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Ketones as Molecular Co-catalysts for Boosting Exciton-Involved Photocatalytic Molecular Oxygen Activation

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Abstract: Excitonic processes of semiconductors open up the possibility for pursuing photocatalytic organic syntheses. However, the insufficient spin relaxation and robust nonradiative decays in semiconductors place restrictions on both quantum yield and selectivity of these reactions. Herein, by taking polymeric carbon nitride (PCN)/acetone as a prototypical system, we propose that extrinsic aliphatic ketones can serve as molecular co-catalysts for synergistically promoting spin-flip transition and suppressing nonradiative energy losses. Spectroscopic investigations indicate that hot excitons in PCN can be transferred to ketones, while triplet excitons in ketones can be transferred to PCN reversely. As such, exhibit PCN/ketone systems considerable triplet-exciton accumulation and extended visible-light response, leading to excellent performance in exciton-involved photocatalysis like singlet oxygen generation. This work provides a fundamental understanding of energy harvesting in semiconductor/molecule systems, and paves the way for optimizing exciton-involved photocatalysis via molecular co-catalyst design.

Introduction

Semiconductor-based photocatalytic organic synthesis has recently attracted tremendous interest, owing to its great potential in converting solar energy to chemical energy.^[1-7] For the activation of molecular intermediates or substrates, excitonic aspect in photoexcited semiconductors exhibits incomparable advantage, by virtue of the feasible spin-involved energy transfer.^[7-9] However, the insufficient spin relaxation and the robust nonradiative decays in semiconductors usually lead to deficient excitonic spin-state control and fast photoinduced species depopulation. Such features set limitations to not only quantum efficiency but also selectivity of photocatalytic reactions. For instance, owing to the unique spin configuration, triplet excitons are usually involved in selective activation processes.^[8,9] Unfortunately, the generally low intersystem crossing (ISC) efficiencies lead to intrinsically faint triplet exciton generation, which clearly exerts a negative effect on the relevant photocatalytic activities. In respect of the nonradiative decays,

exciton–exciton annihilation (EEA) arising from the correlations between excitons represents a crucial process that is adverse to photocatalytic performance. Traditionally, EEA gives rise to the formation of high-lying excitons (i.e., hot excitons) via the inelastic collisions of low-lying excitons. The resulting hot excitons then cool rapidly to low-lying excitonic states through internal conversion, which leads to undesired energy losses in the systems.^[10,11] Therefore, searching effective strategies for regulating these excitonic processes in the systems is urgently needed.

To date tremendous efforts have been devoted to excitonic regulation in semiconductors.^[12-19] As for the regulation of spinstate relaxation, much attention has been paid to the manipulation of spin-orbit coupling and singlet-triplet energy gap, which results in optimized strategies including structural modification and heavy-atom incorporation for promoting ISC $\ensuremath{\mathsf{efficiency}}\xspace{\ensuremath{^{[12-15]}}}$ As for the regulation of nonradiative decays, the factors like dielectric environment and exciton density/diffusion are considered to be critical to EEA rate, which leaves optimized strategies such as phase engineering, substrate control, and excitation regulation.^[16-19] However, in terms of photocatalysis, the applicability of the above strategies is guite limited: regardless of their feasibility, these strategies interfere with the investigation of the intrinsic properties of catalysts, and the accompanying changes in such aspects as charge-carrier mobility, surface area, stability, and band gap would complicate the result interpretation. Most importantly, to the best of our knowledge, the synergistically controllable optimization of spin relaxation and nonradiative decays has never been achieved.

Recently the coupling between semiconductor and molecule has been demonstrated to be favorable for achieving highefficiency exciton-involved energy utilization.^[20-23] Considering that electronic structures of organic molecules vary substantially according to types of functional groups, it is rational to regulate excitonic aspect of semiconductor-based photocatalysts by introducing molecular co-catalysts with appropriate energy levels and configurations. Here we focused our attention on a common category of compounds, aliphatic ketones. Due to the presence of carbonyl group, ketones tend to possess excited states

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exhibiting mixed $\pi\pi^*$ and $n\pi^*$ configurations, which can result in high ISC yields and hence efficient triplet exciton generation.^[24,25] mixed configurations could Moreover. such establish considerable coupling between high-lying excitonic states of semiconductors and discrete excited states of ketones. Such a coupling enables potential extraction of hot excitons competing with energy loss through internal conversion. Besides, the high stabilities of aliphatic ketones further promise their photocatalytic applications. All these advantages hint that aliphatic ketones can serve as molecular co-catalysts for synergistically optimizing the spin relaxation and nonradiative decay processes in semiconductor-based photocatalysts, as depicted in Scheme 1.



