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Building Oxime-Ni²⁺ Complex on Polymeric Carbon Nitride: Molecular-Level Design of Highly Efficient Hydrogen Generation Photocatalysts

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ABSTRACT:

We report an effective strategy to in-situ construct oxime-Ni²⁺ complex unit on polymeric carbon nitride (PCN) as molecular catalyst for highly efficient hydrogen evolution reaction (HER). The PCN was functionalized with oxime groups that allowed for immobilizing Ni²⁺ to form oxime-Ni²⁺ complex units on the PCN surface with uniform distribution. The electrochemical characterizations reveal that these oxime-Ni²⁺ units can effectively capture photogenerated electrons from PCN, and serve as active catalytic sites for proton reduction. Notably, the oxime-Ni²⁺ enriched PCN showed even higher activities for photocatalytic hydrogen evolution than the Pt-loaded PCN. This work provides a new way to synthesize low-cost photocatalysts with surface grafting of noble-metal-free molecular HER catalysts for efficient light-driven hydrogen generation.

KEYWORDS: photocatalytic hydrogen production, polymeric carbon nitride, oxime-Ni²⁺ moieties, solar fuels production, artificial photosynthesis

1. INTRODUCTION

Sunlight-driven H_2 generation from water has attracted great attention due to its potential as one of the most promising strategies to solve the global energy and environmental problems.¹⁻³ In particular, photocatalytic hydrogen evolution reaction (HER) using semiconductor photocatalysts is an ideal approach to harvest, convert, and store solar energy in a form of clean fuel as H_2 .^{4, 5} In the past decade, the polymeric carbon nitride (PCN) has been extensively explored as a visible-light-responsive photocatalyst for water splitting due to high stability, sustainability, easy functionality, and suitable band energy levels.⁶⁻¹² However, pristine PCN alone shows very low efficiency for photocatalytic HER because it is lack of surface active sites for effective HER.⁸

To solve this issue, noble metal catalysts (e.g. Pt, Au, Pd et al.) are commonly deposited onto PCN surface to boost HER activity.¹³⁻¹⁵ But the high cost of these noble metals restricted future applications. Alternatively, researchers have attempted combination of PCN with some low-cost transitional metal (e.g. Ni, Co) based complexes or compounds, including NiS_x ,¹⁶ CoS_x ,¹⁷ $Ni(dmgh)_2$,¹⁸ cobaloxime,¹⁹ and nickel(II) bis(diphosphine) complexes.²⁰ Nevertheless, these catalysts were commonly attaching on PCN surfaces in a format of particulates with the creation of heterojunctions. By this way, the HER efficiency is restricted by the interfacial area and the capability of extracting photoelectrons from PCN. In addition, the actual utilization rate of transition metal in the particulate format is relatively low because only a small portion of surface metal ions could be active and involved for HER. Therefore, to maximize HER efficiency, it is critical to have abundant metal ions directly couple with the PCN surface.

Previous literatures have shown that some metal ions can be inserted into suitable cavity sites of PCN surface through coordination interactions with nearby N and C atoms.²¹⁻²³ However, the coordination effect, in particular for Ni and Co, is relatively weak with the PCN

structure, thus it is hardly enriching and stabilizing these metals on PCN surfaces. Herein, in this work, we modified the PCN surface with oxime functional groups (**Scheme 1**) that can effectively capture Ni^{2+} through strong coordination interactions.²⁴⁻²⁶ As a result, the covalently grafted oxime- Ni^{2+} complex structures are enriched and uniformly distributed on PCN surfaces, and serve as active catalytic sites for HER by using photoelectrons from excited PCN. Significantly, the resulted PCN-oxime- Ni^{2+} sample showed even higher photocatalytic activity for HER than Pt-loaded PCN under the same conditions. Such a rationally designed strategy for PCN functionalization to graft molecular HER catalysts on the surface would be promising in guiding future development of low-cost photocatalyst for highly efficient solar hydrogen production.

