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## Polymeric Donor-Acceptor Hetero-structures for Enhanced Photocatalytic H<sub>2</sub> Evolution without using Pt Cocatalysts

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**Abstract:** Polymeric carbon nitride (CN) is a promising material for photocatalytic water splitting. However, CN in its pristine form tends to show moderate activity due to fast recombination of the charge carriers. The design of efficient photocatalytic system is therefore highly desired, but it remains a great challenge in chemistry till now. Here we found that pyrene-based polymer, could serve as electron donor to accelerate the interface charge carrier transfer of CN. The construction of donor-acceptor (D-A) heterojunction is confirmed to significantly restrain the charge recombination and thus improves the proton reduction process. This study provides a promising strategy to achieve solar  $H_2$  production in an efficient and low-cost manner.

Solar hydrogen production from water has attracted worldwide research attention to meet the urgent need of carbonneutral energy.<sup>1,2</sup> The key bottleneck of this technique however relies on the development of low-cost, sustainable and stable materials, which could catalyze the water splitting reaction in an efficient and cost-effective manner.<sup>3</sup> During the past few decades, many photocatalysts (mainly metal-based materials) have been developed for photocatalytic water splitting.<sup>4-6</sup> However, till now, the activities of most materials are still in their infancy and more breakthroughs are involved to achieve high efficiency.

Polymeric carbon nitride (CN), an alternative polymeric photocatalyst, has attracted particular attentions since 2009 owing to the excellent advantages such as metal-free, low-cost, visible light active and suitable band structures for water splitting.7-10 Unfortunately, this material is only merely active in its pristine form. Besides, most of the CNs are amorphous in its structure, that means disorder in structure and abundant of surface defects, which normally lead to the rapid charge carrier recombination and insufficient performance. Till now. achievements have been obtained after rational modification of the structure and properties. For instance, the apparent quantum efficiency for H<sub>2</sub> evolution can be largely enhanced upon modification of the composition and structure by strategies like doping, copolymerization, hybridization and sensitization.11 However, most of the materials are only barely active or inactive in the absence of Pt as cocatalyst.<sup>12</sup> The development of new catalysts without the aid of Pt is therefore of great significant, but it still remains a great challenge.

Recently, some conjugated polymers beyond of CN, such as pyrene-based conjugated microporous polymers,<sup>13</sup> bipyridyl-

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based conjugated polymers,<sup>14</sup> benzothiadizole-based conjugated polymers,15 and a series of co-polymers of 1,4phenylene and 2,5- thiophene (named P1-18)<sup>16</sup> are also proved as good photocatalysts for solar water splitting. One of the advantages of the copolymers is that the structure and properties could be systemically controlled at molecular level over a continuous change of monomer's ratio.<sup>17</sup> For instance, Cooper and coauthors recently reported that the band gap of the pyrene-based polymers could be easily tuned from 1.94-2.95 eV by control the ratio of the starting monomers, which means the optical absorption tail could be extended to as long as 640 nm. Interestingly, these polymers show H<sub>2</sub> evolution activities under light irradiation in the absence of any noble metal. However, the performance was extremely restrained as a result of the fast recombination of the charge carriers. A general way to prolong the charge carrier life-time is to construct donor-acceptor (D-A) heterojunction, which allows fast electron transfer from electron donor to electron acceptor and prevent bulk charge carrier recombination.15,18,19



 $\label{eq:scheme-sche$ 

Indeed, some well-known organic semiconductors, including Poly(3-hexylthiophene),<sup>20</sup> polypyrrole,<sup>21</sup> graphitized poly(3-hexylthiophene),23 poly(3,4polyacrylonitrile,22 ethylenedioxythiophene),<sup>24</sup> and liner polyfluorene family polymers<sup>25</sup> coupled with CN to construct D-A polymeric heterojunctions were evaluated effective for photocatalytic hydrogen production owing to fast charge transfer and sufficient excited electrons arrived at interface for surface redox reactions. These D-A heterojunctions, even though show excellent performance, mainly rely on noble metal Pt as a cocatalyst to catalyze the proton reduction process. We therefore deduce that visible light H<sub>2</sub> production from water would be achieved when pyrene-based polymers are anchored with CN to facilitate the interface charge carrier transfer and promote the H<sub>2</sub> production kinetics. The molecular structure and band positions of CN and PyP<sub>x</sub> are presented in scheme 1, confirming the construction of

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type-II heterojunction and efficient charge transfer at interfaces.

