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Modulating Location of Single Copper Atoms in Polymeric Carbon Nitride for Enhanced Photoredox Catalysis

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ABSTRACT: Introducing single-atom metals (SAMs) is a promising strategy to improve photocatalysis of polymeric carbon nitride (PCN), but current studies are limited to loading SAMs on the surface of PCN to serve as active sites. Herein, we report an intercalation-structured hollow carbon nitride sphere composed of carbon nitride nanosheets (HCNS) with atomically dispersed Cu₁N₃ moieties embedded within nanosheets (Cu1@HCNS) prepared by a facile molecular assembly approach. It exhibits far superior photoredox catalysis to the pristine HCNS and the modified HCNS with Cu₁N₃ moieties anchored on the surface of nanosheets (Cu1/HCNS) for solar hydrogen production (3261 μ mol g⁻¹ h⁻¹ rate with 7.1% of apparent quantum yield), in which the embedded single-atom Cu acts



as a modifier to effectively modulate the electron structure and remarkably promote interfacial charge transfer of PCN rather than act as active sites to facilitate surface reaction. It can be extended to the nonoxygen coupling of benzylamine and derivants to corresponding imines, and the unexpectedly high reaction rate is achieved. The promoting effect strongly depends on the location of single-atom Cu in the PCN, and the coordination method is a very effective strategy to introduce single-atom metals in terms of the improvement in photocatalysis of PCN owing to the intensified metal—PCN interaction. This work opens up a window for further improving the photocatalytic efficiency of carbon nitride in terms of solar fuel production and clean organic synthesis.

KEYWORDS: carbon nitride, single-atom copper, location effect, hydrogen evolution, nonoxygen coupling, imine, photocatalysis

1. INTRODUCTION

Solar water splitting and photosynthesis are considered as quite promising strategies to address energy and environmental crisis.¹⁻⁴ Designing efficient, stable, environmentally friendly, and cheap photocatalysts is the key to the practical application of photocatalytic technology.¹⁻⁷ Recently, polymeric carbon nitride (PCN) has been regarded as an attractive candidate for photocatalysts owing to its many merits like adjustable electronic structure, good thermal and chemical stability, environmental benignity, and facile preparation from abundant and cheap starting materials.⁸⁻¹¹ Unfortunately, the bulk PCN exhibited inferior photocatalysis owing to the insufficient light absorption, sluggish carrier transfer, rapid recombination of photoinduced charge carriers, and low specific surface area.⁸⁻¹² To improve the photocatalysis of PCN, various strategies have been proposed, including doping,^{10,12–16} fabricating macro– micro-nanostructures,^{17–20} and creating heterojunctions.²¹ However, the photocatalytic efficiency is still far from the requirement for the practical applications in water splitting and selective photosynthesis.

Nowadays, single-atom catalysts are widely used in various reactions due to their unique electronic properties and high atomic utilization.^{22–25} Introducing single-atom metal (SAM) into PCN is a promising strategy to improve its photo-catalysis.^{26–28} However, current studies are mainly limited to loading SAMs on the surface of PCN to act as active sites to

facilitate surface reactions.^{26–39} Although the reaction rate per gram metal is efficiently improved owing to atomic dispersion, the rate per gram PCN is still very low, now that loading superhigh amount of SAM remains a huge challenge. Recently, Dontsova et al.⁴⁰ reported a facile method for preparing a single-atom Ag merged joint electronic system (Ag/TCMmpg-CN) by anchoring Ag atoms on layers of carbon nitride via electrostatic interaction using silver tricyanomethanide as a reactive comonomer, which adjusts the electronic structure and promotes charge transfer in some degree. Depositing 3 wt % Pt as cocatalyst (active sites), Ag/TCM-mpg-CN just shows a 3.6 times higher hydrogen rate (HER) compared to pristine mpg-CN, but the HER only reaches 720 μ mol g⁻¹ h⁻¹, which is quite a low value. The weak SAM-PCN interaction may weaken its promoting effect. Subsequently, the electrostatic adsorption method was extended to diverse Ag/TCMcontaining PCN systems for photocatalytic degradation of pollutants⁴¹⁻⁴³ but rarely used in hydrogen evolution or photosynthesis. Moreover, the adsorbed single Ag atoms by