2. EXPERIMENTAL SECTION

2.1. Synthesis of PCN_0 Sample.

CN bulk powder was prepared by direct heating of urea at 550 °C for 4 h in an alumina crucible with a cover. Further heat treatment was performed at 500 °C for 4 h, and the obtained pale yellow powder was denoted as PCN_0 .

2.2. Synthesis of the $\text{PCN}_0\text{:Ni}$ sample.

Typically, 50 mg PCN_0 was dispersed in 30 mL DI water with ultrasonication for 30 min, and then 1 mL of NiCl_2 aqueous solution (0.21 mol/L) was added into the PCN_0 suspension system. The mixture was then transferred into an autoclave with Teflon liner and maintained at 120 °C for 6 h. After washing and drying, the collected sample was denoted as $\text{PCN}_0\text{:Ni}$.

2.3. Synthesis of the PCN-NOH:Ni sample.

After hydrothermal treatment of PCN₀ for 12h at 180°C, the obtained sample was denoted as PCN-O. Then the PCN-NOH sample was obtained by oxime-functionalization of PCN-O under reflux condition. The synthetic approach of PCN-NOH:Ni sample is the same with that of PCN₀:Ni by replacing PCN₀ with PCN-NOH. More experimental details, including detailed synthetic methods, characterizations, photocatalytic test of HER activity, electrochemical analyses, and theoretical calculations, are presented in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Functionalization of PCN with Oxime Groups.

The raw PCN nanosheets (denoted as PCN₀) were prepared by thermally exfoliating bulk g-C₃N₄ samples at 500 °C for 4 h. The microscopic examinations (Figure S1) prove the sheet-like morphology with a thickness of 3~4 nm. The XRD pattern of PCN₀ (Figure 1) shows two typical signature peaks of g-C₃N₄ at 27.6° and 13.0°, corresponding to interlayer stacking of aromatic segments and in-plane packing of tri-s-triazine units, respectively.

Hydrothermal treatment of PCN₀ was carried out at 180 °C for 12h with product denoted as PCN-O to introduce C=O functional group, as evidenced by the new FTIR peaks appearing at 1656 cm⁻¹ (amide, O=C-NH_x), 1720 cm⁻¹ (carbonyl, N₂C=O) and 1782 (carboxylic, -COOH) cm⁻¹ in the FT-IR spectrum (Figure 2).²⁷ These C=O groups might be generated through hydrolysis of amine groups (C-NH_x) and subsequent oxidation of C-OH in some melem units. Meanwhile, the in-plane packing peak in the XRD pattern shifts from 13.6° to 10.6°, suggesting that the unit cell length at c-axis increases from 0.675 nm to 0.83 nm after hydrothermal treatment.²⁸⁻³⁰ Upon reacting with hydroxylamine (NH₂OH), some C=O moieties are converted to oxime (=N-OH)

groups. The product, denoted as PCN-NOH, showed a new FTIR peak at 980 cm^{-1} , corresponding to the stretching mode of N-O bond.²⁹

The surface function group changes are further investigated by XPS analyses (Figure 3). For C1s, all samples show a strong peak at 288.1 eV, corresponding to the major sp^2 -hybridized carbon in N-C=N of tri-s-triazine rings.³¹⁻³³ The peak at 284.6 eV is ascribed to adventitious carbon. Comparing to PCN₀, the PCN-O shows an additional peak at 289.3 eV (Figure 3a), indicating the formation of C=O groups, which breeds another new peak at 288.7 eV for C=N-OH in PCN-NOH. The formation of oxime (=N-OH) groups can also be supported by the binding energy at 401.2 eV in the N1s XPS spectrum (Figure 3b) and the peak at 532.4 eV in the O1s spectrum (Figure 3c).^{34, 35} Besides, the solid-state ^{13}C NMR analysis was conducted (Figure S2). Both PCN₀ and PCN-NOH showed two clear peaks at 165.2 and 156.7 ppm, corresponding to the C atoms of -CN₃ and -CN₂(NH_x), respectively. Also, the signal peaks at 164.3 and 154.1 ppm can be assigned to the C atoms of C=O and C=N-OH group, respectively.³⁶⁻³⁸ In short, the PCN structure has been successfully functionalized with oxime groups according to the above characterization results.

