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Nickel-decorated g- C_3N_4 hollow sphere as an efficient photocatalyst for 1039/D0NJ01218A hydrogen evolution and oxidation of amines to imines

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Abstract

Photocatalysts composed of earth-abundant elements are highly desired for photocatalytic hydrogen evolution as well as oxidation of amines to imines without requirement of precious metal. Herein, non-precious metal Ni decorated g-C₃N₄ hollow spheres (Ni-CNHS) with different Ni contents were prepared by a simple calcination strategy followed with photoreduction loading of metal Ni. Under visible light illumination, Ni-CNHS exhibited efficient photocatalytic performance for oxidation of amines to imines and hydrogen production from water splitting using triethanolamine as sacrificial agent. The optimal amount of Ni was 0.41 wt% with a H₂-production rate of **596** μ mol·g⁻¹·h⁻¹ and the conversion rate of benzylamine of 61.3%. The probable photocatalytic mechanism of Ni-CNHS was investigated. This work provides the possibility to construct a great performance non-noble metal photocatalysts for hydrogen production and organic synthesis.

Keywords: g-C₃N₄; Ni; Photocatalyst; Hydrogen; Oxidation of amines

1. Introduction

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As a novel metal-free semiconductor photocatalyst, graphite carbon nitride $(g-C_3N_4)$ has regarded as a promising material for photocatalytic reaction due to the excellent optical and electronic properties and suitable bandgap [1-8]. However, the rapid recombination of photoexcited electron-hole pairs and the low specific surface area in bulk g-C₃N₄ result in a low photocatalytic performance. Numerous efforts such as element doping [9], heterojunction construction [10], cocatalyst loading [11,12], morphological tuning [13] and functional group grafting [14-15] have been developed to enhance the photocatalytic performance of g-C₃N₄.

Cocatalysts are often used to accelerate the separation efficiency of photogenerated electron-hole pairs and thus enhance the photocatalytic performance of semiconductor. Among various cocatalysts, noble metals, such as Pt, Au and Pd, frequently exhibit outstanding performance. However, high price seriously limits their large-scale industrial application. Among all noble-metal-free cocatalysts, nickel-based cocatalysts have attracted great attention due to their high activity, stability and low cost [16]. In the past years, metal Ni [17-22] and several Ni compounds have been proven to be effective cocatalysts in g-C₃N₄-based photocatalytic system [23,24], such as Ni₂P [25-27], Ni(OH)₂ [28], Ni₃N [29,30], NiB [31], NiO [32], NiS₂ [33,34], NiS [35], and Ni₃C [36]. These important studies revealed significant advantages of Ni-based materials as cocatalysts of g-C₃N₄ for efficient hydrogen production.

Morphology control has been proved to be one of effective methods to overcome the shortcomings of bulk $g-C_3N_4$ through increasing the specific surface area.

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Recently, hollow g-C₃N₄ nanospheres have attracted more attention due to its Unique structural features [37,38]. For example, hollow g-C₃N₄ nanospheres have been successfully prepared using SiO₂ particles as templates [13,39,40] or by template-free molecular cooperative assembly [41]. Compared with bulk g-C₃N₄, hollow g-C₃N₄ nanospheres exhibited enhanced photocatalytic activity for H₂ production, dye degradation, and CO₂ reduction under visible light irradiation, because the hollow spherical structure usually possessed larger interior and exterior surface area. Therefore, it is great significant to develop a convenient method to synthesize hollow g-C₃N₄ nanospheres.

Imines and their derivatives are important industrial intermediates, which are commonly used in the synthesis of fine chemicals, dyes and pharmaceuticals [42,43]. However, traditional synthesis process involves unstable carbonyl compounds and environmentally unfriendly catalysts [44]. Direct photocatalytic oxidation of amines to imines can provide an economical and green way. For example, $Fe(bpy)_3/g-C_3N_4$ showed high selectivity for photocatalytic oxidation of amines to imines under mild reaction condition [45]. Xu *et al.* found highly selective coupling of benzylamines in air in the presence of core-shell structured CdS@C₃N₄ [46]. Zhang *et al.* reported that decoration of cyano-groups in g-C₃N₄ nanosheets could accelerate the generation of charge carriers and enhance the photocatalytic performance for oxidation of amines to imines [47]. Porous layer-structured g-C₃N₄ also exhibited high activity for the oxidative coupling of amines to imines [48]. Although some examples of Ni/g-C₃N₄ nanocomposites for photocatalytic H₂ production have been reported [17-22],

however, to our knowledge, there is rare report on Ni/g- C_3N_4 composite with dual applications in both hydrogen generation and selective oxidation of amine.

In this work, metal Ni decorated $g-C_3N_4$ hollow spheres (Ni-CNHS) were synthesized via a simple calcination and subsequent photoreduction process, which exhibited superior photocatalytic performance and stability towards hydrogen generation and selective oxidation of amine under visible light illumination. The loading amount of Ni was optimized. The active species in benzylamine oxidation process and possible photocatalytic mechanism have been investigated. This work highlights the potential of non-noble metal co-photocatalyst for organic synthesis and hydrogen evolution.

