A Facile and Green Combined Strategy for Improving Photocatalytic Activity of Carbon Nitride

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Supporting Information

ABSTRACT: We first report an efficient combined strategy that simultaneously integrates copolymerization, doping, and molecular self-assembly for the development of carbon-doping petal-like carbon nitride photocatalysts using melamine (MA), cyanuric acid (CA), and 2,4,6-triaminopyrimidine (TAP) as the starting precursors and water as the only green solvent. The morphology, textural, optical, and electronic properties of carbon nitride could be engineered by rationally manipulating the doping content of TAP. In the process of molecular self-assembly, TAP can insert the aggregate edge easily according to the results of density functional theory (DFT) calculations. The edgedetermination effect of TAP made it easier for the modified carbon nitride materials to form petal-like nanosheets with porous structures and large BET surface areas. In addition, the incorporation of TAP also contributed to tuning the electronic band structures of carbon nitrides and enhancing the separation efficiency of photogenerated carriers. The as-prepared materials exhibited excellent photocatalytic activities in the degradation of tetracycline hydrochloride (TC-HCl) and rhodamine B (RhB). This work may not only offer universally powerful and stable photocatalysts for applications but also develop a new combined strategy to fabricate efficient photocatalysts in a facile and green way.

INTRODUCTION

Semiconductor-based photocatalysis, as a feasible and green technology in which the inexhaustible and clean solar energy can be harvested and utilized, has gained considerable attention for addressing the increasing challenges in energy shortage and environmental pollution. As we all know, it is the key factor to fabricate highly efficient and enough robust photocatalysts to carry out numerous catalytic reactions. Since the pioneering work in 2009 for visible-light photocatalytic water splitting, graphitic carbon nitride (g-C3N4) has been considered as the next generation photocatalyst and also a step to achieve sustainability for artificial photosynthesis and environmental remediation. As a metal-free polymeric photocatalyst, g-C3N4 exhibits lots of excellent features, such as facile synthesis, high chemical and thermal stability, abundant and inexpensive building elements, proper electronic band structure for visible-light-responsive flexible supramolecular networks for fine-tuning material properties, and so on. However, the bulk g-C3N4 material prepared by direct polycondensation from nitrogen-rich precursors generally yields only rather disorganized textures with low surface areas as well as less active sites, which significantly restrict its applications. Thus, considerable and continuing efforts have been devoted to improve the activity of g-C3N4, such as doping with heteroatoms, constructing heterostructures, fabricating copolymers, thermal etching, cocatalyst loading, and so on. In particular, doping carbon nitride with nonmetal elements (such as P, N, Br, O, C, B, I, S, and so on) has been regarded as one efficient strategy for improving the photocatalytic activity of g-C3N4, which allows researchers to engineer the molecular and electronic structure and finally to enhance optical absorption and accelerate charge mobility without destroying the major construction and architecture of the g-C3N4 polymer. Mostly, the effect of heteroatom doping on the photocatalytic performance of g-C3N4 is affected by the prepared methods as well as the selected precursors. However, it is difficult to control heteroatoms in the particular site of the network of g-C3N4. Besides, the process of doping often contains the mixing of different precursors through physical methods, such as mechanical stirring or grinding, which cannot be controlled with uniform dopant distribution to the carbon nitride framework. Therefore, it remains a great challenge to realize efficient and precise control of the heteroatom in the framework of g-C3N4 for fine-tuning of its intrinsic electronic structure and thus its photocatalytic property.

Molecular self-assembly of monomers through noncovalent interactions is in fact a promising route for atomically precise fabrication of materials with desired properties through the bottom-up approach. The cyanuric acid–melamine (CM) complex is one of the best known molecular aggregates...
consisting of a hydrogen bond, which is powerful to control molecular self-assembly due to its reversibility, specificity, and directionality. Recently, the exploitation of CM hydrogen-bonded complexes and other derivatives opens new opportunities for the research of carbon nitride. Shalom et al. and other researchers have reported the CM-derived carbon nitride exhibited well-organized morphology, hollow structure, high surface area, and superior photocatalytic activities. 2,4,6-Triaminopyrimidine (TAP) has a molecular structure similar to melamine (MA). Ho et al. have successfully prepared C-doped g-C₃N₄ for precise substitution of nitrogen in the skeleton of tri-s-triazine with carbon through copolymerization of MA and TAP, while it is not easy to mix uniformly in an agate mortar in the molecular level. Bhunia and co-workers reported a triazine-based carbon nitride material with different C/N ratios by varying the monomer composition ratio between MA and TAP. However it is time-consuming and process-inefficient, and also it requires environmentally hazardous reagents. These pioneering works inspire us to develop new strategy to synthesize modified carbon nitride photocatalysts, which may integrate carbon doping, molecular assembly, and copolymerization with three monomers, thus further enhancing the photocatalytic activity.