Scheme 1. Schematic illustration of acetone as co-catalyst for excitonic regulation in PCN, where HET and TET denote hot exciton transfer and triplet exciton transfer, respectively.

Herein, we proposed that ketones can serve as molecular co-catalysts to optimize exciton-involved photocatalytic reactions. By taking polymeric carbon nitride (PCN)/acetone as a prototypical system, we demonstrated that extrinsic acetone can extract exciton-exciton annihilation (EEA)-induced hot excitons from PCN and donate triplet excitons reversely. Such processes lead to synergistic optimization of spin relaxation and nonradiative decays in the system, thereby leaving highlyefficiency triplet exciton harvesting and promoted visible light response. Not only that, acetone also executes quite limited impact on the intrinsic charge-carrier-involved photoexcitation processes in PCN, endowing the system with selective excitonic regulation. Benefiting from these, the PCN/ketone systems excellent performance in exciton-involved exhibited photocatalytic singlet oxygen (¹O₂) generation. The results not only establish an in-depth understanding of exciton-involved photocatalysis, but also present a synergistic optimization strategy for gaining efficient solar energy utilization via molecular co-catalyst design.

Results and Discussion

PCN samples used in this work were obtained through the typical thermal condensation of melamine (see details in Supporting Information). The structural properties and chemical compositions of the samples were confirmed according to the XRD, FT-IR, and XPS characterizations (Supporting Note 1 and Figure S1). To examine our proposal, we first investigated the

photocatalytic molecular oxygen activation of PCN and PCN/acetone systems, using methyl orange (MO) as the probe molecule. As a typical azo dye, MO can be oxidized by reactive oxygen species (ROS) or photoinduced holes, which can result in absorbance reduction in 350-520 nm. As shown in Figure 1a, the absorbance reduction clearly indicated the consumption of MO molecules by both PCN and PCN/acetone, while the latter exhibited an obvious promotion in the consumption rate. The absorbance evolution at 417 nm was used to estimate the MO consumption. The negligible absorbance changes under blankand acetone-condition (Figure 1b) ruled out the existence of direct interactions between acetone and MO molecules. The distinctly different absorbance evolution observed in a set of control tests under Ar- and O₂-atmosphere (Figure 1c) demonstrated that ROS is mainly responsible for the MO consumption. As compared with the situations under oxygencontaining conditions (that is, air and O_2), the MO degradation under Ar atmosphere showed a notable suppression. Considering the non-existence of ${}^{1}O_{2}$ or superoxide radical (O_{2}^{-}), we attribute the consumption of probe molecule under Ar atmosphere to the photoinduced-hole-involved MO degradation mechanism (see details in Supporting Note 2 and Figure S2). The addition of carotene (a well-known scavenger of ${}^{1}O_{2}$) apparently slowed down the degradation of MO molecules, revealing that the dominant reactive species in the PCN/acetone case should be ${}^{1}O_{2}$.



Figure 1. Photocatalytic molecular oxygen activation. (a) Time-dependent absorption spectra of MO oxidation with PCN and PCN/acetone in air. (b) Evolutions of the 417-nm absorbance of MO solution with different catalysts. (c) Evolutions of the 417-nm absorbance of MO solution with PCN/acetone under different atmospheres or in the presence of carotene. (d) ESR-trapping tests of different samples in the presence of TEMP.

