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Water-Dispersed Conjugated Polyelectrolyte for Visible-Light Hydrogen Production

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Conjugated polymer-based photocatalysts have shown great potential in H₂ production via water splitting, but an intrinsic drawback of conventional hydrophobic polymer photocatalysts is their poor wettability and relatively large particle size in aqueous media, which is favorable for charge recombination with limited interfacial reaction efficiency. Herein, a well-dispersed organic water reduction system using cationic conjugated polyelectrolyte as the photocatalyst has been reported for the first time. In comparison to a model polymer (PFBT) bearing the same conjugated backbone, the polyelectrolyte exhibits significantly enhanced photocatalytic efficiency due to the extended light absorption and improved charge separation of the polymer aggregates.

Photolysis of water for the generation of clean H₂ holds great promise for solving worldwide energy crisis and environmental concerns.[1–6] Over the past decades, enormous semiconducting materials have been investigated in this field. Among them, eco- friendly organic conjugated polymers (CPs) are of particular interest owing to their unique advantages of light weight, easy fabrication, low cost, and tunable optoelectronic properties.[7–12] Since g-C₃N₄ was first reported for H₂ production,[13] significant progress has been made due to the remarkable development of novel CPs, including covalent organic frameworks (COFs),[14–19] conjugated porous polymers (CPPs),[20–27] linear CPs,[28–30] etc. Nevertheless, these highly crosslinking polymer photocatalysts unexceptionally exist in the form of large particles and show uneven dispersion in aqueous solution. It is widely accepted that electron–hole pair dissociation in the semiconductor to generate free charges is crucial for photocatalytic processes. The charge separation efficiencies of bulk polymer particles always suffer from undesirable recombination due to their large sizes.[31] To overcome these problems, the investigation of water-dis- persible nanoscale polymer particles for water splitting reaction is very essential.

Conjugated polyelectrolytes (CPEs) are charged CPs consisting of delocalized electron backbone with pendant ionic groups, which have attracted considerable attention for various applications in biolog- ical imaging, sensing and therapy, as well as optoelectronic devices.[32–37] The π -conjugated backbone offers CPEs with light-harvesting and charge transport capabilities of CPs, while the pendant-charged side chains ensure their unique dispersi- bility in highly polar media. The structural features of CPEs allow facile creation of homogeneous multiphase photocatalytic systems for water splitting. Further- more, the photophysical properties of CPEs, including energy levels, light absorption, and charge carriers transport character- istics, can be readily fine tuned by the modification of

π -conjugated structures. In addition, the CPEs possess excellent photostability, which provides another requisite for photocatalysis

Enlightened by these advantages of CPEs, in this contribution, we present a simple but effective strategy for the conversion of conventional CP into hydrophilic CPE, which shows highly dispersibility in aqueous solution and significantly improved photocatalytic hydrogen generation efficiency in comparison with polymer bearing the same backbone. The model polymer PFBT, precursor polymer PFBT-C6, and target polymer PFBT-CPE are shown in Scheme 1. Detailed synthesis of the three polymers can be found in the Supporting Information. Suzuki–Miyaura coupling between 2,7-dibromofluorene and bis-(pinacolato)diboron yielded 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihydrofluorene, which was further copolymerized with 4,7-dibromo-2,1,3-benzothiadiazole catalyzed by Pd(PPh₃)₄ in DMF afforded poly(9,9-dihydrofluorene-alt-benzothiadiazole) (PFBT) in 90% yield. Like most of the reported CP photocatalysts, PFBT was poorly dispersed in water and possessed limited conjugated units due to poor solubility in reaction media. To extend the conjugation length, we introduced flexible side chains to the fluorene unit to prepare PFBT-C6, which greatly improved the polymer solubility in toluene and ensured the further growth of polymer chains in reaction. Gel permeation chromatography analysis of PFBT-C6 revealed its number-average molecular weight (M_n) of 23 700 and a polydispersity index (PDI) of 1.40. PFBT-C6 is very soluble in THF, CH₂Cl₂, and toluene. Cationic poly[9,9-bis(6'-N,N,N-trimethylammonium)hexyl)fluorene-alt-4,7-(2,1,3-benzothiadiazole)dibromide] (PFBT-CPE) was synthesized by quaternization of neutral PFBT-C6 with trimethylamine at room temperature for 48 h.[38,39] As reported, the as-prepared PFBT-CPE exhibits good