2. Experimental section

2.1 Materials

All reagents, including melamine, cyanuric acid, dimethyl sulfoxide (DMSO) and nickel chloride hexahydrate (NiCl₂.6H₂O) were analytical grade and used as received without any purification.

2.2 Preparation of g- C_3N_4 hollow sphere

g-C₃N₄ hollow spheres (CNHS) were prepared according to literature [41]. Typically, 0.50 g melamine and 0.51 g cyanuric acid were separately dissolved in 10 mL DMSO. Then, they were mixed, and white precipitates were produced. The white precipitates were collected by filtration and washing with ethanol, which was dried and calcined at 550 °C for 4 h under nitrogen atmosphere. After naturally cooled down

to room temperature, yellow powder was obtained.

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2.3 Preparation of Ni-g-C₃N₄ hollow sphere

50 mg CNHS and a certain amount of NiCl₂.6H₂O were put into a Pyrex reaction cell (250 mL) containing 100 mL TEOA aqueous solution (10 vol%), which was then sealed and evacuated to remove the internal air. After irradiation for 1 h by using a 300 W PLS-XE300 Xe lamp, xNi-CNHS catalysts were obtained. The synthesis process of xNi-CNHS is shown in Fig. 1. The content of Ni was adjusted by controlling the amount of added NiCl₂.6H₂O. The actual mass ratio of Ni in xNi-CNHS samples was determined by atomic absorption spectrum (Varian, AA-110), which are 0.17, 0.30, 0.41, 0.56 and 0.68 wt%, respectively. These samples were then denoted as 0.17Ni-CNHS, 0.3Ni-CNHS, 0.41Ni-CNHS, 0.56Ni-CNHS and 0.68Ni-CNHS.



Fig.1. Schematic diagram of the synthesis of xNi-CNHS photocatalysts.

2.4 Characterization

The crystallization of samples was analyzed on an X-ray diffractometer (DX-2700X, Fangyuan, China). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained on a FE-SEM GEMINI ULTRA 55 Field emission scanning electron microscope and a JEOL

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JEM-2100 transmission electron microscope, respectively. X-ray photoelectron^{2001,101039/DONJ01218A} spectra (XPS) were collected on the AXIS Ultra from Kratos. UV-vis diffuse reflectance spectra (DRS) were measured with a SHIMADZU spectrophotometer (UV-2450). Porous parameters were obtained by nitrogen adsorption-desorption test at -196 °C on an ASAP2020 Micromeritics analyzer. Photoluminescence spectra (PL) and time-resolved decay curves were recorded on a HORIBA Fluomax-4 fluorescence spectrometer. The electrochemical tests were characterized on an electrochemical workstation (CHI660E, China).

2.5 Photocatalytic activity

The photocatalytic performance of xNi-CNHS was evaluated by hydrogen production and selective oxidation of amine under visible light irradiation provided by a 300 W Xenon lamp ($\lambda > 420$ nm).

The photocatalytic hydrogen production was tested on a Perfect Labsolar- H_2 water splitting system according to our previous work [49]. Typically, 50 mg photocatalyst was added into a Pyrex reaction cell containing 100 mL of TEOA aqueous solution (10 vol%), which was then sealed and evacuated. Afterwards, the suspension was irradiated under constant stirring. The generated H_2 was periodically measured on line using a GC9800 gas chromatography (Kechuang, China).

The photocatalytic oxidation of amines was performed at room temperature. Typically, 5 mg photocatalyst and 0.05 mmol amine were dispersed into 5 mL CH₃CN in a 10 mL quartz tube, which was then illuminated under continuous stirring for 5 h. After the reaction, the photocatalyst was removed by centrifugation, and the

 supernatant was examined by GC (Shimadzu GC-2014), NMR (Zhongke^{DQ}Niujin^{View Article Online} WNMR-I 400) and HRMS (Waters Xevo G2-S) measurements.

3. Results and discussion

3.1 Structural and morphology characterizations

The phase structure of as-prepared xNi-CNHS was firstly analyzed by XRD measurements. CNHS and xNi-CNHS samples exhibit a strong diffraction peak located at 27.5° and a small peak at 13.2° corresponding to (002) and (100) plane of $g-C_3N_4$ (Fig. 2), originating from the interlayer stacking of aromatic structure and an in-plane structural packing motifs of the continuous heptazine network, respectively [20]. However, no peaks of metal Ni were detected in all xNi-CNHS samples. This may be due to the low loading of Ni on CNHS.



Fig. 2. XRD patterns of CNHS and xNi-CNHS composites with different Ni contents.