Furthermore, electron spin resonance (ESR)-trapping tests provided evidence for the photocatalytic ROS generation. In detail, 2,2,6,6-tetramethylpiperidine (TEMP) was adopted as the trapping agent for detecting ¹O₂. As displayed in Figure 1d, the triplet signals originating from typical 1:1:1 2,2,6,6photocatalytic ¹O₂ tetramethylpiperidine-N-oxyl verified generation in PCN. Notably, PCN/acetone exhibited significantly promoted ¹O₂ production, in accordance with the above results. Negligible ¹O₂ was detected in the acetone case because of the ill-matched excitonic energy levels between acetone and

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molecular oxygen. This phenomenon confirms that the PCN component is the main photocatalyst for ¹O₂ generation in the PCN/acetone system. In addition, 5,5-dimethyl-1-pyrroline-Noxide (DMPO) was used as the trapping agent for detecting photoinduced-electron-related O2⁻⁻ generation. As shown in Figure S3, PCN/acetone exhibited a slight increase (~10%) in O2⁻ generation as compared to PCN. This can be related to the increased yield of free carriers due to the increased long-lived exciton concentration (via a route of exciton dissociation). Obviously, such a slight increase cannot be responsible for the distinct difference in MO degradation. Moreover, their similar O2⁻⁻ production indicates that acetone executes quite limited impact on the intrinsic charge-carrier-involved photoexcitation processes in PCN. The above results verified the promoted exciton-involved photocatalysis in the PCN/acetone system as expected.



Figure 2. Photoluminescence measurements of different samples in acetonitrile at room temperature (excitation at 300 nm). (a) Prompt fluorescence spectra. (b) Time-resolved fluorescence spectra monitored at 410 nm. (c) Phosphorescence spectra (delay time: 10 µs). (d) Time-resolved phosphorescence spectra monitored at 485 nm; Inset: magnified view of the initial-stage decay traces.

To gain insights into the promoted photocatalytic ¹O₂, we interrogated the photoexcitation processes of PCN and PCN/acetone systems by using photoluminescence spectroscopy. According to the UV-vis spectra of PCN and acetone (Figure S4), the excitation wavelength was selected at 300 nm, ensuring excitation of both samples. Figure 2a displays representative prompt fluorescence spectra of PCN, acetone, and PCN/acetone. As for PCN and acetone, the fluorescence spectra peaking at 445 and 410 nm are related to the emissions from the lowest singlet excitonic states and excimer, [26,27] respectively. Strikingly, PCN/acetone exhibited an obvious suppression in the 445-nm emission, rather than the enhancement observed in other donor-acceptor systems. [28,29] Given the low absorbance of the system, the suppression would not originate from the tiny difference in their UV-vis spectra (Figure S5). Moreover, the contribution from the acetone component turned out to exhibit no significant variation, which might be linked to its low quantum yield.^[26] To gain insights into such changes, we further measured the photoluminescence

excitation spectra of PCN and PCN/acetone monitored at 445 nm. As shown in Figure S6, the emission intensity of PCN/acetone exhibited obvious reduction in the region below 325 nm. This threshold value coincided with the optical absorption edge of acetone that corresponds to its lowest singlet excited state (S1).^[26] The slight reduction in the region above 325 nm is most likely due to the processes associated with EEA in the PCN/acetone system, which endows the system with potential visible light response (further discussion on this issue will be given later). Besides, for both the emission and excitation spectra, PCN and PCN/acetone systems exhibit similar spectral profiles, which clearly demonstrate that the introduction of acetone does not affect the intrinsic excitonic bands of the polymeric semiconductor. To further understand the involved excitonic processes, we carried out the time-resolved fluorescence measurements by monitoring emission at 410 nm (Figure 2b and Table S1). Here, a bi-exponential function was employed to fit the decay in the acetone case (given the potential fluorophore-fluorophore interactions), vielding an average lifetime of ~2.25 ns in accordance with the previous reports.^[26,30] As for bare PCN, the bi-exponential fitting vielded an average lifetime of ~0.66 ns. Notably, the PCN/acetone case exhibited a very similar decay (~0.68 ns) to the PCN case (i.e., in terms of both time constants and statistical weights, see Table S1). The absence of acetone's kinetic feature suggested the occurrence of an effective energy transfer from excited molecular acetone to PCN.