3.2. Immobilization of Ni²⁺ by Oxime on PCN

To incorporate nickel ions onto the PCN surface, we treated the samples (PCN₀ and PCN-NOH) by NiCl₂ solution under the hydrothermal condition at 120°C. The obtained samples are denoted as PCN₀:Ni and PCN-NOH:Ni, respectively. The nickel ion attachment did not obviously alter the characteristic spectroscopic features of the samples. The existence of Ni²⁺ can be confirmed by the Ni 2p XPS spectra (Figure 3d). The PCN-NOH:Ni shows a peak at 855.6 eV, which is lower than that for PCN₀:Ni (856.0 eV), suggesting different coordination environment of Ni²⁺ between these two samples.¹⁸ For PCN-NOH:Ni, the three signature XPS-signals (C1s, N1s, and O1s)

corresponding to C=N-OH were all shifted to higher binding energy (Figure S3, Table S1), as compared with PCN-NOH, further confirming the strong interaction between Ni²⁺ and oxime.

The redox behaviors of the oxime-Ni²⁺ structure on PCN were studied by cyclic voltammetry (CV) at a scan rate of 100 mV s⁻¹ as shown in Figure S4. For PCN-NOH:Ni, the CV curve has two pairs of redox peaks. One locates at -0.195 V & -0.805 V (vs. RHE), corresponding to Ni²⁺/Ni⁺ redox process.³⁹⁻⁴² Another appears at 0.412 V & 0.200 V (vs. RHE) which can be attributed to the redox reaction of Ni²⁺/Ni³⁺.⁴³ The results show that electron transfer of Ni²⁺/Ni⁺ or Ni²⁺/Ni³⁺ in electrolysis is a quasi-reversible process too.⁴⁴ In comparison, the Ni²⁺/Ni⁺ redox peak for PCN₀:Ni was observed at -0.776V & -0.305 V (vs. RHE). The relatively more negatively potential and higher current density for PCN-NOH:Ni also suggests the strong interaction between Ni²⁺ and oxime groups on PCN surfaces.

The morphology and microstructure of the PCN₀:Ni and PCN-NOH:Ni samples were examined by SEM and TEM (Figure S5), and did not present obvious change as compared to the original PCN sample. Figure 4 shows the images of high-angle annular dark-field scanning TEM (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping, which indicate a large amount of Ni uniformly distributed on the surface of PCN-NOH:Ni. In comparison, the Ni signal density on PCN₀:Ni is much lower than that on PCN-NOH:Ni, suggesting that oxime-functionalization can greatly increase the immobilized Ni²⁺ amount on the PCN surface (Table S2). Consistently, by using ICP-OES, we have determined the actual loading amount of nickel in PCN-NOH:Ni as 2.7 wt%, which is more than 3 times higher than that in PCN₀:Ni (0.8 wt%). Also, we note that the peak at 27.6° (PCN-NOH) in the XRD pattern slightly shifts to

27.8° (PCN-NOH:Ni), suggesting that the coordination interaction between Ni²⁺ and oxime slightly reduces interlayer distance (Figure S6).

