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Organic Polymer Dots as Photocatalysts for Visible Light-Driven Hydrogen Generation

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Abstract: *For the first time, organic semiconducting polymer dots (Pdots) based on poly[(9,9′-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1′,3} thiadiazole)] (PFBT) and polystyrene grafting with carboxyl-group-functionalized ethylene oxide (PS-PEG-COOH) are introduced as a photocatalyst towards visible-light-driven hydrogen generation in a completely organic solvent-free system. With these organic Pdots as the photocatalyst, an impressive initial rate constant of 8.3 mmol h^{-1} g^{-1} was obtained for visible-light-driven hydrogen production, which is 5-orders of magnitude higher than that of pristine PFBT polymer under the same catalytic conditions. Detailed kinetics studies suggest that the productive electron transfer quench of the excited state of Pdots by an electron donor is about 40 %. More importantly, we also found that the Pdots can tolerate oxygen during catalysis, which is crucial for further application of this material for light-driven water splitting.*

Effective utilization of solar energy by storing it in the form of chemical bonds is recognized as one of the most promising methods to construct a clean and renewable energy system.[1] Hydrogen generation through light-driven water splitting is an ideal process to convert and store solar energy owing to its environmentally friendly properties and the high energy density of hydrogen.[2] However, this reaction relies on efficient catalysts for both proton reduction and water oxidation.[1b] Developing efficient photocatalysts for hydrogen generation is therefore crucial. In addition to various molecular assemblies[3] and inorganic semiconductors,[4] a surge of interest in using organic semiconductors for light-driven proton reduction was raised recently, as organic semiconductors hold the advantages of metal-free structure, tunable optical gaps, and material abundance. In 2009, carbon nitride (g-C_3N_4) was first reported as an photocatalyst for hydrogen production by Antonietti and co-workers.[5] Since then, much effort has been spent on improving its performance by chemical modifications and/or introduction of co-catalysts.[6] Organic semiconducting polymers have also been investigated as hydrogen evolution photocatalysts, including Poly(*p*-phenylene)[7], poly(azomethine)s,[8] covalent organic framework,[9] phenyl-triazine oligomers,[10] microporous organic nanorods,[11] heptazine networks,[12] polybenzothiadiazoles,[13] and porous conjugated polymers.[14] Very recently, Cooper and co-workers reported a series of tunable organic photocatalysts for visible light-driven hydrogen production that successfully avoided the use of platinum as a co-catalyst.[15] Subsequent work investigated planarized conjugated polymers, which turned out to be much better photocatalysts for hydrogen evolution.[16] These works showed that linear conjugated organic polymers are able to efficiently catalyze hydrogen evolution without the assistance of any co-catalysts under visible-light irradiation. To further improve the performance of organic semiconductors for hydrogen production, as well as to remove the organic solvent phase, the next generation of organic semiconductor catalysts should have large surface areas and good dispersibility in water.

Polymer dots (Pdots), as derivatives of polymeric micelles,[16] have attracted significant attention owing to their outstanding optical characteristics as bio-fluorescent probes.[17] Several key features of the Pdots are:[17a] 1) facile yet effective synthetic methods; 2) tunable optical gaps by molecular dopants; 3) tunable particle size and surface hydrophilicity; 4) relatively long excited state lifetimes; 5) owing to the large π-conjugated structures, electrons can freely move within the polymer backbone through the overlaps of p-orbital clouds by tunneling, hopping, or other related mechanisms. Considering the outstanding properties of Pdots as well as the inspiration from the aforementioned hydrogen production catalysis, we speculated that Pdots could function as efficient photocatalyst for light-driven hydrogen evolution. In this work, we report the application of water-soluble Pdots based on the conjugated polymer PFBT (Scheme 1) for photocatalytic performance in visible-light-driven hydrogen generation from absolute aqueous solutions. Detailed kinetic studies are also presented to investigate the induction time observed in this system.