Considering that the quantum yield of ISC in acetone is nearly unity,^[26] we carried out phosphorescence measurements to further investigate the triplet exciton-related excitonic aspects in the system. The phosphorescence spectrum of PCN (Figure 2c) obtained at a delay time of 10 µs exhibited a similar spectral profile to that of the prompt fluorescence (Figure S7). This phenomenon indicates the EEA-induced delayed fluorescence feature of the long-lived emission, in accordance with the previous report.^[11] Strikingly, PCN/acetone exhibited a similar emission to PCN. The quenching of the phosphorescence emission from the acetone component clearly indicates the efficient transfer of triplet excitons from excited acetone to PCN. Besides, the nearly identical profiles of the phosphorescence spectra of PCN and PCN/acetone (Figure 2c) suggested that acetone possesses a negligible impact on the distribution of triplet excitonic energy levels of PCN. Time-resolved phosphorescence spectra (monitored at 485 nm, see Figure 2d and Figure S8) also revealed a similar decay tendency between the PCN and PCN/acetone cases. That is, they both exhibited typical multi-stage traces, arising as a result of triplet-triplet annihilation in the polymeric semiconductor.[11] The monomolecular exponential decays after 60 µs can be ascribed to the suppression of triplet-triplet annihilation at low concentrations of triplet excitons, with triplet lifetimes of ~125.2 and 126.6 µs for the PCN and PCN/acetone cases, respectively. Such an observation further confirms that the addition of acetone does not influence the intrinsic radiative relaxation of triplet excitons in PCN. Nevertheless, a subtle difference between the two decay traces was found in the initial stage. As magnified in the inset of Figure 2d, PCN/acetone exhibited a faster decay than PCN: (8.2 ± 0.1) × 10⁴ s⁻¹ vs. (7.4 ± 0.1) × 10⁴ s⁻¹, suggesting the promoted triplet-triplet annihilation rate (with a roughly 11% acceleration) in the former case. Given that molecular acetone does not influence both kinetics and thermodynamics of excitons

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in PCN, such a difference clearly confirms the increased concentration of triplet excitons in PCN/acetone. Moreover, the accelerated decay in the initial stage was found to be closely related to the acetone concentration (Figure S9), which further confirms the positive role of acetone in optimizing triplet exciton generation in the system. According to the above discussion, it is safe to conclude that the extrinsic addition of acetone can significantly enhance the triplet exciton accumulation without affecting the intrinsic excitonic states in PCN.



Figure 3. Ultrafast transient absorption (TA) spectra of PCN and PCN/acetone. (a) Representative TA spectra taken at the 5-ps probe delay; (b) the corresponding kinetic traces taken at 450 nm under 315-nm excitation. (c) Representative TA spectra taken at the 5-ps probe delay; (d) the corresponding kinetic traces taken at 450 nm under 360-nm excitation. The TA signal (i.e., the absorbance change, Δ Abs.) is given in the unit of mOD (OD: optical density).

By virtue of its high sensitivity in tracking the exciton kinetics in semiconductors, femtosecond time-resolved transient absorption (TA) spectroscopy was further employed to interrogate relaxation kinetics of the systems. $^{\left[11,31-36\right] }$ In the pump-probe configuration, the pump wavelengths were chosen at 315 or 360 nm, suitable for exciting the singlet excited state of acetone or not, respectively.^[34] The WLC (410-550 nm) probe monitored the TA spectral evolution, where the probe bleach signals (Figure 3) are known to correlate with the neutral singlet excitons of PCN.^[35,36] Note that the TA signal of PCN/acetone should originate from the PCN component, since no signal was discernible in the whole probing region for acetone. Figure 3a presents the TA spectra taken at a probe delay of 5 ps (pump at 360 nm), where similar spectral profiles confirms that the additional acetone (1 vol%) does not influence the band distributions in PCN. Given that 360-nm locates out of the spectral range for effective excitation of acetone, the reduction in probe bleach of PCN/acetone (relative to bare PCN) would correlate with the EEA-induced energy transfer from PCN to acetone, echoing to the variation in photoluminescence excitation spectra above 325 nm (Figure S6). Such an energy transfer was further evidenced by the subtle difference in relaxation kinetics (Figure 3b), from which one can see a slight acceleration of photoinduced species consumption in PCN/acetone as compared to bare PCN. Moreover, a sub-