In this study, we designed a series of hybrid polymers based on pyrene-based polymers (PyP<sub>x</sub>, x=1, 2, 3, 4, represents different ratio of the monomers) coupled with CN to fabricate the D-A heterojunciton (more details see experimental section). As will be discussed below,  $PyP_2/CN$  shows best activity for visible light H<sub>2</sub> evolution. Thus, we will focus on detail examination of the structure and properties of this polymer.

In the first place, the resultant PyP2/CN catalysts were subjected to several characterizations to study the texture, morphology, optical, and electronic properties. SEM and TEM were carried out to explore the morphology of the PyP2/CN hybrids. As shown in Fig. 1a, CN shows typical stacking of the wrinkled layers by van der waals's force. PyP2 itself shows much smaller particle size (40-100 nm, Fig. 1b) in comparison with CN (several hundred nanometers). It can be observed clearly that PyP2 nano-particles were successfully deposited on CN (Fig. 1c and d) via an in-situ deposition strategy. TEM images (Fig. 1e and f) further confirm the successful construction of amorphous D-A type polymeric junction between CN and PyP<sub>2</sub>. The elemental mapping analysis in the dark illustrates the homogenous dispersion of C and N elements (Fig S2). Anchoring  $PyP_2$  on the surface of CN can also increase the specific surface area (from 72  $m^2\ g^{\text{-1}}$  of CN to 120  $m^2\ g^{\text{-1}}$  of PyP<sub>2</sub>/CN) (Fig. S3). The successful creation of different PyP<sub>x</sub>/CN composites can also be proved by SEM images as shown in Fig. S4. After incorporation with PyP<sub>2</sub> (loading contents increased from 1 wt. % to 10 wt. %), the skeleton structures of CN are merely changed as certified by XRD, FT-IR and Raman spectra (Fig. S5-7), indicates the robust stability of the polymers. Typically, the locations of two typical diffraction peaks at 13.0° and 27.4° of CN remain unchanged while the peak diffraction intensity was enhanced. We attribute it to the further polymerization in hot DMF.

The chemical states of PyP<sub>2</sub> and CN were characterized by the x-ray photoelectron spectroscopy (XPS) analysis (Fig. S8). After deposited with PyP<sub>2</sub>, the C1s peaks of the PyP<sub>2</sub>/CN at binding energy of 288.5 eV corresponding to N-C=N of CN became weaker. The N 1s XPS peaks at 399.1 and 400.4 eV respectively correspond to aromatic C=N-C coordination and tertiary N-(C)<sub>3</sub> bridging. These two nitrogen species together with the sp<sup>2</sup>-C make up the heptazine heterocyclic (C<sub>6</sub>N<sub>7</sub>) units of CN.<sup>9,26</sup> Note that, comparing to pure CN, the XPS peaks location of the PyP<sub>2</sub>/CN slightly shifts to higher bonding energy positions (~0.4 eV). This shift is usually found in nanocomposite due to the interaction of two or three components. The C/N ratio of PyP<sub>2</sub>/CN is 0.93, which is 0.32 larger than that of CN because of the presence of carbon-rich material PyP<sub>2</sub>.

More structure details of CN, PyP<sub>2</sub> and the PyP<sub>2</sub>/CN were further examined by the solid-state <sup>13</sup>C CP-MAS NMR spectra. As shown in Fig. 2a, the characteristic chemical shifts centered at 164.5 and 156.6 ppm belong to C(e) and C(i) of CN can be observed.<sup>26</sup> A similar slight chemical shift was also found for the PyP<sub>2</sub>/CN hybrids because of the interaction between PyP<sub>2</sub> and CN, in good accordance with the previously discussed Raman spectrum and XPS analysis. Besides, the incorporation of  $PyP_2$  with CN can significantly enhance the visible light absorption as presented in Fig. 2d. The band gap was decreased from 2.84 eV to 2.46 eV, which means more visible photons could be captured by the polymers for subsequent surface redox reactions. Higher  $PyP_2$  contents in composites contribute to more enhanced optical absorption (Fig. S9). Similar enhancement in optical absorption was also revealed when other  $PyP_x$  polymers were deposited on CN (Fig. S10).



Figure 1. SEM images of a) pure CN, b)  $PyP_2$  and c, d) 8 wt. %  $PyP_2/CN$ ; e, f) TEM images of 8 wt. %  $PyP_2/CN$ .