In previous studies, organic solvents such as methanol were introduced as the co-solvent to enhance the dispersibility of the organic polymers or to improve the aqueous miscibility of the organic electron donors.[9b,15,16] To avoid organic co-solvents, we instead adopted water-dispersible PFBT Pdots prepared by modifying a documented strategy,[18b] as shown in Scheme 1. Typically, PFBT was dissolved in THF together with the co-polymer PS-PEG-COOH. The

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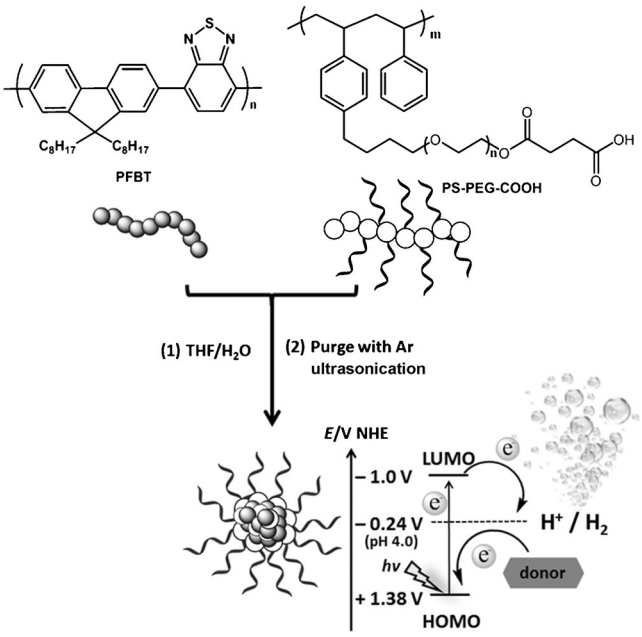

Scheme 1. Preparation of PFBT Pdots and the diagram for light-driven hydrogen generation.

mixture was then poured into distilled water with vigorous stirring; afterwards, the organic solvent in the mixture was purged out by continuous Ar flow in an ultrasonic bath. As a result, a bright green solution was obtained in which the comb-like and amphiphilic polystyrene polymer PS-PEG-COOH enabled the PFBT Pdots to homogenously disperse in water. The particle sizes of the Pdots were investigated by transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements (Figure 1). The data indicate that the PFBT Pdot particles ranged in size from 30 to 50 nm.

The absorption and emission spectra of PFBT Pdots were then measured. As depicted in Figure 2, the formation of PFBT nanoparticles slightly influences its optical properties. Interestingly, the absorption spectrum of the Pdots in water shows a $\approx$20 nm red-shift compared to that in THF, probably owing to the J aggregation of the polymer chain in aqueous solution.[19] It is noteworthy that the absorption edge of the Pdots is extended to approximately 550 nm, surpassing most

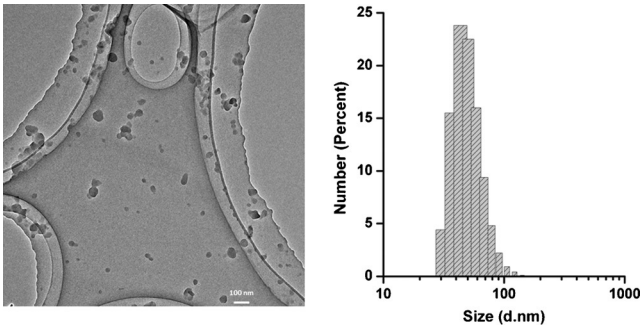

Figure 1. Left: TEM image of PFBT Pdots on a copper alloy TEM sample grid (scale bar: 100 nm). Right: Hydrodynamic diameter of PFBT Pdots measured by DLS.