In this study, we have first developed a simple, new, efficient, and green strategy to prepare modified carbon nitride materials from three common precursor molecules, namely, MA, TAP, and CA, and only water used as a green solvent, as shown in Figure 1. First, TAP and MA that have similar molecular structures of a six-membered aromatic heterocycle were mixed uniformly and sufficiently in water, and meanwhile, CA was solved in water. After mixing the above two solutions, MA, TAP, and CA supramolecular aggregates (MTC) were formed through molecular self-assembly via intermolecular hydrogen bonds. The structures of supramolecular aggregates were first studied by using the density functional theory (DFT) calculations. After polycondensation of the MTC supramolecular aggregates, TAP was successfully copolymerized into the network of carbon nitride for precise substitution of nitrogen in the skeleton of tri-s-triazine with carbon. The obtained modified carbon nitrides exhibited excellent photocatalytic activities in the degradation of tetracycline hydrochloride (TC-HCl) and rhodamine B (RhB). This design strategy is a smart and efficient way to realize the fine-tuning of intrinsic structures and electronic properties and consequently photocatalytic properties of carbon nitride. Also it is anticipated that this metal-free photocatalyst can be a promising candidate for the potential application for the water purification field.

## RESULTS AND DISCUSSION

### Formation of MTC Supramolecular Aggregates and the Synthesis of Carbon Nitrides

TAP has a molecular structure similar to MA. The only difference in the molecular structure is that MA has a 1,3,5-triazine skeleton (C₃N₃), whereas the TAP molecule consists of pyrimidine with two nitrogen atoms in the ring (C₄N₂) (as shown in Figure 1). Based on the high similarity between the molecular structures of MA and TAP, we think that TAP may be a substitute to precursor MA to form supramolecular aggregates with CA.

In order to identify our hypothesis, the optimized structures and complexation energies (E_{comp.'s}) of three aggregate lattice fragments were obtained by DFT calculations. As depicted in Figure 2, complex A, as the lattice fragment of the supramolecular aggregates of MA and TAP, has the lowest
complexation energy of $-98.1 \text{ kcal mol}^{-1}$. According to the possible doped sites of TAP, two typical lattice fragments of the supramolecular aggregates of MA, TAP, and CA were taken into account, that is, complexes B and C, in which TAP occupies the edge and the middle of the aggregates, respectively. The calculated results indicated that the $E_{\text{comp.}}$ of complex B is very close to that of complex A, differing by only $1 \text{ kcal mol}^{-1}$. The $E_{\text{comp.}}$ of complex C, however, is much higher (12.8 kcal mol$^{-1}$) than that of complex A, mainly attributed to the partial breakage of the intermolecular hydrogen bonds in complex C. Therefore, it can be readily concluded that TAP can insert the aggregate edge easily and partly substitute precursor MA to form supramolecular aggregates with CA.

The results of theoretical calculation showed that MA, TAP, and CA can form MTC supramolecular aggregates. Meanwhile, as can be seen from Figure 1, the MA and TAP could be dissolved in water at 90 °C and CA could also be dissolved in water at 90 °C, but after mixing the two solutions, white precipitates could be found. So the experimental results further proved that MA, TAP, and CA can form MTC aggregates.

The obtained MTC aggregates were calcined at 550 °C for 4 h with a heating rate of 5 °C min$^{-1}$ under an nitrogen atmosphere. With the increase of TAP, the color of carbon nitride becomes deeper and 0.01TAP-CM, 0.03TAP-CM, and 0.05TAP-CM become very fluffy (Figure S1, Supporting Information).