dispersion in water. Fourier transform infrared (FTIR) spectroscopy (Figure S3, Supporting Information) shows two characteristic vibration peaks for methylene group at about 2924 and 2850 cm^{-1} for PFBT-C6 and PFBT-CPE. In addition, PFBT-CPE exhibits a broad absorption at about 3418 cm^{-1} , which can be ascribed to the stretching band of the addition of terminal CH_3 .^[37a,b] Thermal gravimetric analysis (Figure S4, Supporting Information) reveals good thermal stabilities for the three polymers, with decomposition temperatures for 5% weight loss all above 200 $^{\circ}\text{C}$. Notably, unlike PFBT and PFBT-C6, PFBT-CPE shows two main decomposition processes during continuous heating, which could attribute to the loss of methyl bromide and the cleavage of side chains, respectively.^[40,41]

The photophysical properties of the three polymers were studied by UV-vis absorption and photoluminescence (PL) spectroscopy, and the relevant results are summarized in Table 1. The absorption peaks of PFBT in $\text{Et}_3\text{N}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixture are located at 309 and 420 nm, ascribing to the fluorene and benzothiadiazole (BT) units in the conjugated backbone, respectively (Figure S6a, Supporting Information). When attaching flexible side chains to the fluorene unit, the maximum absorption band of PFBT-C6 in CH_2Cl_2 is significantly red-shifted to 450 nm due to the extended π -electron delocalization of conjugated backbones (Figure S6b, Supporting Information). Notably, compared to PFBT, PFBT-CPE in $\text{Et}_3\text{N}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixture presents two absorption bands at 319 and 451 nm (Figure 1a). From the absorption edge, optical band gap of roughly 2.18, 2.10, 2.11 eV were estimated for PFBT, PFBT-C6, and PFBT-CPE, respectively (Figure S8, Supporting Information). In addition, the emission of PFBT was centered at 596 nm, which was blue-shifted to 564 nm for PFBT-C6 and 577 nm for PFBT-CPE. This is probably related to the unique π - π stacking of the conjugated backbones after introducing side chain and further quaternization.^[42] The morphology of PFBT-CPE aggregates in $\text{Et}_3\text{N}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$

mixture was studied by SEM and the size distribution was analyzed by dynamic light scattering (DLS). SEM image indicates the formation of uniform nanoparticles (180 nm), which agrees with the DLS results (Figure 1b). In addition, the solution maintains clear after several months, which indicates excellent storage stability of PFBT-CPE.

Subsequently, the cyclic voltammograms were measured for polymer films to evaluate their electronic energy levels. During the cathodic sweeping (Figure 2a), two reversible waves were observed for PFBT and PFBT-CPE. PFBT-C6 (1.35 eV) has a lower onset reduction potential than PFBT-CPE (1.25 eV), which is nearly identical to that of PFBT (1.26 eV). Accordingly, the calculated LUMOs are 3.39, 3.30, 3.40 eV for PFBT, PFBT-C6, and PFBT-CPE, respectively (Figure 2b). In principle, the measured LUMO levels of the three polymers are thermodynamically large enough to enable proton reduction in the photocatalytic reduction.[23]

The photoelectrochemical properties of the polymers were then examined and compared using electrochemical impedance spectroscopy (EIS) and transient photocurrent measurements. As shown in Figure 3a, the radii of the semicircular Nyquist plot for the PFBT-CPE electrode is smaller than PFBT and PFBT-C6, indicating the faster transport of the photoinduced electron and hole pairs, which was further supported by the significantly increased transient photocurrent response in the PFBT-CPE electrode when compared to PFBT and PFBT-C6 (Figure 3b). Accordingly, the improved charge transportation of PFBT-CPE is expected to show good photocatalytic activity.