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charge interaction are not fixed enough, which may lead to leaching during reaction and separation processes. Moreover, Fu et al. reported a new Fe@g-C₃N₄ joint electronic system by anchoring single-atom Fe on the surface of PCN, showing an 18.3 times higher HER of bulk g-C₃N₄.⁴⁴ In contrast, introducing SAM to act as a modifier to adjust the electronic structure and promote interfacial charge transfer rather than as active sites to facilitate surface reaction is regarded as a promising strategy to improve the photocatalysis of PCN but rarely exhibits the possibility for embedding SAM within nanosheets of PCN by strong metal–N bond for more effectively improving solar H₂ production and photosynthesis.

Herein, two kinds of intercalation-structured hollow carbon nitride spheres composed of carbon nitride nanosheetmodified single-atom Cu at distinct distribution locations have been prepared using cheap melamine (ME), cyanuric acid (CA), and copper nitrate as starting materials, featuring Cu_1N_3 species embedded within carbon nitride nanosheets (Cu1@ HCNS) and anchored on the surface of nanosheets (Cu1/ HCNS). Both of them demonstrate the same Cu₁N₃ species fixed by Cu-N bonding and confirmed by aberrationcorrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and X-ray absorption fine structure spectra (XAFS). The distinct distribution locations of Cu₁N₃ species in PCN is confirmed by X-ray photoelectron spectroscopy (XPS) with/without Ar plasma etching. Cu1@HCNS shows 1.6 and 2.7 times higher HER with 7.1% of higher apparent quantum yield (AQY) compared to Cu1/HCNS and pristine HCNS, respectively, which is 35.4 times higher than that over bulk PCN. More interestingly, Cu1@HCNS shows an unexpectedly high benzylamine oxidation rate (BOR) of 10583 μ mol g⁻¹ h⁻¹ for imine production, which is 3.8 and 2.5 times higher than that over Cu1/HCNS and pristine HCNS, respectively. Cu1@HCNS shows a much higher BOR than the reported Pt/metalorganic framework (MOF) and comparable BOR to the reported Ni/CdS,^{45,46} while precious Pt or the toxic and photocorrosive CdS can be avoided. The excellent photocatalysis is extended to diverse benzylamine derivants. Furthermore, we find that the markedly enhanced photoredox catalysis can be ascribed to the modulation of the electronic structure and the promotion of interfacial charge transfer via the introduction of single-atom Cu, and the promoting effect strongly depends on the distribution location of Cu₁N₃ species. Differing from refs 40-44, in this work, the SAM is embedded within nanosheets of PCN via Cu-N bonding rather than embedding SAM by electrostatic adsorption or anchoring it on the surface of PCN. This work paves a new way to design highly efficient and expensive PCN photocatalysts for solar hydrogen production and photosynthesis.

2. RESULTS AND DISCUSSION

The preparation process of Cu1@HCNS and Cu1/HCNS is schematically illustrated in Figure 1a, and experimental details are provided in the Supporting Information. Typically, Cu1@ HCNS was fabricated by a facile molecular assembly approach, including the assembly of ME, CA, and copper nitrate (1) and the polymerization (2). To investigate the effect of location of single-atom Cu on the nature and photocatalysis of Cumodified HCNS, the coordination state of the loading singleatom Cu on the surface of carbon nitride nanosheets of Cu1/ HCNS must be the same as that of Cu1@HCNS. To obtain the same Cu coordination state under the premise of as minor