3.3. Photocatalytic HER Performance

The activities of photocatalytic HER for all samples (10 mg) were measured in the aqueous solution with triethanolamine (TEOA, 10 vol%, 10 mL), and shown in Figure 5. The as-prepared samples PCN₀ and PCN-NOH showed a very low H₂ evolution rate (14 and 38 μmol·g⁻¹·h⁻¹) due to the lack of HER active sites. Loading of Ni²⁺ on PCN₀ (PCN₀:Ni) drastically increases the H₂ evolution rate to 80 μmol·g⁻¹·h⁻¹. Notably, the higher Ni²⁺-enriched sample, PCN-NOH:Ni, presented about 4 times further enhancement of the H₂ evolution rate (320 μmol·g⁻¹·h⁻¹), which is even higher than that from the 0.5 wt% Pt loaded PCN-NOH (denoted as PCN-NOH:Pt) sample (286 μmol·g⁻¹·h⁻¹). To further investigate the influence of Ni content in PCN-NOH:Ni sample on its photocatalytic activity, we compared the photocatalytic HER rate of catalysts PCN-NOH:Ni with different Ni content. As shown in Figure S7, the HER rate increases with higher Ni content (from 0.2% to 2.7%). The BET surface area of all samples was estimated by N₂ adsorption-desorption measurements (Figure S8, Table S3). The surface area of PCN-NOH:Ni (81.7 m² g⁻¹) is considerably smaller than that of PCN₀:Ni (144.2 m² g⁻¹), suggesting that the surface area does not contribute to the enhanced HER activities by the oxime-Ni²⁺ functional structures.

These results indicate that the oxime-Ni²⁺ interactions can not only enable enrichment of Ni²⁺ on PCN surfaces, but also allow for effectively utilizing photoelectrons from excited PCN to promote the HER activity. The apparent quantum efficiency (AQE) reaches 5.11 % at a wavelength of 365 nm, and gradually decreases to 0.4% at 470 nm (Figure S9). The long-term stability of PCN-NOH:Ni was verified

by four cycling tests with well-preserved activities over 20 h (Figure S10). Additionally, to study the structure of the used sample, we have characterized the PCN-NOH:Ni sample after photocatalytic reactions by XPS and TEM (as shown in Figure S11 and S12). Compared with the fresh photocatalyst, the sample after photocatalytic HER showed no shift in the binding energy, and no clear difference on the TEM image. These results indicate that PCN-NOH:Ni catalyst is highly robust in the present photocatalytic HER system.

3.4. Electrochemical and Photoluminescence Analysis

The series of reactions for surface modification of PCN and Ni²⁺-loading should have induced considerable changes in the electronic and structural properties of PCN, which could also influence the photocatalytic HER activities besides the key role from enrichment of the oxime-Ni²⁺. Thus, it is necessary to explore the contributions from other factors, such as band energy levels and charge transfer resistance et al. Figure 6a depicts the UV-vis spectra of all the samples. The derived bandgap energy plots (Figure 6b) indicate that the oxime-functionalization of PCN via hydrothermal treatment enlarges the bandgap of PCN by comparing PCN₀ and PCN-NOH. While Ni²⁺-loading process only slightly increases the bandgap by comparing the samples before (PCN₀ and PCN-NOH) and after Ni²⁺ loading (PCN₀:Ni and PCN-NOH:Ni). The flat-band potentials were estimated by Mott-Schottky plots (Figure 6c) to calculate the band energy levels of the samples (Table S4). As illustrated in Figure 6d, the oxime-functionalized PCN shows a slightly higher conduction band (CB) level than the original PCN₀, suggesting that the proton reduction reaction is thermodynamically more favored on PCN-NOH under UV-vis irradiation. We have also carried out simulations by density functional theory (DFT) to investigate the molecular frontier orbit (FMO) and HOMO–LUMO levels, as shown in Figure S13 and Table S5. The LUMO level of oxime-Ni²⁺

(−2.98 eV) units in PCN-NOH:Ni is lower than that of the N-Ni²⁺ coordination unit in PCN₀:Ni (−2.89 eV), which suggests that the oxime-Ni²⁺ unit has better electron affinity and allows for more easily capturing electrons from the PCN.^{45, 46}

HER overpotential is another critical factor that can greatly influence the photocatalytic HER activity. Figure 7a shows the linear sweep voltammetry (LSV) curves. Obviously, the PCN-NOH:Ni sample exhibits the lowest overpotential at the same cathodic current density as compared to PCN₀:Ni and Pt-loaded PCN-NOH. The electrocatalytic kinetics for HER is examined by Tafel plots. The HER Tafel slope is an inherent property of the catalyst and is obtained from the Tafel equation:⁴⁷

$$\eta = a + b \log |j| \quad (1)$$

where η is the overpotential, b is the Tafel slope, and j is the current density.