The charge carrier properties of CN and PyP<sub>2</sub>/CN were then examined by room temperature photoluminescence (PL) spectra (Fig. 2c, Fig. S11). A strong PL emission peak at approximately 460 nm was observed for the pristine CN, because of the radiative recombination of photo-excited charge carriers. Interestingly, the combination of PyP<sub>2</sub> with CN could efficiently restrain the charge carrier recombination as evidenced by the dramatically decreased PL emission intensity. Under visible light irradiation, the excited electrons could fast transfer from electron donor (PyP<sub>2</sub>) to electron acceptor (CN) while holes quickly move in a different direction (Scheme S3). Which means the construction of the D-A heterojunction can significantly restrain the charge recombination and thus improves the proton

reduction process. By contrast, the emission of the PyP<sub>2</sub>/CN shows a Stokes shift from 420 nm to 514 nm, certificating that the introduction of stronger electron-rich PyP2 could greatly enhance the optical absorption. In order to elucidate the formation and migration dynamics behaviour of photoinduced charge carriers in the PyP2/CN photocatalysts, we further measured the lifetime of the charge carriers in excited PyP<sub>2</sub>/CN hybrids by means of room temperature time-resolved transient fluorescence spectroscopy as shown in Figure 2d. The average decay lifetime in excited CN and PyP2/CN sample was 2.78 and 2.60 ns, respectively. The shorter decay lifetime in the hybrid reveals the photogenerated electrons could be faster transported in the D-A heterojunction, consequently suppresses the charge recombination in CN and improves the photocatalytic H<sub>2</sub> generation.<sup>27,28</sup>



Figure 2 a) Solid-state <sup>13</sup>C CP-MAS NMR, b) UV-Vis DRS, c) Room temperature PL spectra of pure CN, PyP<sub>2</sub> and 8 wt. % PyP<sub>2</sub>/CN samples, d) time-resolved PL spectra recorded of pure CN and 8 wt. % PyP<sub>2</sub>/CN samples at 298 K

With regards to band engineering of the PyP2/CN, the presence of unpaired electrons in the hybrids was monitored by electron paramagnetic resonance (EPR) spectra (Fig. 3a). One single Lorentzian line centered at a g-factor value of 2.0035 was detected for pristine CN, 2.0032 for PyP2 and 2.0036 for PyP<sub>2</sub>/CN in the magnetic field from 3480 to 3540 G (Fig. S12). The changed g-factor of PyP2/CN because the strong interaction between PyP<sub>2</sub> and CN. This g value is solely assigned to an unpaired electron on the sp<sup>2</sup>-C atom in the typical heptazine unit of CN.8,28 Compared with pure CN, the intensity of Lorentzian line of PyP2/CN hybrids was enhanced, presumably due to the redistribution of  $\pi$ -electrons within the hybrid by band offsets. The EPR signals of both CN and PyP2/CN samples were further increased under visible light irradiation illustrating the generation of unpaired electrons on the  $\pi$ -conjugated aromatic rings and efficient photo-induced generation of charge carrier pairs.<sup>12</sup>

![](_page_3_Figure_6.jpeg)

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Figure 3 a) Room temperature EPR spectra of CN and 8 wt. % PyP2/CN samples, b) Polarization curves in the dark, c) photocurrent performance, d) Nyquist plots of electrochemical impedance spectroscopy in the dark of CN and 8 wt. % PyP2/CN electrodes vs SCE.

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To demonstrate their feasibility in technologically important applications, we investigated the electrocatalytic HER properties of PyP2/CN hybrids electrode in a typical three-electrode cell (0.2m Na<sub>2</sub>SO<sub>4</sub>), and Pt and saturated calomel electrode (SCE) serve as the counter and reference electrode, respectively. Before electrochemical reactions, the electrolyte solution was bubbled with Ar for 30 min to remove the air. The obtained polarization curves of CN, and 8 wt. % PyP2/CN were tested and showed in Figure 3b. Obviously, PyP2/CN sample shows lower overpotential during electrochemical tests thus a much higher activity in comparison with pure CN. This result indicates that efficiently PyP<sub>2</sub>/CN can electrocatalyze  $H_2$ evolution. electrochemical measurements consequently. Other and electrochemical impedance spectroscopy (EIS) were also carried out. Fig. 3c displays the photocurrent generation of both pure and PyP<sub>2</sub> optimized CN samples. As expected, a strengthened photocurrent was determined for the PyP2/CN sample, which means accelerated generation and separation of photoinduced e<sup>-</sup>-h<sup>+</sup> pairs at CN/water interfaces. In Fig. 3d, semicircular Nynguist plots showed a remarkably decreased radius when a certain amount of PyP<sub>2</sub> was decorated on CN, indicating enhanced charge transfer rate. Thus, the fast charge recombination of polymeric CN photocatalysts has been addressed by the construction of D-A heteroiunctions, and thus improves photoeletrochemical properties of PyP<sub>2</sub>/CN samples. These conclusions predict the electrochemical impedance of the semiconductor is optimized when an efficient PyP2/CN hybrid is well created.

