Enhanced Built-in Electric Field Promotes Photocatalytic Hydrogen Performance of Polymers Derived from the Introduction of B←N Coordination Bond

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High concentrations of active carriers on the surface of a semiconductor through energy/electron transfer are the core process in the photocatalytic hydrogen production from water. However, it remains a challenge to significantly improve photocatalytic performance by modifying simple molecular modulation. Herein, a new strategy is proposed to enhance the photocatalytic hydrogen evolution performance using boron and nitrogen elements to construct B←N coordination bonds. Experimental results show that polynaphthopyridine borane (PNBN) possessing B←N coordination bonds shows a hydrogen evolution rate of 217.4 μmol h⁻¹, which is significantly higher than that of the comparison materials 0 μmol h⁻¹ for polyphenylpyridazine (PNCC) and 0.66 μmol h⁻¹ for polypyridynaphthalene (PNNC), mainly attributed to the formation of a strong built-in electric field that promotes the separation of photo-generated electrons/holes. This work opens up new prospects for the design of highly efficient polymeric photocatalysts at the molecular level.

1. Introduction

Visible light-driven hydrogen evolution using semiconductors from water is an important synthesis technology of renewable clean energy with great potential to solve the growing energy and environmental issues worldwide. Photocatalysts are key to the ability to achieve this process. Therefore, the development of efficient photocatalysts has become one of the current research hotspots in the field of photocatalysis. The performance of photocatalysts is influenced by various factors, including light absorption ability, the separation and transport ability of photo-generated electrons/holes, and the surface catalytic ability, among which the separation and transport ability of photo-generated electrons/holes are crucial to the influence of the hydrogen evolution performance of photocatalysts. Recently, conjugated polymer photocatalysts have received much attention as a potential alternative to conventional inorganic semiconductor materials. It has been found that the introduction of heteroatoms into the conjugated backbone of polymers to tune the electronic structure of the materials can effectively improve the separation and transport properties of photo-generated electrons/holes. For example, pyridine, pyrazine, triazine, and heptazine, which contain nitrogen (N)-heterocycles with C=N double bonds, are often used as effective building blocks for photocatalysts due to their high electron affinity leading to enhanced the transport ability of photo-generated carriers. However, it remains a challenge to significantly alter the separation and transport capacity of...
photo-generated carriers by simple molecular modulation and thus achieve a breakthrough in photocatalytic performance.

A common strategy to improve photocatalytic hydrogen production performance is to use alternating electron-accepting units and electron-donating units along the backbone to construct donor–accept (D–A)-type conjugated polymer photocatalysts,[16,25,26] The electronic push–pull ability of the D–A structure to increase charge separation and transport is strongly related to the formation of strong molecular dipoles. However, obtaining polymeric photocatalysts with strong dipoles at the molecular level is still not easy. Recently, our group reported a series of novel conjugated materials with organoboron acceptors and exhibited excellent photocatalytic performance, in which the introduction of organoboron acceptors facilitated the separation and transport of photo-generated carriers.[27–29] Accordingly, polymers PNCC, PNNC, and PNBN were stable in air and exhibited off-white, light green, and orange-yellow apparent colors, respectively. The solid-state $^{13}$C cross-polarization magic angle spinning ($^{13}$C CP/MAS NMR) spectra confirm that the broad signal peaks in the range of 115–145 ppm can be attributed to the aromatic carbon signals of polymer skeleton.[37] Moreover, the chemical shifts of PNCC at 148 and 156 ppm are attributed to the signal of adjacent carbon on the N atom, which is caused by the lowering of the electron density of the adjacent carbon by the N atom. Due to the lower symmetry, PNBN shows multiple complex peaks of aromatic carbon signals in the high frequency region. Meanwhile, the signal at around 20 ppm can be referred to as the characteristic peak of methyl (Figure 2a). In addition, high-resolution N 1s X-ray photoelectron spectroscopies (XPS) showed binding energy peaks at 394.9 and 396.7 eV for polymer PNCC and PNBN, respectively, while sample PNCC showed no binding energy peak between 390 and 400 eV, suggesting the presence of pyridine nitrogen in polymers PNCC and PNBN and the existence of different structural forms (Figure 2b).[38] A clear binding energy peak at 184.9 eV was further observed for PNBN in the B 1s XPS spectrum, while PNCC and PNBN had only residual signal peaks for the terminal groups (Bpin and bromine). These results indicate the successful synthesis of N, B-doped polymer structures (Figure S2, Supporting Information). Furthermore, in the Fourier-transform infrared (FTIR) spectrum of PNBN, the characteristic-stretching vibrational peak of the C–H bond on the methyl group is located at 2900 cm$^{-1}$ as well as the bending vibrational peak at 1490 cm$^{-1}$, further indicating the formation of the polymeric N, B-doped structure (Figure S3, Supporting Information).[39,40] Powder X-ray diffraction (XRD) patterns show (Figure S4, Supporting Information) that the polymers PNCC and PNBN are amorphous.[17] Scanning electron microscopy (SEM) showed that these polymers aggregated into irregular nanoparticles (Figure S5, Supporting Information). The high-resolution TEM images of PNCC, PNNC, and PNBN were tested and showed that none of the three polymers had significant lattice stripes (Figure S6, Supporting Information). Thus PNCC, PNNC, and PNBN, like most organic polymer materials, do not have ordered crystallinity.