**Structure and Morphology Characterization.** Morphological characteristics of the different materials were investigated by SEM and TEM. As illustrated in Figure 3, the CN sample exhibits aggregated morphology consisting of block large particles and no porosity is observed on the surface (Figure 3a), which is the typical structure characteristic of g-C$_3$N$_4$ synthesized by direct thermal polymerization. Far different from CN, all xTAP-CM materials exhibit porous, loose, curve, and homogeneous morphology composed of nanosheets (Figure 3b–f). Thanks to many gas bubbles produced during thermal condensation under high temperature and the edge-termination effect of TAP, all xTAP-CM materials exhibit porous and loose morphology composed of nanosheets. In addition, the atmosphere originated from the interior of the reaction system, and the condition of polycondensation was more homogeneous than common thermal condensation, so we obtained regular and homogeneous morphology. Ho et al. have reported the g-C$_3$N$_4$ layer self-organized into nanotubes with a wrinkled appearance when the TAP was incorporated. So the curve morphology of xTAP-CM materials is in agreement with Ho et al.’s results and also reveals the successful integration of TAP rings into the CN network again. Moreover, we can find the configuration of the curve structure is dependent on the TAP contents. For 0.01TAP, the carbon nitride displays a loose stacked structure and layers were partially curved (Figure 3c). When the TAP content was increased to 0.03 or 0.05, the layers of carbon nitride sufficiently assembled into a curve structure and exhibited homogeneous petal-like morphology with porous texture (Figure 3d,e). Further increasing TAP content to 0.07, the layers of carbon nitride become smaller and begin to collapse or destroy (Figure 3f). The differences of morphology further confirm the successful incorporation of TAP. Furthermore, the basic sheet edge tends to bend, which may be caused as a result of minimizing the surface energy of the sheet and porous structure formation. Obviously, the morphology of the carbon nitride could be modified by rationally manipulating the doping content of TAP, which is a facile way to tune the microstructures. This result is supplemented by TEM images for CN and 0.03TAP-CM (Figure 3g,h). Clearly, the pristine CN exhibits the compact stacking of layered sheet morphology (Figure 3g) that changes to a thin, curve, silk-like nanostructure (Figure 3h) after TAP doping.

The XRD patterns of the different materials are displayed in Figure 4a,b. The xTAP-CM materials show distinctly different XRD patterns from CN. CN gives two typical diffraction peaks at around 13.0 and 27.2° as reported previously, which are attributed to the in-plane structural packing motif and the interlayer stacking of aromatic systems, respectively. Impressively, the two obvious peaks become very weak in the xTAP-CM, which demonstrate structure defects and the absence of long-range order in the atomic arrangements. We may infer the multiple effects of too many gas bubbles produced during thermal condensation significantly disrupted the long-range atomic order in directions both perpendicular and parallel to layers, which agrees with the SEM results. Notably, 0.07TAP-CM exhibits the weakest peaks, which may be ascribed to the collapsed or destroyed structures. In addition, the main peak displays a slight shift to higher angles from 27.2 to 27.5°, corresponding to a reduction in the stacking distance of layers.
The microstructures of the different materials were further characterized by FTIR technology to investigate the effect of TAP incorporation. As shown in Figure 4c,d, all FTIR spectra of the as-prepared samples showed similar characteristic vibrational peaks. The multiple bands in the range from about 1230 to 1650 cm\(^{-1}\) correspond to the stretching modes of typical aromatic C\(\text{−}N\) heterocycles.\(^{10g,18}\) The peak at approximately 808 cm\(^{-1}\) is assigned to the characteristic breathing mode of tri-s-triazine units.\(^{19}\) The broad bands located in the range from 3000 to 3650 cm\(^{-1}\) originate from the stretching vibrations of N−H and O−H bonds, associated with uncondensed amino groups (−NH\(_2\) or −NH groups) and adsorbed H\(_2\)O molecules.\(^{18−20}\) It is obvious that the characteristic absorbance for the C−N heterocycles remained almost unchanged after incorporating with TAP. These results suggest that the TAP incorporation did not severely alter the core chemical skeleton of carbon nitride. However, the evident enhanced absorption in 3000 to 3650 cm\(^{-1}\) can be considered as an indicator of modified carbon nitride materials with enlarged open-up surfaces and more uncondensed amino groups.\(^{18}\) In addition, the peak at \(\sim\)1380 cm\(^{-1}\) becomes obviously enhanced compared to CN, which may be the influence of TAP incorporated to the supramolecular complex. Furthermore, the peak at \(\sim\)808 cm\(^{-1}\) is another typical characteristic peak of the heptazine unit, and we can find that the peaks for modified g-C\(_3\)N\(_4\) materials slightly shift from 808 to 814 cm\(^{-1}\) by the introduction of TAP.