The morphology and microstructure of CNHS and 0.41Ni-CNHS were examined by SEM and TEM observation. Fig. 3a and 3b show typical SEM images of CNHS, which reveal its uniform hollow structure with a diameter of 1-3 μ m. The 0.41Ni-CNHS possesses similar morphology and size (see the TEM image in Fig. 3c).

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From the HRTEM image shown in Fig. 3d, we observe several lattice fringes on the surface of 0.41Ni-CNHS with a lattice spacing of 0.205 nm, which is consistent with the (111) plane of metal Ni [19].



Fig. 3. (a, b) SEM images of CNHS, (c) TEM image and (d) HRTEM image of 0.41Ni-CNHS.

The composition of 0.41Ni-CNHS was further analyzed by XPS measurement. The XPS survey spectrum shows that the 0.41Ni-CNHS mainly contains C, N, O, and Ni elements (Fig. 4a). **The peak of O 1s comes from the surface-adsorbed H₂O and CO₂ on 0.41Ni-CNHS [49]**. In the C 1s spectrum (Fig. 4b), two peaks at 284.5 eV and 287.9 eV can be assigned to the sp²-bonded C=C species and the N-C=N bond in g-C₃N₄ structure, respectively [17, 18]. Fig. 4c presents the N 1s spectrum, where the peaks at 398.5, 399.7, 401.0, and 404.1 eV can be attributed to the N species in C=N-C, N-(C)₃ and C-N-H groups and positive charge localization in heptazine rings, respectively [31]. The regional spectrum of Ni 2p is plotted in Fig. 4d. **The strongest**

peak at 852.3 eV (Ni⁰ 2p_{3/2}), together with that at 870.1 eV (Ni⁰ 2p_{1/2}), correspond to the metallic Ni. In addition, the satellite signals at 858.1 eV for Ni⁰ 2p_{3/2} and 876.2 eV for Ni⁰ 2p_{1/2} are also detected [50-52].



Fig. 4. Survey XPS spectrum (a), regional spectrum of C 1s (b), N 1s (c) and Ni 2p (d) of

0.41Ni-CNHS.

The specific surface area (S_{BET}) and pore structure of CNHS and xNi-CNHS were determined by performing N₂ adsorption-desorption measurement. All samples exhibit type IV isotherm with a H3-type hysteresis loop, indicating the existence of mesopores and macropores [28]. The N₂ adsorption-desorption isotherms of CNHS and 0.41Ni-CNHS are shown in Fig. 5. They both have a wide distribution in the pore size with the range of 2 to 100 nm (Inset in Fig. 5). The corresponding S_{BET} and pore

volume of CNHS and xNi-CNHS samples are listed in Table 1. Clearly, the $B_{BET}^{View Article Online}$ value gradually decreases with the loading of Ni.



Fig. 5. The N₂ adsorption-desorption isotherm and pore size distribution (inset) of CNHS and

0.41Ni-CNHS.

Table 1. S_{BET} and pore volume of the as-prepared samples

Sample	$S_{\rm BET}({ m m}^2.{ m g}^{-1})$	Pore volume (cm ³ .g ⁻¹)
CNHS	107.0	0.694
0.17Ni-CNHS	101.8	0.654
0.3Ni-CNHS	89.6	0.593
0.41Ni-CNHS	86.8	0.592
0.56Ni-CNHS	76.1	0.576
0.68Ni-CNHS	74.4	0.553

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The UV-vis DRS of CNHS and xNi-CNHS are presented in Fig. 6a.^{10144039/DONJ01218A} absorption edge of CNHS locates at about 435 nm. After loading metal Ni, xNi-CNHSs display a greatly enhanced light-harvesting ability across the whole optical spectrum. After careful fitting the Tauc plots of 0.41Ni-CNHS and CNHS, we find they roughly have the same bandgap energy of 2.82 eV (Fig. 6b), which shows that the loading of Ni does not change the energy band structure of CNHS.



Fig. 6. (a) UV-vis DRS of CNHS and xNi-CNHSs; (b) Tauc plots of CNHS and 0.41Ni-CNHS.

3.2 Photocatalytic activity

The photocatalytic activity of xNi-CNHS samples was first evaluated by H_2 production from water splitting using TEOA as sacrificial agent. The rates of H_2 generation over different samples are presented in Fig. 7a. Pure CNHS produces trace amount of H_2 . After Ni loading, H_2 is smoothly generated. The H_2 -production rate of 0.17Ni-CNHS is **216** µmol·g⁻¹·h⁻¹. With an increasing amount of Ni loading, the H_2 -production rate markedly rises. And 0.41Ni-CNHS exhibits the highest rate of **596** µmol·g⁻¹·h⁻¹. However, it decreases when excess Ni is loaded. The effect of metal-loading amount on the H_2 -evolution rate has been investigated by several

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groups. For example, Chen et al. considered that the existence of an optimal Pt loading amount for H₂ evolution originated from the contradiction between the increased electrons trapped by Pt and the reduced active sites for methanol adsorption with increasing the Pt-loading amount [53]. Some authors thought that with successive loading, metal particles may act as recombination centers of charge carriers, and less semiconductor surface may be available for photoabsorption [54-57]. Therefore, the reaction rate is decreased. Moreover, some groups indicated that the effects of the intrinsic electronic properties, the particle size and dispersion of metal cocatalysts should be also taken into account [56-60]. In the present work, excessive loaded Ni may act as shielding for photoabsorption of semiconductor surface and recombination centers of photogenerated electrons and holes [54-57], which is supported by the transient photocurrent response and photoluminescence intensity of xNi-CNHS composites presented in section 3.3. The photocatalytic activity is thus decreased. However, no clear explanation is yet known, and further study is needed.