The normalized UV–Vis diffuse reflectance spectra of the samples PNCC, PNNC, and PNBN in the solid state were shown in Figure 2c, where all polymers exhibit intrinsic absorption originating from aromatic π→π* electron transitions with maximum.

### 2. Results and Discussion

Polymers PNCC, PNNC, and PNBN were prepared by Pd(0)-catalyzed Suzuki–Miyaura polymerization in N,N-dimethylformamide (DMF) in the presence of K$_2$CO$_3$, at 100 °C for 2 days (Synthesis details are available in the Supporting Information section). The polymers PNCC, PNNC, and PNBN were tested and showed that none of the three polymers had significant lattice stripes (Figure S5, Supporting Information). The high-resolution TEM images of PNCC, PNNC, and PNBN were tested and showed that none of the three polymers had significant lattice stripes (Figure S6, Supporting Information). Thus PNCC, PNNC, and PNBN, like most organic polymer materials, do not have ordered crystallinity.

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absorption wavelengths of 424 (PNCC), 468 (PNNC), and 547 nm (PNBN), respectively. The optical band gaps estimated using the Tauc plot equation were 3.04 eV (PNCC), 2.76 eV (PNNC), and 2.33 eV (PNBN) (Figure S8, Supporting Information), indicating that these polymers have sufficient thermodynamic driving force for the photocatalytic water-splitting reaction (theoretically 1.23 eV). With the stepwise introduction of N and B atoms, the absorption spectra of samples are significantly red-shifted and the optical band gap \( (E_{\text{g}}) \) becomes progressively narrower. This trend of evolution may arise for two reasons: first, the formation of B←N coordination bonds fixes the skeleton structure and expands the overall conjugation of the structure, second, the introduction of B←N units alters the donor–acceptor properties of the whole molecule and enhances the intramolecular and intermolecular charge transfer (CT) ability.

Density functional theory (DFT) was used to calculate the electronic structure of polymer fragments at the B3LYP/6-311G (d, p) level (Figure 2d). The highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of both MNCC1-DFT (fragment of polyphenylnaphthalene) and MNNC1-DFT (fragment of polypyridynaphthalene) are uniformly distributed in the aromatic backbone. In contrast, the HOMO and LUMO of MNBN1-DFT (fragment of polynaphthopyridine borane) are located on the naphthyl moiety and pyridyl moieties, respectively. The polarity distribution of the frontier orbitals predicts that the polymer PNBN has a distinct D–A characteristic, which facilitates the spatial separation of charges. In addition, the HOMO energy of MNBN1-DFT is reduced by 0.36 and 0.33 eV compared with the all-carbon structure MNCC1-DFT and the nitrogen-doped MNNC1-DFT, respectively, indicating that the boronized variant PNBN has a higher electron affinity. The calculated results for the longer fragment structure (MNCC2-DFT, MNNC2-DFT, and MNBN2-DFT) show a similar trend (Table S2, Supporting Information). Furthermore, molecular planarity calculations investigated their discrepancies in electron conjugation ability (Figures S10–S13, Supporting Information). The introduction of B←N coordination bond limits the rotation of naphthyl and pyridine groups, allowing polymer PNBN to exhibit the good planarity with low molecular planarity parameter (MPP = 0.065 Å) and span of deviation from plane (SDP = 0.232 Å). Thus, the intramolecular B←N coordination bond can rigidify a conjugated system consisting of multiple aromatic rings. All results show that the formation of B←N coordination bonds has the potential to promote the photocatalytic hydrogen production performance.