Figure 1. (a) Schematic fabrication of Cu1@HCNS and Cu1/HCNS graphitic carbon nitride materials with single-atom copper modification. (b) SEM and (c) TEM images of Cu1@HCNS. (d) SEM and (e) TEM images of Cu1/HCNS. (f, g) HRTEM images of Cu1@HCNS (f) and Cu1/HCNS (g). (h, i) HAADF-STEM images of Cu1@HCNS (h) and Cu1/HCNS (i).

as affecting the structure of HCNS, Cu1/HCNS was also prepared by a molecular assembly method, except for an impregnation process that was inserted, now that Cu1@HCNS was prepared by molecular assembly. To avoid the effect of twice calcination on carbon nitride, the desired amount of Cu-ME-CA complex was impregnated on the precursor of HCNS rather than directly on HCNS. The detailed process includes assembly of ME and CA (3), impregnation of ME-Cu complex with subsequent fixation by CA via assembly (4), and polymerization (5). Moreover, pristine HCNS and Cu nanoparticle (NP)-embedded HCNS were also prepared.

The intercalation-structured hollow carbon nitride spheres composed of carbon nitride nanosheets are verified by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figures 1b-e and S1). As illustrated in the high-resolution TEM (HRTEM) images (Figure 1f,g), no Cu NP is observed on Cu1@HCNS and Cu1/HCNS, but obvious Cu NPs are observed on Cu_{NP}@ HCNS (Figure S1d, highlighted by yellow circles). As a powerful tool for identifying single-atoms,⁴⁷ the atomically dispersed Cu sites on both Cu1@HCNS and Cu1/HCNS are identified as bright spots (highlighted by yellow circles) by HAADF-STEM (Figure 1h,i). However, Cu1/HCNS shows much denser single Cu atoms compared to Cu1@HCNS, although they have similar Cu loadings measured by inductively coupled plasma-optical emission spectrometry (ICP-OES; 0.85 and 1.03 wt % for Cu1@HCNS and Cu1/ HCNS, respectively). This implies the distinct Cu distribution locations that were confirmed by XPS measurements. Figure S2 shows two X-ray diffraction peaks appearing at 13.1 and 27.4°, assigned to g-C₃N₄. The morphology and main matrix of g-C₃N₄ are not greatly affected compared to HCNS, although the introduction of Cu distorts the g-C₃N₄ crystal. N₂ adsorption-desorption and elemental analysis results (Figure S3 and Table S1) demonstrate that both Cu1@HCNS and

Cu1/HCNS have similar textural properties and N/C ratio compared to HCNS, and no obvious difference is observed after single Cu atoms are introduced. However, Cu_{NP} @HCNS shows distinct textural properties and elemental components compared to the other samples, which might be owing to the presence of the reducing agent in the assembly process.

The N 1s X-ray photoelectron spectroscopy (XPS) peak of Cu1@HCNS and Cu1/HCNS assigned to pyridinic N shifts to lower binding energy than that of HCNS (Figure S4), indicating that Cu atoms may coordinate with pyridinic N to form the Cu $-N_x$ moieties.^{48–51} A new peak at 399.0 eV appears on the N 1s XPS of Cu1@HCNS and Cu1/HCNS samples in contrast to HCNS and can be resolved (Figure 2a–



Figure 2. (a–c) N 1s XPS spectra of Cu1@HCNS (a), Cu1/HCNS (b), and HCNS (c). (d) Cu 2p XPS spectra of Cu1@HCNS and Cu1/HCNS materials with/without Ar plasma etching for XPS measurement. (e) Normalized Cu K-edge XANES spectra. (f) k^3 -Weighted Fourier transform spectra from Cu K-edge EXAFS. (g, h) Corresponding EXAFS fitting curve of Cu1@HCNS (g) and Cu1/HCNS (h). (i) Model of Cu₁N₃ sites in Cu1@HCNS and Cu1/HCNS.