The H₂ production rates of 0.41Ni-CNHS and some reported Ni compounds/g-C₃N₄ photocatalysts are listed in Table S1. 0.41Ni-CNHS exhibits higher activity compared with Ni/g-C₃N₄ [20-22], Ni₂P/g-C₃N₄ [25-27], Ni(OH)₂/g-C₃N₄ [28], Ni₃N/g-C₃N₄ [29,30], NiB/g-C₃N₄ [31], NiO/g-C₃N₄ [32], NiS₂/g-C₃N₄ [33], Ni₃C/g-C₃N₄ [36] **and 0.5%Ni-1.0%NiS/g-C₃N₄ [61]**. This may be resulted from the hollow spherical structure and its large S_{BET} . However, our 0.41Ni-CNHS exhibits poorer performance than Ni-C₃N₄ composites, this may be due

to the chemically bonded nickel cocatalyst through Ni-S-C-N chemical bonds $[17]_{,}^{View Article Online}$ doping of S and Ni [18] and high nickel loading [19] in g-C₃N₄ lattice.

To evaluate the stability of 0.41Ni-CNHS, cycling photocatalytic reaction was performed under visible light irradiation for a total of 25 hours. The reaction system was evacuated after every 5 h. The results are presented in Fig. 7b. Clearly, H_2 is continuously produced without obvious decrease after five cycles, reflecting that 0.41Ni-CNHS is a promising stable photocatalyst towards water splitting.



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Fig. 7. (a) Rates of H₂-production over xNi-CNHS composites, (b) Stability of 0.41Ni-CNHS for H₂-production.

The photocatalytic performance of xNi-CNHS samples was further investigated by the selective oxidation of amines to imines using benzylamine as the model substrate. As shown in Table 2, the pure CHNS shows relatively low conversion rate of 25.1%. It is gradually enhanced with Ni loading in CNHS. The optimal loading amount of Ni (0.41Ni-CNHS) is 0.41 wt% and the corresponding optimal conversion

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rate is 61.3% with 99% selectivity, which is about 2.4 times as high as those of CNHS. However, the conversion rate shows a declining tendency with further increasing of Ni loading in xNi-CNHS composites. Such phenomenon is also found for H₂ evolution as described above. No imine was obtained without adding photocatalyst or in the dark, demonstrating that the selective oxidation of benzylamine is induced by xNi-CNHS composites under visible light.

Table 2. Photocatalytic selective oxidation of benzylamine. Reaction condition: 0.05 mmol benzylamine, 5 mg photocatalyst, 5 mL CH₃CN, irradiation for 5 h.

	NH ₂ catalyst visible light, air, 1	RT	
Entry	Catalyst	Conv. (%)	Sel. (%)
1	CNHS	25.1	>99
2	0.17Ni-CNHS	51.3	>99
3	0.3Ni-CNHS	56.1	>99
4	0.41Ni-CNHS	61.3	99
5	0.56Ni-CNHS	58.8	>99
6	0.68Ni-CNHS	56.7	99
7ª	-	0	-
8 ^b	0.41Ni-CNHS	0	-

^aWithout catalyst; ^b In the dark.

Table 3. Photocatalytic selective oxidation of various amines over 0.41Ni-CNHS. Reaction



The photocatalytic activity of 0.41Ni-CNHS was further explored for various benzylamine derivatives under the same reaction condition (Table 3). All kinds of benzylamines can be efficiently converted into their corresponding imines (selectivity \geq 98%), which were determined by NMR and HRMS measurements (**Fig. S1-S24**).

 The electronic effect of the reaction was checked. Obviously, the amines bearing electron-donating groups on the benzene ring reacted better than those with electron-withdrawing groups. Moreover, the reaction with sterically encumbered benzylamine with orth-methyl group afforded the desired product in less conversion rate [62-63].



Fig. 8. (a) Control experiments by introducing different scavengers in photocatalytic benzylamine oxidation over 0.41Ni-CNHS. (b) The amount of H₂O₂ generated by 0.41Ni-CNHS and CNHS.