The photocatalytic activities of the D-A polymers were evaluated in an assay of visible-light-induced H<sub>2</sub> evolution from water in the presence of the sacrificial electron donor (triethanolamine, TEOA). Note that, no cocatalyst (normally Pt) was involved in the current process of water splitting. Fig. 4a shows a typical volcano relationship between hydrogen

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evolution rate (HER) and the loading content of PyP<sub>2</sub>. Firstly, gradual increase in the HER took place when the incorporation amounts of PyP<sub>2</sub> were increased from 3 wt. % to 8 wt. %. The optimum HER (30 µmol h<sup>-1</sup>) of the hybrids was achieved when the loading amount was certified as 8 wt. %, 15-fold higher than that of CN (2 µmol h<sup>-1</sup>). It's not exceptional that further increasing the loading contents of PyP<sub>2</sub> lead to decrease in the photocatalytic activities because of the "covering effect".<sup>12</sup> The heavy coverage of the active sites on CN surface could cause the decreased H<sub>2</sub> production rate by growth of high percentage of PyP<sub>2</sub> on CN surface. The similar tendency could be tested in another PyP<sub>2</sub>/CNM hybrid (CNM is CN prepared from melamine, see more details in experimental section) (Fig. S13).

To demonstrate the stability and reusability of the samples, a typical time course for hydrogen production was conducted using PyP<sub>2</sub>/CN catalyst under visible-light irradiation ( $\lambda$ >420nm). Repeating experiments were allowed for a total of 16 hours by four consecutive operations under the same reaction conditions. As shown in Fig. 4b, a slight deactivation with time was noticed in the first three runs. When an appropriate amount of TEOA was added to the reaction solution, the activity of hydrogen evolution improved in the fourth run. Note that no obvious change in material structures was observed through XRD and FTIR examinations for the sample before and after reaction (Fig. S14). This means that the decrease in the activity after the first three runs is mainly due to the decreased concentration of sacrificial electron donor TEOA. As shown in Fig. S15, there is no evident deactivation with time was noticed in the first four runs when an appropriate amount of TEOA was added after every cycle. Therefore, the (photo)-chemical stability of the PyP<sub>2</sub>/CN hybrid as an organic photocatalyst is acceptable for light-trigged hydrogen generation.

Controlled experiments were shown in Fig. 4c. To further underline the importance of in-situ synthesis of PyP2/CN,  $\mathsf{PyP}_2\text{+}\mathsf{CN}$  (physical-mixture of  $\mathsf{PyP}_2$  and  $\mathsf{CN})$  or  $\mathsf{PyP}_2\text{-}\mathsf{CN}$ (obtained by two-step impregnation) were also examined for hydrogen evolution. From the picture we can see no significant enhancement in the activity in comparison with pure CN, indicating in-situ deposition is important to establish tight adhesion on the surface of CN, which subsequently facilitate the charge carrier transfer from bulk to interface. Besides, to exclude the effect of residual palladium (generated from Suzuki-Miyaura synthesis) in PyP2, we further examined the activity of CN in the presence of same amounts of Pd as that in the synthesis of  $PyP_2$ . Results reveal that  $Pd(PPh_3)_4+CN$ (physical-mixture of CN and Pd(PPh<sub>3</sub>)<sub>4</sub>) or Pd(PPh<sub>3</sub>)<sub>4</sub>-CN (prepared by impregnation) or Pd(PPh<sub>3</sub>)<sub>4</sub>/CN (in-situ method of CN and Pd(PPh<sub>3</sub>)<sub>4</sub>) all only merely improve photocatalytic activity, illustrating Pd only merely contribute to the present excellent performance.