c), implying the formation of Cu-N bond.⁵⁰⁻⁵² The quantitative results for the N 1s XPS of Cu1@HCNS, Cu1/ HCNS, and bare HCNS presented in Table S2 demonstrate that both Cu1@HCNS and Cu1/HCNS show similar content in terms of oxidized N, graphitic N, and pyrrolic N but decreasing pyridinic N percentage in comparison with bare HCNS, further implying the coordination of Cu and pyridinic N. In addition, we can clearly see that Cu1@HCNS shows a much lower Cu-N percentage, although they have a similar Cu loading. To further determine the location of single Cu atoms on Cu1@HCNS and Cu1/HCNS, the Cu 2p XPS spectra of Ar plasma etched samples were collected (Figure 2d). The Ar plasma etching process was performed for 10 s, and the etching depth of the two samples is ca. 6 nm. The Cu1@HCNS shows a significantly increasing Cu 2p peak intensity after it suffers from Ar plasma etching, while no detectable change occurs on Cu1/HCNS before and after etching. This unambiguously confirms that the single Cu atoms are embedded within nanosheets of Cu1@HCNS, while the Cu atoms are anchored on the surface of nanosheets of Cu1/ HCNS. This is consistent with the HAADF-STEM results (Figure 1h,i).

X-ray absorption spectroscopy (XAS) experiments were performed to further explore the electronic structure and local coordination state of Cu species in Cu1@HCNS and Cu1/ HCNS samples. X-ray absorption near-edge spectra (XANES) of Cu1@HCNS and Cu1/HCNS show a similar edge shape (Figure 2e), indicating the same coordination configuration of single-atom Cu. The extended X-ray absorption fine structure (EXAFS) spectra reveal no Cu–Cu signal in both Cu1@ HCNS and Cu1/HCNS (Figure 2f). Moreover, the EXAFS fitting curve in R space for Cu1@HCNS and Cu1/HCNS samples demonstrates that the Cu–N coordination and the isolated Cu atom is coordinated with three N atoms (Figure 2g,h and Table S3). In addition, the isolated Cu₁N₃ coordination state was further modeled by density functional theory (Figure 2i).

The photocatalytic activity of the two single Cu atommodified HCNS catalysts with distinct Cu distribution locations was tested using triethanolamine (TEOA) as a sacrificial agent and 3 wt % Pt as a cocatalyst under visible light (Figure 3a). CuNP@HCNS, HCNS, and buck PCN (BCN)



Figure 3. (a) Time-dependent H_2 evolution over the 3 wt % Ptdeposited PCN samples including Cu1@HCNS, Cu1/HCNS, HCNS, Cu_{NP}@HCNS, and BCN under visible light irradiation. (b) Wavelength-dependent AQY of the photocatalytic H_2 evolution (right axis) and UV/vis light absorption spectrum (left axis) over Cu1@HCNS.

were tested as a benchmark for comparison. Only trace H₂ is produced on Cu_{NP}@HCNS, originating from the destroyed semiconductor structure confirmed by remarkably changing textural properties and elemental components (Figure S3 and Table S1), although it has a similar morphology to HCNS (Figure S1c). Both the single Cu atom-modified HCNS show much superior photocatalytic activity to pristine HCNS for H₂ evolution, originating from the promoting effect of introducing single-atom Cu. More interestingly, Cu1@HCNS shows 1.6 times higher HER (3261 μ mol g⁻¹ h⁻¹) compared to Cu1/ HCNS (2097 μ mol g⁻¹ h⁻¹), suggesting that the promoting effect strongly depends on the distribution location of Cu₁N₃ species. Moreover, almost no H_2 can be produced on Cu1@ HCNS in the absence of Pt cocatalyst, implying that the embedded Cu does not act as active sites for H_2 evolution and thus differs from the reported results.^{29–39} Cu1@HCNS shows 7.1% of AQY at $\lambda = 420$ nm (Figure 3b). The developed Cu1@HCNS shows superior photocatalytic performance to the previously reported doped PCN photocatalysts for H₂ production, including Fe@g-C3N4 with single-atom Fe loaded on the surface of carbon nitride and 1% Ag/TCM-mpg-CN with single-atom Ag embedded into PCN by electrostatic adsorption (Table S4).