In order to study the mechanism of photocatalytic benzylamine oxidation, control experiments were carried out to determine the active species in benzylamine oxidation process. Fig. 8a shows that the conversion rate of benzylamine drops quickly from 61.3% to 12.1% after adding *p*-benzoquinone (capturing $\cdot O_2^-$) into the photoreaction system, indicating that $\cdot O_2^-$ is the main active species. However, when $K_2S_2O_8$ (electron scavenger) or ammonium oxalate (hole scavenger) is added, the conversion rate exhibits moderate reduction. It can be inferred that both photogenerated holes and electrons are also involved in benzylamine oxidation. In addition, H_2O_2 was detected based on iodimetry [64]. As shown in Fig. 8b,

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0.41Ni-CNHS produces more H₂O₂ than CNHS does.

3.3 Possible mechanism for photocatalytic reaction

Based on the above characterization and photocatalytic activity, the mechanism for the photocatalytic redox reaction over Ni-CNHS composite is proposed (Fig. 9). Under visible light irradiation, CNHS generates holes in the valence band (VB) and electrons in the conduction band (CB). The excited electrons in CB will transfer to metal Ni and thereby reducing H⁺ to H₂ (Fig. 9a). And the VB holes are consumed by TEOA. While in benzylamine oxidation (Fig. 9b), the photoexcited electrons reduce O_2 to $\cdot O_2^-$. Meanwhile, the photoexcited holes oxidize benzylamine to benzylammonium cation radicals, which react with $\cdot O_2^-$ to generate Ph-CH=NH intermediate and H₂O₂. Finally, Ph-CH=NH intermediate combines with benzylamine to yield the corresponding N-benzylidenebenzylamine [65-69].



Fig. 9. Schematic illustration of photocatalytic mechanism for (a) H₂ evolution and (b) oxidation

of amine over Ni-CNHS composite under visible light irradiation.

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In order to support the mechanism of photocatalytic benzylamine oxidation^{2000000001218A} reaction, we conducted HRMS experiment to characterize intermediate produced by benzylamine after irradiation 3 h. Besides the start material (benzylamine) and product (N-benzylidenebenzylamine), Ph-CH=NH intermediate was detected (Fig. 10), indicating that Ph-CH=NH is a key intermediate during photocatalytic benzylamine oxidation.



Fig. 10. HRMS spectrum of benzylamine (a), phenylmethanimine (b) and *N*-benzylidenebenzylamine (c).

Photoluminescence (PL) spectrum is usually adopted to study the recombination of photogenerated electron-hole pairs. Therefore, CNHS and **xNi-CNHS composites** were further characterized by performing PL measurements under 350 nm excitation wavelength. Seen from Fig. 11a, they both possess a broad luminescence band in the region of 400-600 nm, corresponding to the recombination of electron-hole pairs. **The**

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maximum quenching is observed for 0.41Ni-CNHS, implying the maximum reduction in the recombination rate of electron-hole pairs. The PL intensity increases in the following order: 0.41Ni-CNHS < 0.56Ni-CNHS < 0.3Ni-CNHS < 0.68Ni-CNHS < 0.17Ni-CNHS < CNHS, which is in good agreement with the photocatalytic activities of these samples. We speculate the intimate contact between Ni and CNHS is favorable for the rapid transfer of charges, thereby promoting the separation of photoexcited electrons and holes [23].



Fig. 11. (a) Steady state PL spectra of CNHS and xNi-CNHS photocatalysts and (b) time-resolved

transient PL decay of CNHS and 0.41Ni-CNHS.

Time-resolved transient fluorescence lifetimes of CNHS and 0.41Ni-CNHS were measured to further reveal the transfer efficiency of photoexcited electrons and holes. As shown in Fig. 11b, the average lifetime τ_{av} is obtained according to reference [36]: $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, where τ_1 and τ_2 are the emission lifetimes, and A_1 and A_2 are the corresponding amplitudes, respectively. The average PL lifetime of CNHS and 0.41Ni-CNHS is 4.56 and 3.38 ns, respectively. The fast component (τ_1) can be attributed to the radiative recombination process of CB

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electrons and VB holes. The slow component (τ_2) is believed to be the radiative recombination of long-lived electron-hole pairs in CNHS [70]. The shorter PL lifetime reveals the faster electron transfer from CNHS to Ni, thus enhancing the photocatalytic performance of CNHS.

To gain deeper insight into the charge transfer between CNHS and Ni, the transient photocurrent responses of CNHS and xNi-CNHS composites were measured. The *I*-t curves with four cycles of on/off irradiation ($\lambda > 420$ nm) are shown in Fig. 12a. The photocurrent density of 0.41Ni-CNHS is 1.2 µA·cm⁻², significantly higher than that of CNHS (0.2 μ A·cm⁻²) and other xNi-CNHS. The enhanced transient photocurrent density could be attributed to the fact that the loaded Ni could effectively accelerate charge transfer through Ni-CNHS interface [19]. In addition, the electrochemical impedance spectroscopy (EIS) of Nyquist diagram (Fig. 12b) clearly shows that the arc radii of 0.41Ni-CNHS is smaller than that of CNHS, which means higher efficiency in photogenerated charge separation and electron transfer in 0.41Ni-CNHS [49]. These results are consistent with the above PL measurement.