The compositions and surface chemical states of the different samples were studied by XPS to determine the effect of TAP incorporation on the chemical skeleton of carbon nitride. In the XPS survey spectra (Figure S2, Supporting Information), we can find three main peaks at \(\sim\)288, 398, and 532 eV, which belong to the C 1s, N 1s, and O 1s signals, respectively. As shown in Table 1, the C/N molar ratios increased when TAP content increased, which is consistent with the result of the substitution of partial N atoms by C atoms in the framework of carbon nitride. In addition, the peak at \(\sim\)808 cm\(^{-1}\) becomes obviously enhanced compared to CN, which may be the influence of TAP incorporated to the supramolecular complex. Furthermore, the peak at \(\sim\)808 cm\(^{-1}\) is another typical characteristic peak of the heptazine unit, and we can find that the peaks for modified g-C\(_3\)N\(_4\) materials slightly shift from 808 to 814 cm\(^{-1}\) by the introduction of TAP.

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## Table 1. Elements Containing from XPS and Relative Content of Various Species Obtained from XPS Data (%)

| sample     | C   | N   | C/N | C=N−C | N(−C)\(_3\) | NH\(_2\) | NH\(_2\)/N(−C)\(_3\) |
|------------|-----|-----|-----|-------|-------------|---------|---------------------|
| CN         | 40.210 | 56.920 | 0.706 | 0.704 | 0.217 | 0.079 | 0.364 |
| CM         | 39.000 | 59.170 | 0.659 | 0.682 | 0.227 | 0.090 | 0.400 |
| 0.01TAP-CM | 41.458 | 56.649 | 0.732 | 0.722 | 0.198 | 0.080 | 0.405 |
| 0.03TAP-CM | 41.555 | 56.646 | 0.734 | 0.729 | 0.188 | 0.083 | 0.444 |
| 0.05TAP-CM | 42.242 | 55.624 | 0.759 | 0.718 | 0.197 | 0.085 | 0.432 |
| 0.07TAP-CM | 42.164 | 54.955 | 0.767 | 0.718 | 0.197 | 0.085 | 0.432 |
nitride when MA was substituted by TAP. The chemical groups and bonding characteristics were further confirmed by the high-resolution C 1s (Figure S3, Supporting Information) and N 1s spectra (Figure 5a−f). The C 1s spectra could be peak-fitted into four components: the main one located at ∼288.3 eV was attributed to sp²-hybridized C from the s-triazine heterocycle, whereas the wide component at ∼293.5 eV could be ascribed to its π → π* satellite band; the peak with a low intensity at ∼286.3 eV was related to the C−NH₃⁺ and the weak component at ∼284.8 eV was associated with surface carbon impurities. However, the binding energy of xTAP-CM materials for the C 1s XPS at 288.3 eV shifted slightly to lower energy (288.2 eV), and the peak at 286.3 eV reversely shifted to higher energy (286.9 eV) when TAP incorporation increased, which are well consistent with the reported literature. The N 1s XPS spectra (Figure 5a−f) can be fitted into four peaks. The main component (∼398.7 eV) corresponded to sp²-hybridized N from the heterocycle and was also accompanied by a wide π → π* satellite band at 404.4 eV. The peaks at 400.0 and 401.1 eV corresponded to the tertiary N in the form of N(−C)₃ and uncondensed amino functional groups (NH₂ or NH), respectively. The absorption associated with different nitrogen moieties could identify the defect types to some degree, as well as the uncondensed amino groups. N-associated species were quantified using deconvoluted N 1s spectra (Table 1). A higher ratio of NH₃⁺/N(−C)₃ demonstrates a smaller polymerization degree, meanwhile more uncondensed amino groups. It can be found that xTAP-CM materials all show larger values of NH₃⁺/N(−C)₃. The phenomena can be attributed to the edge-
termination effect of TAP, which results in the low degree of polymerization and large amount of amino groups. The XPS results are consistent with the SEM, XRD, and FTIR results.

