortion proved by the structural characterizations (Figures 1b,c and S1), resulting in a different electron affinity in the location domains of the polymer structure proved by the ESP spectra (Figure S12) for higher charge mobility.⁸³

Taken together, it can be seen that the singlet exciton dissociation efficiency, electron concentration, photocurrent as well as H_2 evolution rate of HM-d(3) are about three times as high as that of HM(0), suggesting that the free charge carriers dissociated from the majority of excitons can participate in the HER. It also confirms that the difference in PC performance mainly resulting from the exciton dynamic difference rather than Pt because: (1) difference exist in each step of the exciton dynamics, and it becomes significant when accumulated together; (2) PEC and MS measurements without Pt have very similar results to HER activity with Pt. Furthermore, the above results indicate a remarkable agreement between various techniques (TA, PF, DFT, PEC and PC) for exploring the effects of $-C\equiv N$ defects on exciton dynamics.

4. CONCLUSIONS

The $-C\equiv N$ defect concentration-dependent exciton dynamics involved in the PC process in HM has been systematically explored by the comprehensive studies from TA, PF, and PEC experiments as well as DFT simulations, highlighting the significant role of defects in the overall exciton dynamics by multiple band structure regulation. With increasing defect concentration, the defect-mediated TS is capable of generating more singlet excitons by narrowing the band gap and benefits most singlet excitons transferring to the TS rather than T_1 through the ISC process in a short time owing to the smaller transition energy, followed by producing free charge carriers from a robust exciton dissociation process owing to the built-in electric field between $-C\equiv N$ and neighboring $-NH-$ groups with different electronegativities and suppresses the singlet exciton recombination by trapping the electrons involved in excitons until reaching to the highest electron concentration as well as the HER activity. However, excess defects act as recombination centers, leading to severe exciton recombination and resulting in decreased HER activity. This study offers a new insight into regulating exciton dynamics by defect engineering and presents a useful picture in its undertaking of better understanding this relatively unknown design principle, which helps to lay the groundwork for future structural design of photocatalysts for high-efficiency energy conversion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c08830>.

Experimental details, fabrication of photocatalysts, characterizations (including PF, TA, and structure characterizations), PC and PEC measurements, DFT calculation, XPS spectra, C/N atomic ratio and $-C\equiv N$ concentration table, SEM images, N_2 adsorption–desorption isotherms and corresponding pore size distribution curves, photostability test, UV–vis absorp-

tion spectra and Tauc plots, TA spectra, calculated frontier molecular orbitals, oscillator strength table, steady-state delayed PF spectra at 77 K with different delay times, Gaussian fit of PF emission spectra at 300 K, fitted ultrafast absorption decay components at 710 and 764 nm, ESP-mapped molecular vdW surfaces, singlet and triplet exciton binding energies of the two samples revealed by DFT calculations, steady-state PF spectra with or without the hole scavenger (TEOA) at 300 K, fitted PF decay components at 300 K, comparison of average radiative lifetimes derived from TA and time-resolved PF results, S_1 and T_n transition configurations, D_e and D_o value of selected T_n and the major ISC channel revealed by DFT calculations, and energy levels and calculated band structures (PDF)

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Notes

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