 Fig. 12. (a) Transient photocurrent response and (b) EIS profile of CNHS and 0.41Ni-CNHS.

Fig. S25 presents the plots of the normalized photocatalytic activity, S_{BET} , optical absorption, photocurrent density, and PL intensity of xNi-CNHS/CNHS versus Ni amount. With an increasing amount of Ni loading, the H₂-production rate and conversion rate of benzylamine both first rise and then decline, and 0.41Ni-CNHS exhibits the best activity. They are in good agreement with the variation of photocurrent density, optical absorption in visible light region and quenched PL intensity. However, a continuous decrease in the S_{BET} value with increasing Ni amount is observed. Therefore, it is reasonable to conclude that the visible light absorption and the separation of photogenerated electrons and holes play key roles in the photocatalytic performance of the xNi-CNHS composites.

4. Conclusions

In this paper, xNi-CNHS photocatalysts were prepared by calcination of melamine-cyanuric acid supramolecular aggregates followed by loading Ni using photodeposition method. The diameter of CNHS was 1-3 μ m observed from SEM and TEM images. The loading of metal Ni on CNHS was confirmed by HRTEM and XPS measurements, and the loaded amount of Ni was determined by AAS. The optimal 0.41Ni-CNHS composite exhibited the best and stable photocatalytic performance with the H₂-evolution rate of 596 μ mol·g⁻¹·h⁻¹. The conversion rate of benzylamine over 0.41Ni-CNHS was 61.3%, which was about 2.4 times as high as those of CNHS.

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Based on experiments for active species capture in benzylamine oxidation, and PL, transient photocurrent and EIS measurements, we proposed the photocatalytic mechanism of benzylamine oxidation and H₂ generation in the presence of Ni-CNHS. This work provides a novel insight for designing non-noble-metal photocatalyst for H₂-evolution and organic synthesis.

Conflicts of interest

There are no conflicts to declare.

References

- W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong and S. P. Chai, Chem. Rev., 2016, [1] 116, 7159-7329.
- [2] X. B. Chen, S. H. Shen, L. J. Guo and S. S. Mao, Chem. Rev., 2010, 110, 6503-6570.
- [3] J. W. Fu, J. G. Yu, C. J. Jiang and B. Cheng, Adv. Energy Mater., 2018, 3, 1701503.
- J. J. Zhu, P. Xiao, H. L. Li and S.A.C. Carabineiro, ACS Appl. Mater. [4] Interfaces, 2014, 6, 16449-16465.
- [5] D. Masih, Y. Y. Ma and S. Rohani, Appl. Catal. B, 2017, 206, 556-588.
- [6] G. Mamba and A. K. Mishra, Appl. Catal. B, 2016, 198, 347-377.
- J. Q. Wen, J. Xie, X. B. Chen and X. Li, Appl. Surf. Sci., 2017, 391, 72-123. [7]
- [8] S. Kumar, S. Karthikeyan and F. A. Lee, Catalysts, 2018, 8, 74.

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- [9] L. B. Jiang, X. Z. Yuan, Y. Pan, J. Liang, G. M. Zeng, Z. B. Wu and H, Wang, *Appl. Catal. B*, 2017, 217, 388-406.
- [10] A. L. Yuan, H. Lei, F. N. Xi, J. Y. Liu, L. S. Qin, Z. Chen and X. P. Dong, J. Colloid Interface Sci., 2019, 548, 56-65.
- [11] K. X. Li, Z. X. Zeng, L. S. Yan, S. L. Luo, X. B. Luo, M. X. Huo and Y. H. Guo, *Appl. Catal. B*, 2015, 165, 428-437.
- [12] X. Li, J. G. Yu, M. Jaroniec and X. B. Chen, Chem. Rev., 2019, 119, 3962-4179.
- [13] J. H. Sun, J. S. Zhang, M. W. Zhang, M. Antonietti, X. Z. Fu and X. C. Wang, *Nat. Commun.*, 2012, 3, 1139.
- [14] C. K. Yao, A. L. Yuan, Z. S. Wang, H. Lei, L. Zhang, L. M. Guo and X. P. Dong, J. Mater. Chem. A, 2019, 7, 13071-13079.
- [15] C. K. Yao, R. Wang, Z. S. Wang, H. Lei, L. X. P. Dong and C. Z. He, J. Mater. Chem. A, 2019, 7, 27547-27559.
- [16] J. R. Ran, J. Zhang, J. G. Yu, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2014, 43, 7787-7812.
- [17] M. H. Vu, M. Sakar, C. C. Nguyen and T. O. Do, ACS Sustain. Chem. Eng., 2018, 6, 4194-4203.
- [18] C. Z. Sun, H. Zhang, H. Liu, X. X. Zheng, W. X. Zou, L. Dong and L. Qi, Appl. Catal. B, 2018, 235, 66-74.
- [19] L. G. Kong, Y. M. Dong, P. P. Jiang, G. L. Wang, H. Z. Zhang and N. Zhao, J. Mater. Chem. A, 2016, 4, 9998-10007.