Considering the good photophysical property and excellent dispersion of PFBT-CPE, we investigated its application for photocatalytic hydrogen evolution, which was performed using 300 W xenon arc lamp with a 420 nm cut-off filter as light source and Et₃N as hole scavenger (Table 1). No H₂ was detected either in dark or without polymer

photocatalysts in the Et₃N/CH₃OH/ H₂O (1/1/1, v/v/v) mixture. In addition, negligible hydrogen was produced in the mixture of methanol and H₂O (Table S1, Supporting Information). As illustrated in Figure 4a, PFBT-CPE exhibits a stable H₂ release rate of 512 mmol h⁻¹ g⁻¹ in three runs of 15 h without noble-metal loading. Furthermore, PFBT-CPE could be reused for two additional runs without noticeable decrease in its photocatalytic efficiency. No apparent change of the UV-vis (Figure S9, Supporting Information) and ¹H NMR spectra (Figure S10, Supporting Information) of PFBT-CPE could be observed. In comparison, PFBT showed a relatively lower HER of 165 mmol h⁻¹ g⁻¹, which can mainly be ascribed to its wide band gap and large particle size. An extremely poor photocatalytic efficiency of 12 mmol h⁻¹ g⁻¹ for PFBT-C6 was measured in the same photocatalytic condition. It is probably due to the pronounced hydrophobic nature of PFBT-C6 (larger particles in the catalytic medium), which blocks the active sites on the polymer conjugated backbone attached with long C6 side chain. In addition, different sacrificial agents or solvents were also studied for PFBT-CPE. No H₂ was observed when employing ascorbic acid, while PFBT-CPE in (C₂H₅)₂NH/ H₂O and 10% vol TEOA/H₂O were found to yield lower activities of 83 and 268 mmol h⁻¹ g⁻¹, respectively (Table S1, Supporting Information). The wavelength dependent apparent quantum yields (AQY) for PFBT-CPE were investigated under monochromatic visible light irradiation. As displayed in Figure 4b, PFBT-CPE has an AQY of 0.19% at 400 nm, whereas 0.30 and 0.46% were calculated at 420 and 450 nm, respectively. When employing monochromatic light at 500 nm, only residual H₂ could be detected, indicating that the incident photons contributing to the proton reduction reaction are mainly below 500 nm, which agree with its absorption spectrum.

To investigate charge carrier photo-generation dynamics in the absence and presence of sacrificial agent Et₃N in the photocatalytic system, ultrafast transient absorption spectroscopy

copy was measured in the visible spectral region. Figure 5 (left panel) shows two positive bands at around 450 and 600 nm, and two photoinduced absorption (PIA) bands below 550 nm and beyond 600 nm. The positive band at 450 nm corresponds to the absorption of the PFBT-CPE as illustrated in Figure 1a and hence interpreted as a ground state bleaching (GSB) due to the depletion of the excitonic ground state. The broad PIA feature at greater wavelength (beyond 600 nm) can be attributed to the charge absorption in the photocatalytic system. Meanwhile, the spectra also show the formation of stimulated emission (SE) in a wavelength region corresponding to photoluminescence (λ_{max} 600 nm). Although the spectral profiles of both samples show similar features, their carrier dynamics are different. Monitoring the transient dynamics of the GSB and PIA band would allow us to trace the evolution of these photoexcited species. As displayed in the right panel of Figure 5, even though photobleaching (PB) of both samples decay with almost the same trend at the earlier time, the sample containing Et3N exhibits longer tail dynamics ($\tau_3 > 2$ ns), which indicates the formation of long-lived charges that escaped charge recombination as result of Et3N presence.[46] Similar to PB signal, PIA of photogenerated charges probed at 700 nm also shows a long-lived tail ($\tau_3 > 2$ ns) upon introduction of Et3N. The appearance of a long-lived photoinduced absorption band beyond 600 nm indicates enhancement of free charge generation in photocatalytic system. The SE feature provides further evidence that charge recombination in this system is incredibly suppressed. In the absence of Et3N, the SE decay is only less than 50 ps, while it lasts beyond 1 ns with the addition of Et3N. This indicates that SE which arises due to excitons recombination has been reduced and contribute to proton reduction after electron separation from the exciton.[45]

The transient absorption spectroscopy (TAS) results here indicate a significant impact of the sacrificial agent Et₃N in the photocatalytic process. We believed the study is useful to reveal charge carrier dynamic in the photocatalytic process.