The molecular electrostatic potential (MESP) on the surface of molecules, van der Waals (vdW) is essential for the study and prediction of intermolecular interactions. As shown in the Figure 3a, electrostatic potential (ESP) of the three model structures differed significantly. MNCC1-DFT and MNBN1-DFT had more significant potential difference compared with the weak electrostatic interaction of MNCC1-DFT. In the ESP area distribution diagram, we find that the percentage of positive charge of MNBN1-DFT increases significantly due to the introduction of
boron, with a maximum potential difference of 55.13 eV (Figure S14, Supporting Information). The results of the MESP show that the pyridine group in the backbone of MNBN1-DFT apparently has more electron positivity than the naphthalene group, thus indicating that the B←N coordination enhances the electron-accepting nature of the pyridine ring. In addition, the molecular dipole moment of the material changes with the doping of N and B. The calculation shows that the dipole of MNBN1-DFT is 4.96 Debye, which is 4.93 and 3.06 Debye higher than the dipoles of MNCC1-DFT (0.13 Debye) and MNNC1-DFT (1.90 Debye), respectively (Figure 3a). The results of the ESP distribution and molecular dipole moment demonstrate at a theoretical level that a large built-in electric field is formed in the polymer PNBN. On the other hand, Zhang et al.\cite{48,49} found that the built-in electric field of the material is positively correlated with the zeta potential and surface potential. The surface potentials of the three materials obtained by Kelvin probe atomic force microscope (AFM) were 19.8 mV for PNCC, 31.7 mV for PNNC, and 55.7 mV for PNBN, respectively (Figure 3b). Obviously, PNBN has the largest surface potential. Subsequently, the zeta potential of polymers PNCC, PNNC, and PNBN detected with KPFM. c) Zeta potential of polymers PNCC, PNNC, and PNBN in H2O. d) Comparison of photocurrent behaviors of polymers PNCC, PNNC, and PNBN under visible light (λ > 420 nm, 100 mW cm−2).

Figure 3. a) Molecular dipole and MESP values mapped on vdW surface of MNCC1-DFT, MNNC1-DFT, and MNBN1-DFT. b) Surface potential of polymers PNCC, PNNC, and PNBN detected with KPFM. c) Zeta potential of polymers PNCC, PNNC, and PNBN in H2O. d) Comparison of photocurrent behaviors of polymers PNCC, PNNC, and PNBN under visible light (λ > 420 nm, 100 mW cm−2).
of the polymers in water was tested. As shown in Figure 3c, the zeta potential of PNBN (−32.36 mW) was 2.5 times higher than that of PNCC (−12.91 mW) and 2.4 times higher than that of PNNC (−13.29 mW). In other words, the catalyst PNBN shows the strongest built-in electric field. The enhanced built-in electric field results in a higher charge separation efficiency on the PNBN surface, much higher than that of PNNC and PNCC. This result is also demonstrated by the photocurrent intensity (Figure 3d) and electrochemical impedance spectroscopy (EIS) (Figure S16, Supporting Information), the photocurrent intensity of the PNBN is 0.25 μA cm⁻², ten times that of the PNCC and 30 times higher than that of PNNC. The diameter of semicircular Nyquist plots of the PNBN at high frequency is smaller than that of PNCC and PNNC, indicating higher charge separation efficiency and lower charge transfer resistance. These results imply that the polymer PNBN possessing B←N coordination bonds is likely to have the best photocatalytic hydrogen evolution activity.