To get insights into the influence of single Cu atoms on the Cu-modified HCNS catalysts, the optical, electronic, electrochemical, and photoelectrochemical properties were systematically investigated. UV/vis absorption spectra demonstrate that both Cu1@HCNS and Cu1/HCNS show a red shift of absorption edge and intensive visible light absorption in contrast to pristine HCNS (Figure 4a), which facilitates more



Figure 4. (a) UV/vis absorption spectra and corresponding Taus plots (inset). (b) Schematic diagram of the band structure. (c) Steady-state photoluminescence (PL) spectra. (d) Time-resolved transient PL spectra. (e) Electrochemical impedance spectra and (f) transient photocurrent response of Cu1@HCNS, Cu1/HCNS, and HCNS.

charge carrier generation. Embedding single Cu atoms within carbon nitride nanosheets is more effective to promote light absorption than anchoring them on the nanosheets. The band gap energy (E_{α}) was estimated by the transformational Taus plots acquired from Kuberka-Munk function (Figure 4a, inset). Cu1@HCNS shows lower E_{σ} (2.65 eV) than Cu1/ HCNS (2.71 eV) and HCNS (2.75 eV), originating from the adjustment of the electronic structure by Cu-carbon nitride interaction. The flat band potentials of the samples were measured by Mott-Schottky plots at frequencies of 1.0, 1.2, and 1.5 kHz (Figure S5). Apparently, the conduction band (CB) potentials of Cu1@HCNS, Cu1/HCNS, and HCNS were determined to be -0.7, -0.65 and -0.48 V vs Ag/AgCl, respectively, where an estimated flat band potential was directly used as the CB potential for n-type semiconductor.^{53–55} The valence band (VB) edge potential of the samples was measured by VB XPS (Figure S6). The VB energy levels of Cu1@HCNS, Cu1/HCNS, and HCNS were determined to be 1.95, 2.05, and 2.30 eV, respectively. The corresponding band structure alignments of Cu1@HCNS, Cu1/HCNS, and HCNS are schematically depicted in Figure 4b. All samples satisfy the required thermodynamic condition for water reduction and oxidation, and more negative CB of Cu1@HCNS is beneficial to solar hydrogen production.

In addition to the effect of the band gap structure, the distribution location of single Cu atoms in HCNS is also expected to affect the separation of photoinduced charge carriers. Thus, the steady-state photoluminescence (PL) spectra were employed to reveal the photophysical characteristics of the electron-hole pairs (Figure 4c). Both Cu1@ HCNS and Cu1/HCNS show a much lower PL intensity than HCNS, indicating the efficiently suppressed recombination of electron-hole pairs.⁵³⁻⁵⁵ Especially, the implantation of Cu1N3 within carbon nitride nanosheets is more effective than anchoring them on the surface of nanosheets regarding the inhibition of the recombination of charge carriers. Furthermore, the shorter average PL lifetimes of Cu1@ HCNS and Cu1/HCNS than that of HCNS owing to the modulation of electronic structure coupled with the weaker PL is indicative of fast PL quenching, which might originate from the improved charge separation.⁵⁵ This highlights the role of rapid charge transfer by the promoting effect of the introduction of single Cu atoms depending on the Cu distribution location. As a consequence, photocatalytic H_2 production is promoted. $^{53-55}$

The electrochemical impedance measurements (EIS) were performed to further evaluate the charge-transfer properties (Figure 4e). Owing to modulating the electronic structure, Cu1@HCNS showed a much smaller arc radius than HCNS, suggesting its lower resistance for fast charge transfer.⁴⁰ Cu1/HCNS shows a slightly higher resistance than HCNS, which might originate from the interfacial resistance between the Cu-anchored outside surface of PCN and the electrolyte. Combining the effective improvement in light absorption, separation of charge carriers, and conductivity owing to the adjusted electronic structure by embedding Cu1N3 within carbon nitride nanosheets and promoting charge transfer at the interface of Cu and carbon nitride,44 Cu1@HCNS shows a much higher transient photocurrent response (Figure 4f). It endows Cu1@HCNS with far superior photocatalysis in H₂ production. Moreover, the results demonstrate that the promoting effect of the introduction of single-atom Cu strongly depends on the Cu location.