 /iew Article Online

- [20] L. L. Bi, D. D. Meng, Q. J. Bu, Y. H. Lin, D. J. Wang and T. F. Xie, Phys. Chem. Chem. Phys., 2016, 18, 31534-31541.
- [21] L. L. Bi, D. D. Xu, L. J. Zhang, Y. H. Lin, D. J. Wang and T. F. Xie, *Phys. Chem. Chem. Phys.*, 2015, 17, 29899-29905.
- [22] A. Indra, P. W. Menezes, K. Kailasam, D. Hollmann, M. Schröder, A. Thomas,A. Brückner and M. Driess, *Chem. Commun.*, 2015, 52, 104-107.
- [23] R. C. Shen, J. Xie, Q. J. Xiang, X. B. Chen, J. Z. Jiang and X. Li, *Chinese J. Catal.*, 2019, 40, 240-288.
- [24] L. Yang, H. H. Li, Y. Yu and H. W. Yu, Catal. Commun., 2018, 110, 51-54.
- [25] P. Ye, X. L. Liu, J. Iocozzia, Y. P. Yuan, L. Gu, G. S. Xu and Z. Q. Lin, J. Mater. Chem. A, 2017, 5, 8493-8498.
- [26] A. Indra, A. Acharjya, P. W. Menezes, C. Merschjann, D. Hollmann, M. Schwarze, M. Aktas, A. Friedrich, S. Lochbrunner, A. Thomas and M. Driess, *Angew. Chemie Int. Ed.*, 2017, 56, 1653-1657.
- [27] W. J. Wang, T. C. An, G. Y. Li, D. H. Xia, H. J. Zhao, J. C. Yu and P. K. Wong, *Appl. Catal. B*, 2017, 217, 570-580.
- [28] J. G. Yu, S. H. Wang, B. Cheng, Z. Lin and F. Huang, Catal. Sci. Technol., 2013, 3, 1782-1789.
- [29] J. H. Ge, Y. J. Liu, D. C. Jiang, L. Zhang and P. W. Du, *Chinese J. Catal.*, 2019, 40, 160-167.
- [30] L. Chen, H. J. Huang, Y. H. Zheng, W. H. Sun, Y. Zhao, P. S. Francis and X. X.Wang, *Dalt. Trans.*, 2018, 47, 12188-12196.

- Pathlighed on 260 May 2020 Downloaded by Uppradia Unikeraty 0 6 8 2 9 5 4 8 2 1 0 6 8 2 9 5 4
- [31] Q. H. Zhu, B. C. Qiu, M. M. Du, M. Y. Xing and J. L. Zhang, *Ind. Eng.* Chem. *Res.*, 2018, 57, 8125-8130.
- [32] J. N. Liu, Q. H. Jia, J. L. Long, X. X. Wang, Z. W. Gao and Q. Gu, *Appl. Catal. B*, 2018, 222, 35-43.
- [33] L. S. Yin, Y. P. Yuan, S. W. Cao, Z. Y. Zhang and C. Xue, *RSC Adv.*, 2014, 4, 6127-6132.
- [34] H. T. Li, M. Wang, Y. P. Wei and F. Long, J. Colloid Interface Sci., 2019, 534, 343-349.
- [35] J. D. Hong, Y. S. Wang, Y. B. Wang, W. Zhang and R. Xu, ChemSusChem, 2013, 6, 2263-2268.
- [36] K. L. He, J. Xie, Z. Q. Liu, N. Li, X. B. Chen, J. Hu and X. Li, J. Mater. Chem. A, 2018, 6, 13110-13122.

New Journal of Chemistry Accepted Manuscript

- [37] X. W. Lou, L. A. Archer and Z. C. Yang, Adv. Mater., 2010, 20, 3987-4019.
- [38] X. J. Wang, J. Feng, Y. C. Bai, Q. Zhang and Y. D. Yin, *Chem. Rev.*, 2016, 116, 10983–11060.
- [39] D. D. Zheng, C. Y. Pang, Y. X. Liu and X. C. Wang, *Chem. Commun.*, 2015, 51, 9706-9709.
- [40] D. D. Zheng, C. J. Huang and X. C. Wang, *Nanoscale*, 2015, 7, 465-470.
- [41] Y. S. Jun, E. Z. Lee, X. C. Wang, W. H. Hong, G. D. Stucky and A. Thomas, *Adv. Funct. Mater.*, 2013, 23, 3661-3667.
- [42] S. I. Murahashi, Angew. Chemie Int. Ed., 1995, 34, 2443-2465.
- [43] M. Largeron and M. B. Fleury, *Science*, 2013, 43, 339.