The pore structures and BET surface areas of the different samples were obtained by N₂ adsorption–desorption measurements. As shown in Figure 6a, xTAP-CM materials exhibit type IV isotherms with extremely high adsorption capacities in the high relative pressure ($P/P₀$) from 0.8 to 1), indicating the presence of abundant mesopores and macropores. As compared to bulk CN, the BET surface areas of xTAP-CM materials present an obvious increase. Especially, the BET surface area of 0.03TAP-CM is calculated to be 95 m² g⁻¹, which is more than 15 times that of CN (6 m² g⁻¹). The large BET surface area of xTAP-CM materials can be attributed to the edge-termination effect of TAP as well as the large amount of bubbles of polycondensation. The BET surface areas of 0.05TAP-CM and 0.07TAP-CM are calculated to be 84 and 41 m² g⁻¹, respectively. It can be seen that with the increase of TAP, the BET surface area decreased, which may be due to too much incorporation of TAP and the petal-like microstructure that began to collapse or destroy. The BET results are consistent with the SEM results. To further analyze the pore structures of xTAP-CM materials, pore size distribution (PSD) plots were obtained using the Barrett–Joyner–Halenda (BJH) method. Correspondingly, xTAP-CM materials possess much larger pore volumes than CN (Figure 6b). The PSD curves of xTAP-CM materials have a narrow distribution from about 2 to 4 nm and a broad distribution from about 20 to 180 nm, while that of CN shows negligible peaks. Notably, the PSD curve of 0.07TAP-CM exhibits a negligible peak in the region from 20 to 180 nm, which may be also attributed to too much incorporation of TAP and the petal-like microstructure that began to collapse or destroy. The large BET surface area and pore volume could provide more reactive sites and more edge structures, which may effectively adsorb more reactants and which are conducive to mass transfer and charge carrier transfer during the photocatalytic process. 4,15

Optical and Electronic Properties. We studied the optical properties of the different samples by solid-state UV–vis diffuse reflectance spectroscopy (DRS) (Figure 7a,b). As shown in Figure 7a,b, the UV–vis DRS spectra indicate that the absorption edges of xTAP-CM materials display a slight red shift along with a TAP increase, which was consistent with the results reported in the previous literature. 10g This result further confirms the successful incorporation of TAP, and the electronic structure of carbon nitride is remarkably modified. The energy band gaps of the different samples can be determined from the intercept of the tangents to the plots of $(αhυ)^2$ versus $hυ$. As presented in Figure 7c, we can obtain the band gaps of different samples. Overall, the xTAP-CM materials demonstrate narrower band gaps than the CN sample. Furthermore, XPS valence band (VB) XPS spectra were analyzed to investigate the band edges of all the different samples (Figure 7d). According to the results of band gaps and valence band, the electronic band structures of xTAP-CM materials can be schemed (as shown in Figure 7e). It can be seen that the electronic band structures of xTAP-CM materials could be tuned by manipulating the doping content of TAP. From 0.01TAP-CM to 0.07TAP-CM, the band gaps were gradually reduced. A possible reason is the increasing proportion of TAP; the contributions of substituted carbon would decrease the balances of π-conjugated electrons on the triazine rings and accordingly reduced the band gaps on the large doping compounds as observed in the UV–vis absorption spectra. 25 The reduction of band gap energy is beneficial to harvest solar light. Aside from an appropriate band gap, the matching of CB and VB levels of the semiconductor would decrease the balances of conduction and valence bands. Therefore, it is essential to achieve a lower band gap. The XRD results are consistent with the SEM, XRD, and FTIR results. We also measured the PL spectra of 0.01TAP-CM, 0.05TAP-CM, and 0.07TAP-CM (Figure 8a, Supporting Information). It can be seen that, with an increasing amount of TAP added, the fluorescence intensities of 0.01TAP-CM, 0.03TAP-CM, and 0.05TAP-CM gradually increase. It may be due to the more defects produced with the increasing amount of TAP. More defects appear resulting in an increase in radiation recombination and
gradually stronger fluorescence intensity. However, the fluorescence intensity of 0.07TAP-CM obviously decreases. It may be due to the too much incorporation of TAP and nanosheet structures that began to collapse or destroy.