Imines are important building-blocks for fine chemicals, pharmaceuticals, and agrochemicals.^{56,57} Photocatalytic coupling of amines using O2 as an oxidant is considered as an efficient method for imine production, in which O₂ is indispensable because superoxide radicals are required in this process.^{54,58-60} However, the aerobic coupling process inevitably suffers from a risk of handling explosive mixtures containing flammable organic compounds and O₂, which limits its industrial applications. Photocatalytic nonoxygen coupling of amines to imines using H_2O as the oxidant is considered as a promising alternative.^{45,46} The excellent visible light photocatalysis of Cu1@HCNS was further evaluated by the nonoxygen coupling of benzylamine and derivants to their corresponding imines in the presence of water, and the reaction results are listed in Table 1. No reaction occurs in the absence of a catalyst (entry 1). Cu1@HCNS shows 2.5 times higher BOR (entry 4, 10 583 μ mol g⁻¹ h⁻¹) with 96% of imine selectivity compared to HCNS (entry 2, 4267 µmol g⁻ ¹ h⁻¹), which is much higher than that over Pt/MOF^{45} and comparable with that over Ni/CdS.⁴⁶ The use of precious metal or toxic and photocorrosive CdS can be avoided, showing great prospects for industrial applications. In addition, Cu1/HCNS (entry 3, 2807 μ mol g⁻¹ h⁻¹) shows lower BOR than HCNS (entry 2, 4267 μ mol g⁻¹ h⁻¹), although it shows higher HER (Figure 3a), and might be ascribed to its lower oxidation potential than that of HCNS (2.05 eV vs 2.30 eV). Moreover, bare HCNS without Cu introduction shows a Table 1. Visible Light-Driven Nonoxygen Coupling of Benzylamine and Its Derivants to Their Corresponding Imines a

	R	H ₂ H Visibl	e light	N N	R
entry	catalyst	R	BOR^{b} [μ mol g ⁻¹ h ⁻¹]	sel. (%)	$H_2 \text{ rate} \\ [\mu \text{mol } \text{g}^{-1} \text{ h}^{-1}]$
1 ^c		Н			
2	HCNS	Н	4267	95	0.1
3	Cu1/HCNS	Н	2807	86	0.4
4	Cu1@HCNS	Н	10 583	96	0.5
5 ^{<i>d</i>}	Cu1@HCNS	Н	7667	99	8.9
6 ^e	Cu1@HCNS	Н	812	94	
7 ^f	Cu1@HCNS	Н	905	94	
8 ^g	Cu1@HCNS	Н	2414	97	
9 ^h	Cu1@HCNS	Н	4190	86	1.5
10	Cu1@HCNS	p-F	2359	81	0.5
11	Cu1@HCNS	p-Cl	1315	95	0.6
12	Cu1@HCNS	p-Br	4217	98	0.2
13	Cu1@HCNS	o-Me	7900	93	0.1
14	Cu1@HCNS	p-Me	11 242	90	0.5
15	Cu1@HCNS	о- ОМе	1134	86	0.3
16	Cu1@HCNS	<i>р-</i> ОМе	1314	94	0.5

^{*a*}Reaction conditions: 2 mmol substrate, 10 mg of catalyst, 2.8 mL of CH₃CN, 2 mL of H₂O, 4 h, visible light (λ > 420 nm), 20 °C. ^{*b*}Defined as the oxidation rate of benzylamine and its derivants. ^{*c*}No catalyst. ^{*d*}Add Ni as cocatalyst. ^{*c*}Without light irradiation. ^{*f*}Without H₂O. ^{*g*}Ammonium oxalate as hole scavenger. ^{*h*}Isopropanol as hydroxyl radical scavenger.