picosecond (~0.3 ps) internal conversion in PCN was revealed in the initial build-up kinetics (Figure S10), on a timescale comparable to that of energy transfer processes.^[37-39] Note that the accurate timescale of hot-exciton transfer is hardly to be distinguished, owing to the resolution limitation of our pumpprobe system (~100 fs). However, the PCN/acetone case exhibited a less negative TA signal than the bare PCN case at the initial 1-ps stage (Figure S10a), suggesting that a considerable amount of hot excitons transfer from PCN to acetone at a sub-ps timescale. These hot excitons are most likely to originate from EEA, owing to the insufficient photon energy (360 nm) for directly generating hot excitons. These observations suggested that the EEA-induced hot excitons can be transferred from PCN to acetone, thereby opening a pathway for triplet exciton harvesting beyond the direct photoexcitation of acetone. Strikingly, 315-nm excitation turned out to bring on a spectral evolution to the contrary. As shown in Figure 3c, the addition of a tiny amount of acetone led to a pronounced spectral variation below ~515 nm, i.e., more probe bleach emerged for PCN/acetone than for bare PCN. This observation demonstrated that there must be a process of energy transfer from excited acetone to PCN, which results in remarkably promoted accumulation of photoinduced species in the PCN/acetone system. The more negative TA signal for PCN/acetone over the initial 1-ps range under 315-nm excitation (Figure S10b) also confirms the ultrafast energy transfer from acetone to PCN. It is worth pointing out that under 315-nm excitation the EEA-induced energy transfer from PCN to acetone exists concomitantly with the energy transfer from acetone to PCN, whereas the latter should prevail over the former. In line with this argument, the observed kinetics (Figure 3d) revealed prolonged relaxation in PCN/acetone relative to PCN, verifying the effective injection of photoinduced species to the PCN component of PCN/acetone. Therefore, the above TA results and analyses provided confirmative evidences for the excitoninvolved energy transfer in the photoexcited PCN/acetone system.

The finding of the positive role of acetone in optimizing exciton-involved photocatalysis inspired us to interrogate the feasibility of using various aliphatic ketones as co-catalysts to PCN for promoting ¹O₂-involved reactions. Here, oxidative coupling of amines to imines, an extensively studied reaction by virtue of its chemical and biological significances, was selected to assess the relevant photocatalytic performance.^[40,41] It has been reported that ¹O₂ can selectively convert amines into imines via an aldimine-mediated mechanism, where benzaldehyde formed by the hydrolysis of aldimine can react with benzylamine to gives rise to the formation of imine. (Figure S11).^[41] Table 1 lists the conversion rates and selectivities of oxidative coupling reaction under different conditions. In particular, PCN/acetone showed a rate of 95% for benzylamine conversion (entry 1), ~4.5-fold higher than that of PCN (entry 2), and both cases exhibited high imine selectivity (≥ 90%). The formation of imine for bare PCN is ascribed to feasible chargetransfer-mediated pathway, where reactive species including photoinduced hole and O2⁻ are crucial to the reaction (see details in Supporting Note 3 and Figure S12). As for the PCN/acetone case, the conversion rate and selectivity of the reaction are closely related to the concentration of acetone (Figure S13), where higher concentrations led to side or peroxidation reactions. To elucidate the role of ${}^{1}O_{2}$ in the system,