View Article Online

- [44] J. Matsuo, A. Kawana, Y. Fukuda and T. Mukaiyama, *Chem. Lett.*, 2001, 30, 712-713.
- [45] A. Kumar, P. Kumar, C. Joshi, S. Ponnada, A. K. Pathak, A. Ali, B. Sreedhar and S. L. Jain, *Green Chem.*, 2016, 18, 2514-2521.
- [46] Y. Xu, Y. Chen and W. F. Fu, *Appl. Catal. B*, 2018, 236, 176-183.

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- [47] D. Zhang, X. H. Han, T. Dong, X. W. Guo, C. S. Song and Z. K. Zhao, J. Catal., 2018, 366, 237-244.
- [48] Y. Xiao, G. Tian, W. Li, Y. Xie, B. Jiang, C. Tian, D. Zhao and H. Fu, J. Am. Chem. Soc., 2019, 141, 2508-2515.
- [49] W. Peng, S. S. Zhang, Y. B. Shao and J. H. Huang, *Int. J. Hydrogen Energy*, 2018, 43, 22215-22225.
- [50] L. L. Bi, X. P. Gao, Z. C. Ma, L. J. Zhang, D. J. Wang and T. F. Xie, *ChemCatChem*, 2017, 9, 3779-3785.
- [51] K. L. Chen, S. S. Zhang, P. Wen, X. B. Qian and J. H. Huang, J. Phys. Chem. Solids, 2019, 133, 100-107.
- [52] A. N. Mansour, Surf. Sci. Spectra, 1994, 3, 221-230.
- [53] T. Chen, Z. C. Feng, G. P. Wu, J. Y. Shi, G. J. Ma, P. L. Ying and C. Li, J. Phys. Chem. C, 2007, 111, 8005-8014.
- [54] G. R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, J. Photochem. Photobiol. A: Chem., 1995, 89, 177-189.
- [55] K. L. Wang, Z. S. Wei, B. S. Ohtani and E. Kowalska, *Catal. Today*, 2018, 303, 327-333.

View Article Online I. Majeed, M. A. Nadeem, E. Hussain, G. I. N. Waterhouse, A. Badshah, A. [56] Iqbal, M. A. Nadeem and H. Idriss, ChemCatChem, 2016, 8, 3146-3155. Z. H. N. Al-Azri, M. AlOufi, A. Chan, G. I. N. Waterhouse and H. Idriss, [57] ACS Catal., 2019, 9, 3946-3958. M. J. Berr, F. F. Schweinberger, M. DOblinger, K. E. Sanwald, C. Wolff, J. [58] Breimeier, A. S. Crampton, C. J. Ridge, M. Tschurl, U. Heiz, F. Jackel and J. Feldmann, Nano Lett., 2012, 12, 5903-5906. W. T. Chen, A. Chan, D. X. S. Watehouse, J. Llorca, H. Idriss and G. I. N. [59] Waterhouse, J. Catal., 2018, 367, 27-42. K. Katsiev, G. Harrison, Y. Al-Salik, G. Thornton and H. Idriss, ACS [60] Catal., 2019, 9, 8294-8305. [61] J. Q. Wen, J. Xie, H. D. Zhang, A. P. Zhang, Y. J. Liu, X. B. Chen and X. Lin, ACS Appl. Mater. Interfaces, 2017, 9, 14031–14042. L. Ye and Z. Li, ChemCatChem, 2014, 6, 2540-2543. [62] [63] F. Raza, J. H. Park, H. R. Lee, H. I. Kim, S. J. Jeon, J. H. Kim, ACS Catal., 2016, 6, 2754-2759. R. S. Wang, G. H. Qiu, Y. Xiao, X. Q. Tao, W. Peng and B. X. Li, J. Catal., [64]

New Journal of Chemistry Accepted Manuscript

[65] C. Y. Xu, H. Liu, D. D. Li, J. H. Su and H. L. Jiang, Chem. Sci., 2018, 9, 3152-3158.

2019, 374, 378-390.

[66] H. Liu, C. Y. Xu, D. D. Li and H. L. Jiang, *Angew. Chemie Int. Ed.*, 2018, 57, 5379-5383.

View Article Online

- [67] A. L. Yuan, H. Lei, Z. S. Wang and X. P. Dong, J. Colloid Interface Sci., 2020, 560, 40-49
- [68] T. Wang, X. Q. Tao, Y. Xiao, G. H. Qiu, Y. Yang and B. X. Li, Catal. Sci. Technol., 2020, 10, 138-146.
- [69] G. H. Qiu, R. S. Wang, F. Han, X. Q. Tao, Y. Xiao and B. X. Li, *Ind. Eng. Chem. Res.*, 2019, 58, 17389-17398.
- [70] Y. C. Pu, H. C. Fan, T. W. Liu and J. W. Chen, J. Mater. Chem. A, 2017, 5, 25438-25449.



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