The photocatalytic hydrogen production activity of the prepared polymers was evaluated under visible light irradiation (λ > 420 nm) in a mixture of water (H₂O), methanol (CH₃OH), and triethylamine (TEA) (Figure S25, Supporting Information). Polymer PNCC showed almost no hydrogen production under visible light irradiation. In contrast, the HER of the nitrogen-doped PNNC was slightly improved to 0.66 μmol h⁻¹, but the photocatalytic activity was still low. Excitingly, the photocatalytic hydrogen evolution activity of the polymer PNBN was as high as 217.4 μmol h⁻¹ with a turnover number (TON) of 25.74 and a solar-to-hydrogen (STH) conversion efficiency (STH) of 1.05% under the same conditions. The HER of PNBN increased by several orders of magnitude relative to PNCC and PNNC, which may be caused by the better planarity and conjugation of the BN heterocyclic structure due to the introduction of B←N coordination bonds. In addition, dynamic light scattering (DLS) experiments (Figure S25, Supporting Information) were performed in methanol. The smaller particle size of PNBN can also increase the exposure of catalytic sites on the surface. To confirm the source of H₂, mass spectrometry of D₂O was carried out. The prepared catalyst (10.0 mg) was added to 50 mL of a 1:1:1 volume mixture of D₂O, CH₃OH, and TEA solution for the photocatalytic reaction. Mass spectrometric analysis (Figure S26, Supporting Information) of the resulting gas showed a deuterium to hydrogen ratio of 0.9633 and a possible source of H as a result of proton exchange between D₂O and CH₃OH (the carrier gas in the mass spectrometry test is helium; therefore, only H₂ and D₂H can be distinguished.). In addition, the photocatalytic hydrogen evolution rate of PNBN remained significant at 142.2 μmol h⁻¹ when a mixture of 8 vol% TEA in water was used (Figure S27, Supporting Information). These results indicate that in the system of H₂O, CH₃OH, and TEA, the main source of H₂ is H₂O as well as the proton exchange of CH₃OH.

Subsequently, the dependence of the gas evolution rates on the photocatalyst mass, solution pH, and Pt cocatalyst loading was investigated. The results showed a resting point of 0.2 g L⁻¹ for PNBN (Figure S28, Supporting Information). There was no significant effect on photocatalytic hydrogen evolution in the pH range of 8.8–10 (Figure S29, Supporting Information). In contrast, the loading of the cocatalyst has a significant effect on the photocatalytic activity. The results show a tendency to saturate the performance of HER at lower Pt contents, followed by a
Figure 5. a) EPR spectra of polymers PNCC, PNNC, and PNBN for detection of •O₂⁻ radicals in a methanol dispersion. b) Fluorescence quenching spectra of polymers PNCC, PNNC, and PNBN. Insets: schematic representation of the transfer of excitation-generated holes to a sacrificial donor (TEA). Isosurfaces of the charge density difference between the: c) hole/d) electron polaron and ground state of MNBN1-DFT.

decrease at higher Pt concentrations. The optimal HER of PNBN reached 354.1 μmol h⁻¹ when 1 wt% of Pt was added (Figure 4b). PNBN exhibits highly photocatalytic hydrogen production performance compared with the recently reported linear conjugated polymers.⁵⁰⁻⁵³ In addition, the wavelength-dependent HER and apparent quantum yield (AQY) of the polymer PNBN were tested. The results show that the HER is positively correlated with the absorption spectrum (Figure 4c). And the AQYs of PNBN were 10.9, 3.0, 3.2, and 0.3% at 420, 450, 500, and 550 nm, respectively (Figure 4d). The tested AQYs are in good agreement with the absorption spectrum of PNBN, indicating that most of the photons captured by the material are involved in photoreaction. These results suggest that the introduction of N and B in the conjugated backbone may contribute to the separation and transfer of photo-generated carriers, enhancing the photocatalytic hydrogen production activity of the polymer. Meanwhile, the photostability of polymer PNBN was further verified by cycling experiments. Although the structure of the sample PNBN showed some changes after 21 h of photocatalysis, its HER was still much higher than those of PNCC and PNNC (Figure S33, Supporting Information).