higher BOR than Cu1/HCNS, implying that Cu is not the active site for the nonoxygen coupling. Moreover, the oxidative coupling process in the presence of H₂O only produces a small amount of H₂, which might be ascribed to the absence of active sites for hydrogen evolution. The HER is significantly increased from 0.5 to 8.9 μ mol g⁻¹ h⁻¹ when Ni was deposited to provide active sites for H₂ evolution (entry 5). Unfortunately, the deposited Ni leads to a decrease in BOR (2807 μ mol g⁻¹ h⁻¹) and imine selectivity (86%). The secondary amine is the main byproduct owing to the promoted hydrogenation of the as-formed imine over Ni sites. Furthermore, Cu1@HCNS shows excellent photocatalysis in the oxidative coupling of benzylamine derivants to corresponding imines (entries 10–16).

To get insights into the mechanism of the nonoxygen coupling of benzylamine and its derivants, we performed a series of controlled experiments (Table 1). The catalyst, light irradiation, and H₂O play critical roles in this reaction (entries 1, 4, 6, 7). Accordingly, ammonium oxalate and isopropanol were selected as hole and hydroxyl radical scavengers, respectively, to identify active species. The significantly decreased BOR (entries 8 and 9) indicates that holes and/or hydroxyl radicals could be the reactive species for this reaction. However, an extremely low BOR without H₂O participation (entry 7) indicates that holes are to oxidize H_2O into hydroxyl radicals rather than directly oxidize the benzylamine. Therefore, the active species in the nonoxygen coupling reaction is hydroxyl radical. On the basis of the above results, a plausible mechanism for the nonoxygen coupling of benzylamine and derivants to their corresponding imines over Cu1@HCNS

sample is proposed (Figure 5). Under light irradiation, photogenerated electrons are excited from the VB of Cu1@



Figure 5. Plausible reaction mechanism over Cu1@HCNS samples for nonoxygen coupling of amines to imines by water under visible light irradiation.

HCNS to the CB and the corresponding holes leave the VB. The electron reduces H^+ to produce H_2 and holes oxidize H_2O into hydroxyl radicals. The carbon cationic species are produced by the hydroxyl radicals and then couple with benzylamines to produce imines.

3. CONCLUSIONS

In summary, we have prepared two kinds of intercalationstructured hollow carbon nitride spheres modified with atomically dispersed Cu1N3 species at distinct distribution locations by a facile molecular assembly approach using lowcost melamine, cyanuric acid, and copper nitrate as starting materials. The results show that the implantation of single Cu atoms via Cu-N bonding within carbon nitride nanosheets is more effective than anchoring them on the surface of nanosheets regarding the adjustment of the electronic structure and the promotion of interfacial charge transfer to improve visible light photoredox catalysis. As a result, the developed Cu1/HCNS shows 1.6 and 2.7 times higher HER with 7.1% of AQY compared to Cu1/HCNS and pristine HCNS, respectively, which is 35.4 times higher than that over bulk PCN. More interestingly, Cu1@HCNS shows an unexpectedly high benzylamine oxidation rate of 10 583 μ mol g⁻¹ h⁻¹ for the nonoxygen coupling of benzylamine, which is 3.8 and 2.5 times higher than that over Cu1/HCNS and pristine HCNS, respectively. This work paves a new avenue for fabricating more efficient carbon nitride photocatalysts for solar hydrogen evolution and photosynthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c01099.

SEM and TEM images of HCNS and $Cu_{NP}@HCNS$; XRD patterns; N₂ adsorption–desorption and elemental analysis of the as-prepared samples; N 1s XPS spectra; EXAFS fitting data for Cu1@HCNS and Cu1/HCNS samples; summary on photocatalytic performance; Mott–Schottky plots; VB XPS spectra; synthetic procedure; characterization methods of samples; additional characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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