As shown in Figure 7b, the Tafel slope values of the PCN₀, PCN₀:Ni, PCN-O, PCN-NOH:Pt and PCN-NOH:Ni are 294, 179, 223, 140 and 134 mV dec^{−1}, respectively. The lower b value of PCN-NOH:Ni further supports its superior HER performance.⁴⁸⁻⁵⁰ In short, the above results suggest that the oxime-Ni²⁺ complex can effectively take use of the photoelectrons from excited PCN to implement HER on the surface.

The charge-transfer resistance between the electrode and the electrolyte was also investigated through electrochemical impedance spectroscopy (EIS). In the measured Nyquist plots (Figure 7c), the PCN-NOH:Ni sample presents the smallest semicircle diameter, which implies the lowest resistance and supports the excellent HER performance of PCN-NOH:Ni. The comparison of transient photocurrent density for all samples (Figure 8a) follows the same trend of photocatalytic HER activities as PCN-NOH:Ni > PCN₀:Ni > PCN₀. This further suggests that the oxime-Ni²⁺ functional structure can promote photogenerated charge separation of PCN.

Figure 8b shows the photoluminescence (PL) spectra of the samples under excitation at 350 nm. A broad and strong peak centering at around 436 nm is attributed to the strong recombination of electrons at the CB and the holes at valence band (VB) in PCN excitation.¹⁴ Notably, the PCN-NOH:Ni presents much weaker PL signals than other samples, suggesting lower recombination probability of photogenerated charges. In addition, as compared with PCN₀:Ni, the emission band of PCN-NOH:Ni exhibits slight blue-shift from 436 nm to 430 nm, which might be attributed to the slightly larger bandgap of PCN-NOH:Ni.^{51, 52} In Figure 8c, the time-resolved photoluminescence (TRPL) spectrum of three samples was investigated. Obviously, the PL intensities of samples exhibit an exponential decay, and PCN-NOH:Ni displays slower decay kinetics than PCN₀:Ni and PCN₀. The PL lifetimes were obtained by fitting the TRPL curves using a two-exponential function. In Table S6, the average PL lifetimes of PCN₀, PCN₀:Ni and PCN-NOH:Ni were calculated to be 3.13, 4.45 and 5.43 ns, respectively. This result indicated that the positive role of oxime-Ni²⁺ functionalization of PCN can improve the charge separation efficiency. In brief, all of the above testing results suggest that the oxime-Ni²⁺ functionalization of PCN can reduce the charge-transfer resistance, enhance charge separation, lower HER overpotential, longer PL lifetimes, and thus promote the photocatalytic HER activity.

3.5. Proposed Photocatalytic HER Process

Based on the above analysis results, we propose a structural model of oxime-Ni²⁺ in PCN (Scheme 2a) and the charge transfer route in photocatalytic HER (Scheme 2b). Similar to the previously reported nickel-oxime complexes,^{53, 54} in PCN-NOH:Ni, the nickel ion can bridge two nearby melem rings through establishing coordination interaction with the N in the oxime group and another adjacent N in the melem ring. The hydrogen evolution processes over nickel or cobalt complexes should be similar to