Electrochemical impedance spectroscopy (EIS) is a method to explain the electron-transfer efficiency at the electrodes. Generally speaking, the relative size of the arc radius on Nyquist plots corresponds to charge transfer resistance in the study of photocatalysis. The 0.03TAP-CM photocatalyst exhibits the smaller arc radius, implying its lower charge-transfer resistance (as shown in Figure 8b). This result is supplemented by transient photocurrent response measurements that show an enhancement in the current density of 0.03TAP-CM over CN. These results indicate 0.03TAP-CM has less recombination and more efficient separation of photogenerated $\text{h}^+/\text{e}^-$ pairs, and such photoelectrochemical properties are very beneficial for photocatalysis. The more efficient separation of photogenerated $\text{h}^+/\text{e}^-$ pairs can be attributed to the incorporation of TAP, which caused the carbon doping in the carbon nitride materials.

Photocatalytic Activities. In order to estimate the potential capabilities of wastewater treatment, the photocatalytic activities of the as-prepared samples were evaluated via the degradation of aqueous TC-HCl and RhB under light
irradiation. As shown in Figure 9a, the photolysis of TC-HCl under the same experimental conditions without the catalyst indicated that TC-HCl was stable under irradiation after 30 min. For comparison, only about 50% of TC-HCl was degraded in the presence of the CN after 30 min. On the contrary, the photocatalytic activities for xTAP-CM materials were very satisfactory. The photodegradation rates increase with the addition of TAP content in the supramolecular complex and then decrease. Especially for 0.03TAP-CM, when the irradiation time reached only 20 min, more than 95% of TC-HCl was degraded. In order to confirm the universality of the catalyst, we studied the photocatalytic degradation of rhodamine B (RhB), which was a common organic dye. The results also verified the excellent ability of the 0.03TAP-CM material to remove organic pollution in water (Figure 9b). The results demonstrated that the well-defined petal-like microstructure was advantageous to improve its photocatalytic activity.

Figure 8. (a) PL spectra of the CN and 0.03TAP-CM. (b) EIS plots of the CN and 0.03TAP-CM; inset shows the transient photocurrent responses of the CN and 0.03TAP-CM.

Figure 9. (a) Photocatalytic degradation of TC-HCl. (b) Photocatalytic degradation of RhB. (c) Cyclic test on the photocatalytic degradation of TC-HCl using 0.03TAP-CM (20 min irradiation). (d) Trapping experiment of the active species for the degradation of TC-HCl over the 0.03TAP-CM.
The stability of a photocatalyst is also very important for its practical application. The 0.03TAP-CM sample was tested through five consecutive trials (only irradiation for 20 min) to test the reusability and stability (Figure 9c). There is hardly any loss of activity in the photocatalytic performance of 0.03TAP-CM with the reaction time prolonged. The mass loss of catalyst 0.03TAP-CM in recycling experiments may be the major factor affecting the photocatalyst reactivation. Therefore, 0.03TAP-CM can be regarded as a stable high-performance photocatalyst for photodegrading organic pollutants, possessing great prospects in environmental protection.

Photocatalytic Mechanism. It is well known that photogenerated holes (h\(^+\)), superoxide radical (O\(_2^−\)), and hydroxyl radical (OH) are three typical active species for the degradation of pollutants. In order to investigate the photocatalytic mechanism of 0.03TAP-CM and probe the role of various active species, the trapping experiments were conducted. In this study, EDTA-2Na, BQ, and IPA were employed as the scavengers for h\(^+\), O\(_2^−\), and OH, respectively. As stated in Figure 9d, the photocatalytic activity of 0.03TAP-CM was greatly suppressed by the addition of BQ, which indicated that O\(_2^−\) is the main active species in the photocatalytic reaction. Conversely, the photocatalytic efficiency did not change significantly by introduction of IPA and EDTA-2Na, revealing that the OH and h\(^+\) did not play an important role in the degradation. In conclusion, O\(_2^−\) is the major reactive species for the degradation of TC-HCl on the 0.03TAP-CM sample.