In addition, we also compared the activity of  $PyP_2/CN$  with the traditional Pt/CN catalyst. Typically, Pt was deposited on CN by *in-situ* photo-deposition under visible light irradiation and the loading amounts were varied from 3 wt. % to 8 wt. % (Fig. S16). The hydrogen evolution ability of  $PyP_2/CN$  is equally as good as Pt/CN. So we can conclude that our experiment is of great importance. Therewith, we evaluated the wavelength dependence of the optimum 8 wt. %  $PyP_2/CN$  sample for hydrogen evolution under different specific wavelength illuminations (Fig. S17). And the AQY data of the sample play well with the optical absorption. This indicates that the photocatalytic hydrogen evolution reaction is indeed promoted by the photons. To examine the universality of PyP2/CN heterojnction, different CN precursors, CNM, CNT, and CND (synthesized from melamine, thiourea and dicyandiamide) were also used for fabrication of polymeric junctions under identical synthetic conditions (Fig. S18). Results reveal that all the asprepared composites show good photocatalytic H<sub>2</sub> production activities, while the optimum activity was achieved when ureabased CN was used to construct the heterojunction. This is mainly ascribed to the thin nanosheet structure of urea-based CN. Thus, we can conclude the organic heterojunctions are reliable to accelerate charge transfer and provide more active sites, leading to an efficiently facilitation of H<sub>2</sub> production process.

![](_page_4_Figure_9.jpeg)

Figure 4 a) Hydrogen evolution rates using x wt. % PyP<sub>2</sub>/CN samples. b) Stability test of H<sub>2</sub> evolution (evacuation every 4 h) for 8 wt. % PyP<sub>2</sub>/CN photocatalyst under visible-light irradiation ( $\lambda$ ≥420 nm). c) Hydrogen evolution rates using different samples, d) Hydrogen evolution rates of different 8 wt. % PyP<sub>2</sub>/CN.

Furthermore, PyP<sub>x</sub> with different band gaps and morphologies (see more details in experimental section and SEM images in Fig. S2) were also selected to combine with CN. As shown in Fig. 4d, both PyP<sub>1</sub> and PyP<sub>2</sub> are able to promote the H<sub>2</sub> evolution performance of CN, while PyP<sub>3</sub> and PyP<sub>4</sub> can only merely contribute to the activity. It can be observed that the pyrene-pyrene link in PyP<sub>3</sub> and PyP<sub>4</sub> has larger steric hindrance than pyrene-benzene link in PyP1 and PyP2 which causes a great distortion of their structures, and finally leading to weak adhesion on CN (Scheme S2). This means the photo-excited electrons and holes generated in catalysts cannot be separated and transferred at the interface. Therefore, PyP<sub>3</sub>/CN and PyP<sub>4</sub>/CN are mediocre performers in the visible-light-induced H<sub>2</sub> evolution from water.

In summary, an excellent D-A polymeric photocatalyt based on PyP<sub>2</sub>/CN was fabricated via a facile one step in-situ

deposition. Results reveal that the heterojunciton is effective to accelerate the interface charge carrier and thus promote the subsequent redox reactions. Favorable band gap obtained by adjusting the content of PyP<sub>2</sub> lead to good photocatalytic activity for hydrogen evolution under visible light without extra cocatalyst. The  $\pi$ - $\pi$  stacking of PyP<sub>2</sub>/CN hybrids were observed to broaden light absorption, improve the charge carrier transfer and provide more surface active sites thereby resulting in an enhanced activity compared to that of parental CN and PyP<sub>2</sub>. The universality of the polymeric junctions was also examined good when changing different CN substrate and diverse PyP<sub>x</sub> electron donors. Thus, we believe that more conjugated polymers can be used as stable metal-free semiconductors for the fabrication of efficient D-A juncitons with nice photocatalytic performance.

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## COMMUNICATION

А series of D-A polymeric photocatalyts  $(PyP_x/CN)$ were fabricated via a facile one step insitu deposition. Favorable band gap obtained by adjusting the content of PyP2 lead to good photocatalytic activity for hydrogen evolution under visible light without extra cocatalyst. The D-A heterojunciton is effective to accelerate the interface charge carrier and thus promote the subsequent redox reactions.

![](_page_7_Figure_4.jpeg)

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Polymeric Donor-Acceptor Heterostructures for Enhanced Photocatalytic H<sub>2</sub> Evolution without using Pt Cocatalysts

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