In summary, we have demonstrated the great potential of CPEs for photocatalytic hydrogen production, whereby they can absorb visible light and directly transfer photoexcited electrons to drive the proton reduction. A stable hydrogen release rate of 512 mmol h⁻¹ g⁻¹ was achieved under visible light (>420 nm), which was a dramatic increase in comparison with the model polymer PFBT (3.10 times) and precursor polymer PFBT-C6 (42.7 times). Apart from significantly improved photocatalytic performance, other impressive advantages of CPEs are abundant, which include low cost, nontoxic, stable, and sustainably synthesized on a large scale. Inspired by the facile tunable properties and excellent water dispersibility of CPEs, we believe the achievement in this contribution will pave the way for the creation of high efficient homogeneous multiphase photocatalysis in the future.

Acknowledgements

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Table 1. Dispersion in CH₃OH/H₂O (1/1, v/v) mixtures, optical and electrochemical properties as well as hydrogen evolution rates (HERs) of polymers.

Polymers	Dispersion in water/CH ₃ OH HER ($\mu\text{mol h}^{-1} \text{g}^{-1}$) ^{d)}	λ_{abs} (nm) ^{a)}	λ_{em} (nm) ^{a)}	Optical gap (eV) ^{b)}	$E_{\text{red, onset}}$ (V) ^{c)}	
PFBT	Poor	309, 420	596	2.18	−6.06	165
PFBT-C6	Poor	320, 450	565	2.10	−5.50	12
PFBT-CPE	Good	319, 451	588	2.11	−6.12	512

a) PFBT-C6 was CH₂Cl₂ solution, PFBT and PFBT-CPE were Et₃N/CH₃OH/H₂O (1/1/1, v/v/v) mixture; fluorescence measurements of the three samples excited at 380 nm. b) Calculated from the onset of the UV-vis reflectance spectrum ($E_g \approx 1240/\lambda_{\text{onset}}$). c) vs. Ag/Ag⁺ in acetonitrile solution. d) Reaction conditions: 10 mg of photocatalysts suspended in 12 mL of Et₃N/CH₃OH/H₂O (1/1/1, v/v/v) mixture. All the samples were illuminated for 2 h using a 300 W Xe lamp as light source (>420 nm).

Scheme 1. The conversion of hydrophobic polymer PFBT to cationic conjugated polyelectrolyte PFBT-CPE.

Figure 1. a) Normalized UV-vis absorption (solid line) and PL (dashed line, $\lambda_{\text{ex}} = 380$ nm) spectra and (b) DLS results of PFBT-CPE in Et₃N/CH₃OH/ H₂O (1/1/1, v/v/v) solution (inset was the SEM image of PFBT-CPE nanoparticles).

Figure 2. a) Cyclic voltammograms (reduction scans) of polymer films (vs. Ag/Ag⁺) in acetonitrile solution, scan speed: 50 mV s⁻¹; (b) energy diagram of the three polymers. LUMO = $-(E_{\text{red,onset}} - E_{1/2, \text{Fc/Fc}^+})$ = 4.8 eV, where $E_{\text{red,onset}}$ was the onset potentials of the reduction waves; $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g,opt}}$, where $E_{\text{g,opt}}$ was the optical band gap of the polymer.

Figure 3. a) EIS plots and (b) periodic on/off photocurrents response of polymers (>420 nm) electrodes at a 0.6 V bias potential versus Ag/AgCl in 0.5 M Na_2SO_4 aqueous solution.

Figure 4. a) Typical time course of photocatalytic hydrogen production experiment with PFBT-CPE under visible light (>420 nm); (b) merged UV-vis absorption spectra (blue line) and wavelength-specific AQY (black bars) of PFBT-CPE using 40 nm FWHM band-pass filters.

Figure 5. Left panel: transient absorption spectra of PFBT-CPE in the mixture of H₂O/CH₃OH (top) and H₂O/CH₃OH/Et₃N (bottom) at indicated delay time following photoexcitation at 400 nm. Right panel: decay dynamics of photobleaching (fitted by triexponential function) probed at 450 nm (top) and photoinduced absorption (PIA) (bottom) probed at 700 nm.