According to the above experimental results, the mechanism for photocatalytic degradation is proposed (Figure 10).

![Figure 10. Proposed mechanism of photocatalytic process on 0.03TAP-CM photocatalyst under light irradiation.](image)

enhanced photocatalytic performance of 0.03TAP-CM demonstrated above can be explained as the synergistic effects of large BET surface area, porous structure, petal-like morphology, and carbon doping. First, benefiting from the edge-termination effect of TAP as well as the large amount of bubbles in the polycondensation, all the xTAP-CM materials demonstrate large surface areas and porous structures (especially for 0.03TAP-CM), which could provide more reactive sites and more edge structures, and may effectively absorb more reactants. Furthermore, the well-defined and homogeneous petal-like structure could efficiently enhance the reflection and scattering of light in the reaction system, which is in favor of making full use of the light. Third, carbon doping could efficiently enhance the separation of photogenerated h\(^+\)/e\(^−\) pairs. Finally, precise control of doping carbon atoms into the skeleton structure of carbon nitride finely tunes its intrinsic electronic properties. 0.03TAP-CM has the lowest CB value and strongest reduction ability, which is a benefit to produce more O\(_2^−\) active species.

CONCLUSIONS

To conclude, the modified and efficient carbon nitride materials were synthesized by a facile and green method using MA, CA, and TAP as the starting precursors and water as the green solvent. MA, CA, and TAP could form the self-assembly aggregates in water. TAP can insert the aggregate edge easily according to the results of DFT calculations. The morphology, textural, optical, and electronic features of carbon nitride could be modified by rationally manipulating the doping content of TAP. Compared to the common carbon nitride, the optimal modified carbon nitride 0.03TAP-CM had homogeneous petal-like morphology, porous nanostructure, larger BET surface area, more appropriate electronic band structure, and higher separation efficiency of photogenerated carriers. 0.03TAP-CM exhibited excellent photocatalytic activities in the degradation of TC-HCl and RhB. The enhanced photocatalytic activities may be attributed to the edge-termination effect and incorporation of TAP. Overall, this work demonstrates a facile and green preparation strategy that simultaneously integrates copolymerization, doping, and molecular self-assembly. Meanwhile, the new as-prepared photocatalysts, xTAP-CM materials (especially 0.03TAP-CM), demonstrate excellent photocatalytic performances and hold great promise in practical applications of utilizing solar energy for environmental remedy.

EXPERIMENTAL SECTION

Material Preparation. The common g-C\(_3\)N\(_4\) sample was prepared by a previously reported thermal polymerization method. In a typical procedure, the material was synthesized by heating 2.5 g of MA in a sealed quartz crucible under N\(_2\) gas flow to 550 °C for 4 h at a heating rate of 5 °C min\(^{-1}\) and then cooled to room temperature. The product was collected and ground into powder and denoted as CN.

The modified carbon nitride materials were prepared by a new and green approach. First, MA and TAP with different amount ratios of 2.5 - x:x (x = 0, 0.0250, 0.0750, 0.1250, 0.1750, and the total amount remained 2.5 g) were first dissolved and mixed in 100 mL of deionized water under stirring at 90 °C. At the same time, 2.5 g of CA was dissolved in another 100 mL of deionized water under stirring at 90 °C. After complete dissolution, the above solutions were mixed together to give white precipitates. Subsequently, the mixtures were filtered and washed with water. The resulting precipitates were dried at 60 °C in an oven and calcined at 550 °C for 4 h with a heating rate of 5 °C min\(^{-1}\) under a nitrogen atmosphere. When x = 0, the corresponding sample was denoted as CM due to the sample only involving two kinds of precursors (CA and MA). When different amounts of TAP were introduced into the CA and MA system, the resulting samples were labeled xTAP-CM (x denotes the ratio of TAP/(MA + TAP), x = 0.01, 0.03, 0.05, and 0.07).