To gain a better understanding of the photocatalytic process, the transient absorption spectroscopy (TAS) of the polymers were tested. Figures S38–S40 (Supporting Information) show the transient spectra of suspensions of PNCC, PNNC, and PNBN (H₂O/MeOH/TEA) from 1 ps to 5 ns after excitation at 400 nm. After excitation, the negative transient signal of the PNBN between 450 and 600 nm overlaps spectrally with the polymer photoluminescence shown in Figure 1b, and it is therefore mainly classified as stimulated emission from polymer excitons. For all three polymers, they exhibit prominent new positive absorption features around 691 nm being assigned to the active species of hydrogen evolution on the polymer.⁵¹ In addition, the results of the overall decay kinetics of the polymers at 691 nm show that the lifetime of PNBN at 691 nm is considerably longer (223.4 ps) compared with PNCC (81.7 ps) and PNNC (83.2 ps), suggesting that PNBN with B←N bonds is more conducive to photocatalysis. Electron paramagnetic resonance (EPR) experiments were carried out under light in order to further confirm the redox properties of the polymers. According to the results shown in Figure 5a, no signal of DMPO-•O₂⁻ in PNCC and PNNC is detected after light irradiation. The typical signal of •O₂⁻ was found in PNBN, indicating the photo-generated charge carriers in PNBN exhibited strong reduction ability during the photocatalytic process. Unfortunately, we did not detect signals for hydroxyl radicals in any of the three polymers (Figure S41, Supporting Information). This may be due to the difficulty of the polymers to reach the potential for the generation of H₂O/•OH (1.99 eV vs RHE) or OH⁻/•OH (2.38 eV vs RHE) radicals.⁵⁵⁻⁵⁶

In order to clearly verify the high hydrogen production activity of PNBN in the H₂O/CH₃OH/TEA system, we performed fluorescence quenching experiments in solution. As shown in Figure 5b, PNBN exhibited a strong fluorescence peak in the H₂O/CH₃OH mixture at λ = 550 nm. When TEA was added to the PNBN suspension, the fluorescence intensity of PNBN decreased dramatically. This suggests that the presence of TEA can inhibit excitons recombine via the radiative pathway. At the same concentration, PNCC and PNNC still maintain high fluorescence intensities. This is clearly not conducive to charges transfer under the photocatalytic reaction system. The fluorescence quenching results and photocatalytic experiments confirm that the presence of sacrificial agent can greatly influence the electron-hole separation/recombination pathway of PNBN.

In addition, to confirm the role of B←N bond in the photocatalytic process, we calculated the Gibbs free energy change of ...
HER on the B and N sites. As can be observed in Figure S53 (Supporting Information), there is a distinct difference in $\Delta G_{\text{reaction}}$ when the N or B sites of PNNC and PNBN are hydrogenated. The hydrogen-binding free energy at the N and B site of PNBN is 0.62 and 1.67 eV higher than that of the N site of PNNC, respectively, indicating a high overpotential of HER. These results suggest that the formation of B–N bonds in the polymer structure does not lead to stronger hydrogen adsorption like platinum. The B–N coordination bond mainly contributes to improve the planarity of the backbone and enhance the built-in electric field, thus promoting the separation and migration efficiency of the photo-generated carriers.

To investigate the potential reaction sites of PNBN, the electron density difference between the hole/electron polaron and ground state of the polymers fragment were calculated. The charge density differences of both MNCC1-DFT and MNNC1-DFT show a relatively uniform distribution (Figures S54–S55, Supporting Information). In contrast, the electron density difference between the electron/hole polaron and ground state of MNBN1-DFT is concentrated on the pyridine ring and the naphthyl group, which were obviously favorable for the redox reaction (Figures 5c,d). Furthermore, the electron distribution of the electron density difference between the first excited state and the ground state to evaluate the trend of electron leap. According to the simulation results (Figure S59, Supporting Information), electrons of the PNBN are excited mainly from the naphthalene group (yellow region) and finally leap to the pyridine ring (purple region). When these light-generated electrons and holes have a sufficiently high driving force, they undergo proton reduction or oxidation at the expense of the electron donor, respectively. In other words, the reduction reaction of water is more likely to occur on the pyridine ring of PNBN, while the oxidation reaction with the sacrificial agent is more likely to occur on the naphthyl group. These results suggest that a rapid redox reaction can be achieved on the backbone of PNBN, leading to efficient hydrogen evolution.

3. Conclusion

In summary, a D–A-type conjugated polymer photocatalyst with B–N coordination bonds was successfully synthesized. The B–N coordination bonds significantly improved the planarity and rigidity of the conjugated framework and established a strong built-in electric field through the change of electronic structure. This resulted in the polymer PNBN exhibiting excellent hydrogen evolution performance with HER of 217.4 μmol h$^{-1}$ and AQY420 = 10.9%, which is much higher than most of the reported organic conjugated polymer photocatalysts. These results imply that the construction of polar bonds provides a new approach for the design and development of photocatalysts.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

B–N coordination bond, built-in electric field, conjugated polymers, hydrogen, photocatalysts

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