we further performed atmosphere- and scavenger-control tests. As shown in entry 3, the absence of oxygen can greatly suppress both selectivities and conversion rates for both PCN and PCN/acetone, confirming that the oxidative coupling reaction mainly undergoes a ROS-mediated route. Significant reduction of conversion rate in the scavenger-control test (with additional NaN₃, an efficient scavenger of ${}^{1}O_{2}$; entry 4) further verified the crucial role of ¹O₂ in this oxidative coupling process. ESR-trapping tests also provide direct evidence to the crucial role of ¹O₂ in the benzylamine conversion (Figure S14). Note that benzylamine serving as a scavenger of photoinduced hole can lead to exciton dissociation to some extent, which, however, exhibits quite limited impact on the overall excitonic processes in PCN under catalytic condition (see details in Supporting Note 4, Table S2 and Figure S15). Besides, the potential impact of bound benzylamine on the photoexcitation processes of acetone has also been excluded (Supporting Note 5 and Figure S16). The incomplete suppression of the reaction might be ascribed to the concomitant O₂⁻⁻-involved coupling route. Moreover, it is quite interesting that the imine yield in the presence of NaN₃ for PCN/acetone (23%) is guite close to the imine yield for bare PCN (20%), echoing to their similar O2⁻⁻ generation. Such a feature further verifies that the extrinsic acetone does not influence the charge-carrier process involved in photoexcited PCN, but selectively optimizes the excitonic processes therein. To go further, a set of control tests with different amines as substrates were conducted, of which the conversion-rate promotion in PCN/acetone relative to PCN confirmed the generality of acetone as co-catalyst for optimizing the oxidative coupling of amines (see details in Supporting Note 6 and Table S3)

To step further, we selected a wide range of aliphatic ketones to evaluate the scope of ketone-based co-catalysts. Given that the energy levels and ISC rates are variable in different ketones, it can be expected to achieve different cocatalytic activities by using ketones with certain structural factors. Firstly, the impact of carbon chain length was investigated. As shown in entry 5-8, the addition of straight-chain aliphatic ketones including 2-butanone, 2-pentanone, 2-hexanone, and 2heptanone turned out to promote the conversion rates substantially, proving the feasibility of using ketones as molecular co-catalysts. As compared to the acetone case, the lower promotions in these cases can be linked to the lower ISC rates intrinsic to these ketones. Besides, the addition amount of ketones for aerobic oxidative coupling of benzylamine was controlled at 10 µL, which means acetone with lowest molecular weight but similar density lead to the highest molar ratio. For ketones with the same carbon chain length, the position of carbonyl group can bring forth great impact on the relevant photophysical properties, thereby determining the efficiency of triplet exciton-involved energy transfer between ketones and PCN. Taking 2-, 3-, and 4-heptanones as examples (entry 8-10), the corresponding promotions in conversion rate exhibited an obvious progressive decrease. Similar comparison results were also found between 2- and 3-pentanones (entry 6,11). This phenomenon can be ascribed to the reduced ISC rates caused by the restricted vibrational motions in ketones.^[42] Analogously, relatively small promotions were found in the cases with methyl substitution (entry 12,13). Moreover, the isotope effect was examined by comparing the acetone and acetone- d_6 cases (entry 14). The slightly higher conversion rate in the acetone- d_6

case coincided with the longer decay time of triplet acetone- d_6 originating from the reduced stretching vibrations of C–D bonds (as compared to C–H bonds).^[25] The above results confirmed the universality of using ketones as co-catalysts to PCN for optimizing the triplet exciton-involved photocatalysis.

Table conditior	1. Aerobic oxidative	coupling	of benzy	lamine u	nder different
	NH ₂	cat.	N	\mathbf{i}	
Entr	w latens	ketone		PCN/ketone	
LIIU	try ketone	Conv. ^[b]	Select. ^[c]	Conv.	Select.
1	acetone	3	89	95	92
2 ^[d]	J –	-		21	93
3 ^[e]	acetone	trace	trace	27	50
4 ^[f]	acetone	4	82	33	70
5	2-butanone	5	85	69	87
6	2-pentanone	4	82	67	96
7	2-hexanone	3	85	77	85
8	2-heptanone	3	23	75	90
9	3-heptanone	5	88	51	89
10	4-heptanone	6	97	29	85
11	3-pentanone	6	80	34	87
12	4-Methyl-2- pentanone	5	99	35	76
13	5-Methyl-2- hexanone	5	80	44	80
14	acetone- d_6	5	63	97	90

[a] Reaction conditions: benzylamine (0.5 mmol), catalyst (ketone, 10 μ L; or PCN/ketone, 2 mg/10 μ L), acetonitrile (2 mL), O₂ (1 atm), 20 °C, xenon lamp, 3 h. [b] Determined by NMR analyses, using 1,1,2,2-tetrachloroethane as the internal standard, conversion = 1 – [amine]_{terminal}/[amine]_{initial}, mol%. [c] Selectivity = yield_{Imine} × 2/conversion_{amine}, mol%. [d] Without the addition of any ketone. [e] Ar atmosphere. [f] Additional 50 mg of NaN₃.