Material Characterization. The Fourier transform infrared (FTIR) spectra were obtained using a PerkinElmer model 2000 FTIR spectrophotometer. The X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax/Ulma IV diffractometer. The scanning electron microscopy (SEM) images were obtained on a FEI QUANTA F250 scanning
electron microscope. Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2 F30 instrument. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 Xi with a high-performance Al monochromatic source ($h\nu = 1486.6$ eV, 150 W). Brunauer—Emmett—Teller (BET) surface areas were calculated from $N_2$ adsorption—desorption isotherms collected at 77 K using Quantachrome Instruments version 3.0. UV—vis diffuse reflectance spectra were recorded on a Shimadzu UV-3600 spectrophotometer using BaSO$_4$ as the reference sample. The photoluminescence (PL) spectra were measured on an EL FLS980 at room temperature with excitation at 389 nm. The electrochemical impedance spectroscopy (EIS) was carried out and the transient photocurrent responses were obtained, both on an electrochemical workstation (CHI-660D, Shanghai Chenhua Apparatus Co., Ltd.) by using a three-electrode model in which the working electrodes of CN and 0.03TAP-CM were deposited on ITO conductive glass. A Pt electrode was used as the counter electrode, and a saturated Ag/AgCl electrode was the reference electrode. A 300 W Xe lamp was used as a light source. The working electrode was prepared according to the following procedure: 5 mg of photocatalyst and 10 μL of Nafton solution (5 wt %) were dispersed in 1000 μL water/ethanol mixed solvent (3:1 v/v) by 60 min sonication to make slurry. Then, 40 μL of the slurry was dropped onto the ITO conductive glass with an effective working area of 1 cm$^2$ and then dried in air.

**Calculation Methods.** All DFT calculations presented here were carried out with the Gaussian 09 suite of programs. Based on the conductor-like polarizable continuum model (CPCM), geometric structures for the lattice fragments were optimized in aqueous solution using the dispersion corrected B3LYP-D3 theory of level in conjunction with the standard 6-31 + G(d) basis set. The computational methods chosen have been tested extensively and proven to be reliable in solving many biochemical problems. Vibrational frequency calculations were performed to confirm the stationary point as a minimum with all positive frequencies. The complexation interactions were performed to confirm the stationary point as a minimum with all positive frequencies. The complexity of the lattice fragments were calculated through basis set superposition error (BSSE) correction. The dielectric constant used in the calculations was $\varepsilon = 78.4$ for water.

**Photocatalytic Activity Measurement.** The photocatalytic activities of the synthesized samples were evaluated by photodegradation of TC-HCl and RhB at ambient temperature in air. The UV—visible light was provided by a visible light was provided by a 70 W metal halide, which was often used in photocatalysis purification in the coming decades. Nature 2008, 452, 301–310. (b) Ong, W.-J.; Tan, L.-L.; Ng, Y. H.; Yong, S.-T.; Chai, S.-P. Graphitic Carbon Nitride (g-C$_3$N$_4$)-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer To Achieving Sustainability? Chem. Res. 2016, 116, 7159–7329.

The stability of 0.03TAP-CM was checked using the recyclability studies. After each cycle, the catalyst was collected by centrifugation, washed with distilled water, and dried. The recovered catalyst was then directly used for the next cycle of photocatalytic degradation of TC-HCl as stated above.

**Active Species Detection.** The reactive species in the photodegradation of TC-HCl were detected using in situ trapping experiments. The detection process was similar to the photodegradation experimental process except for the addition of scavengers. Three different scavengers, disodium ethylenediaminetetraacetate (EDTA-2Na, hole scavenger), $p$-benzoquinone (BQ, $\cdot$O$_2^-$ radical scavenger), and isopropanol (IPA, OH radical scavenger), were added to the TC-HCl solution prior to illumination in three separate photodegradation systems. The authors gratefully acknowledge the financial support from the Key Project of the Education Department of Sichuan Province (18ZA0474), the Project of Research and Development Fund of Nanchong (18YFJ0041), and the Project of Talents Research Fund of China West Normal University (17YC040 and 17YC010).

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00179.

Sample photograph, XPS survey spectrum, high-resolution C 1s XPS spectra, and PL spectra (PDF)
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