literature studies.^{19, 55-59}. The photoelectrons generated from excited PCN can effectively transfer to the oxime-Ni²⁺ moieties, inducing the reduction of Ni²⁺ to Ni⁺. Then the proton binds with Ni⁺, followed by capturing another photoelectron and reacting with a second proton to form H₂. Since the charge transfer from PCN to oxime-Ni²⁺ is very efficient, we did not observe intermediate status rising from the accumulation of Ni⁺ during the photocatalytic processes. Nevertheless, unlike the traditional molecular HER catalysts which can be readily dissolved in the solution for mechanistic HER studies,^{60, 61} the PCN-oxime-Ni²⁺ system could only be investigated in the solid phase. The detailed mechanism of photocatalytic HER over PCN-NOH:Ni is pending with our further investigation by combining electrochemical and in-situ spectroscopic tools.

4. CONCLUSIONS

In summary, we have successfully functionalized PCN with oxime groups which allow for effective immobilization of Ni²⁺ (2.7 wt%) on the PCN surface with uniform distribution. The obtained PCN sample with oxime-Ni²⁺ showed even higher photocatalytic activity for hydrogen generation than Pt-loaded PCN. The electrochemical characterizations reveal that the covalently grafted oxime-Ni²⁺ units can effectively capture photogenerated electrons from PCN and serve as active catalytic sites for HER. This work with the rational design of PCN functionalization provides a new way to graft molecular HER catalysts on PCN through strong coordination interactions towards highly efficient solar hydrogen production. The strategy may also be extended to other types of molecular catalysts that can be attached on PCN surfaces for a wide range of photocatalytic applications.

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Notes

The authors declare no competing financial interest.

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Figure Captions

Figure 1. XRD patterns of PCN₀, PCN₀:Ni, PCN-NOH and PCN-NOH:Ni samples.

Figure 2. FTIR spectra of PCN₀, PCN₀:Ni, PCN-O, PCN-NOH and PCN-NOH:Ni samples.

Figure 3. a) C1s, b) N1s and c) O1s XPS spectra of PCN₀, PCN-O and PCN-NOH; d) Ni 2p XPS spectra of PCN₀:Ni and PCN-NOH:Ni samples.

Figure 4. HAADF-STEM image and the corresponding EDS element mapping images of a) PCN₀:Ni and b) PCN-NOH:Ni samples.

Figure 5. Photocatalytic hydrogen evolution amount versus irradiation time over PCN₀, PCN₀:Ni, PCN-O, PCN-NOH, PCN-NOH:Ni and PCN-NOH:Pt catalysts.

Figure 6. a) UV–visible absorption spectra converted from diffuse reflection spectra, b) band gap energies, c) Mott-Schottky plots and d) schematic energy levels of PCN₀, PCN₀:Ni, PCN-NOH and PCN-NOH:Ni samples.

Figure 7. a) Linear sweep voltammetry (LSV) curves at the scan rate of 100 mV s⁻¹, b) Tafel plots, and c) Electrochemical impedance spectroscopy (EIS) Nyquist plots of the as-prepared PCN₀, PCN-O, PCN₀:Ni, PCN-NOH:Pt and PCN-NOH:Ni thin films on FTO glass in 0.2 M Na₂SO₄ electrolyte.

Figure 8. a) Transient photocurrent responses at bias of 0 V, b) Photoluminescence, and c) Time-resolved photoluminescence spectra of PCN₀, PCN₀:Ni, and PCN-NOH:Ni samples.

Scheme 1. Schematic illustration on the synthesis of PCN-NOH:Ni catalyst.

Scheme 2. a) The proposed structure of oxime-Ni²⁺ in PCN and the redox cycle of Ni²⁺ during HER; b) schematic diagram of excitation and reactions on PCN-NOH:Ni sample under light irradiation. The photo-holes are sacrificed by TEOA to produce TEOA⁺.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table of Contents

Oxime- Ni^{2+} complex units are constructed and enriched on the polymeric carbon nitride surface and can function as highly efficient molecular catalysts for photocatalytic hydrogen evolution.