Last but not least, we investigated the wavelength-dependent photocatalytic oxidative coupling of benzylamine in order to look deeper into the relevant photoexcitation processes. As shown in Figure 4a, the wavelength-dependent conversion rates of the PCN case were in good agreement with the spectral distribution of the sample absorbance (dashed black line), which exhibited an obvious cut-off wavelength at around 450 nm. Such a feature indicated the low photocatalytic reactivity under visible light illumination, which would be detrimental to the potential applications. As compared to bare PCN, PCN/acetone exhibited remarkable enhancement in conversion rates over a broad region spanning from UV to visible, where the sharp change in the UV could be caused by the photoabsorption of acetone and PCN. Dramatically, the PCN/acetone system exhibited a considerable reactivity under visible light illumination, attributable to the EEA-induced energy transfer from photoexcited PCN to acetone (Figure 4b). Such processes can be understood as follow: under visible light illumination, the selective photoexcitation of the PCN component induces the accumulation of excitons; the strong correlations between these excitons lead to the generation of hot excitons (refer to E_n in the scheme) via an EEA mechanism; then the generated hot

excitons are transferred to acetone, indirectly exciting the acetone component in the system. This understanding is based on the following two facts: (i) the robust EEA in PCN yields a considerable amount of hot excitons with suitable energy level matching that of acetone, and (ii) the sub-picosecond build-up time (~0.3 ps, linked to the internal conversion of hot excitons) enables feasible hot exciton-involved energy transfer from PCN to acetone prior to the relaxation to the lowest excitonic states (refer to E1 in the scheme). This finding confirmed the feasibility of using ketones as co-catalysts to PCN in optimizing the visiblelight-driven, exciton-involved photocatalysis. It should be pointed out that the hot-exciton (generated via direct excitation or EEA) transfer from PCN to acetone also exists under UV-light (below 325 nm) excitation. However, the simultaneous but dominant excitation of acetone enables energy transfer from acetone to PCN, prevailing over the hot-exciton transfer from PCN to acetone.



Figure 4. Photocatalytic mechanism investigations. (a) Wavelength-dependent photocatalytic oxidative coupling of benzylamine, where the dashed black line is the UV-vis spectrum of PCN. (b) Schematic illustration of hot-exciton-involved energy transfer in PCN/acetone (mediated by EEA) under visible light illumination, where GS and IC denote ground state and internal conversion, respectively.

Conclusion

In conclusion, we here propose that ketones can serve as molecular co-catalysts for synergistically promoting spin relaxation and suppressing nonradiative energy losses in semiconductor-based photocatalysts. By taking polymeric carbon nitride (PCN)/acetone as a prototypical system, we demonstrate that the extrinsic introduction of ketones can lead to promoted triplet exciton accumulation and extended visible light response. According to spectroscopic investigations, we attribute such optimizations to two types of exciton-involved energy transfers between PCN and ketones. That is, the energy transfer of exciton-exciton annihilation-induced hot excitons from PCN to acetone and the energy transfer of molecular ketone triplets (whose formation is due to the high intersystem crossing efficiency) to PCN. Owing to these features, the PCN/ketone systems exhibit significantly optimized performance in exciton-involved photocatalytic reactions like singlet oxygen generation. This work brings an in-depth understanding of exciton-involved photocatalysis, and presents a prototypical model for pursing optimized solar energy utilization through introducing extrinsic molecular co-catalysts.

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Keywords: co-catalysts • exciton • energy transfer • singlet oxygen

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RESEARCH ARTICLE

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Ketones can serve as molecular co-catalysts for synergistically suppressing nonradiative energy losses and promoting spin transition. The energy transfer of exciton–exciton annihilation-induced hot excitons from PCN to acetone and the reverse energy transfer of triplet excitons from ketones to PCN are responsible to the optimizations, thereby endowing PCN/ketone systems with excellent performance in exciton-involved photocatalytic reactions.