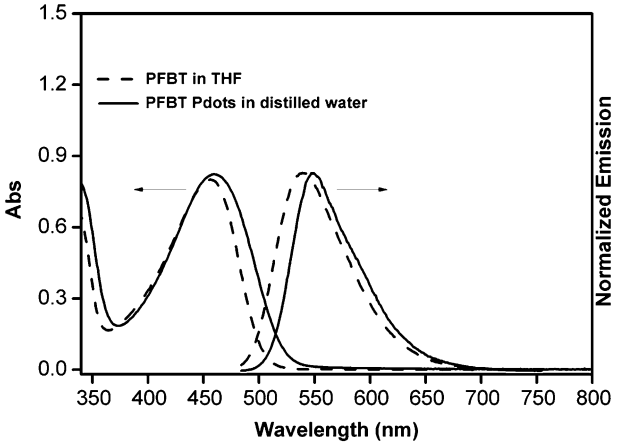

Figure 2. Absorption and emission spectra of PFBT polymer in THF and PFBT Pdots in water.

of the documented organic semiconductors for light-driven hydrogen evolution, and an optical band gap of 2.38 eV was determined. This narrow band gap also enhances the visible-light-harvesting ability of the semiconductor. The minor overlap between the absorption and emission spectra facilitates kinetics studies by tracing the emission quenching.

To evaluate the performance of PFBT Pdots as a photocatalyst for light-driven hydrogen evolution, a typical two-component system was employed. Ascorbic acid was used as a sacrificial electron donor. Figure 3 depicts the kinetic curve of hydrogen generation of the above system. Surprisingly, PFBT Pdots exhibited excellent hydrogen generation performance, and two control experiments indicated that each component shows no activity under the same conditions, confirming the photo-catalytic process of this system. An initial rate constant for hydrogen generation of 8.3 $\pm$

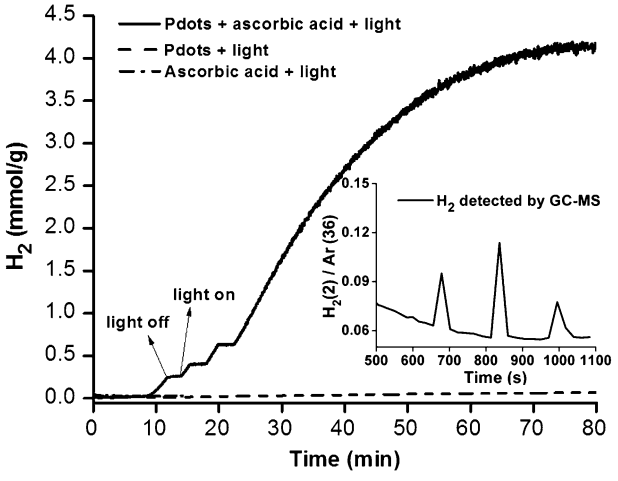

Figure 3. Visible-light-driven hydrogen generation from water at room temperature. Conditions: PFBT Pdots, ca. 16.8 $\mu g\,mL^{-1}$ (Figure S1); ascorbic acid: 0.2 M; pH 4.0 (adjusted with 1 M NaOH), LED lamp: white light ($\lambda > 420$ nm); the kinetic curve is monitored by a hydrogen sensor (see details in the Supporting Information). Inset: H_2 generation confirmed by GC-MS, the three peaks are signals from three injections of the headspace gas in the reaction flask.

0.2 mmol $h^{-1} g^{-1}$ (Figure S2) was obtained, which places the PFBT Pdots among the most efficient photocatalysts to the best of our knowledge (Table S1).[6,7f,8,9b,c,10,14–16] At first glance, the PFBT Pdots lost their activity after one hour of reaction time, and some large particles were formed. Thus, we believe that aggregation is the main reason for the deactivation, and this aggregation is likely due to the photolysis (Figure S3). However, the starting material (PFBT polymer) can be easily recycled just by simply collecting the particles, and the UV/Vis spectrum suggests the PFBT polymer remains stable in chemical structure and composition (Figure S4). The reproduced Pdots from the recycled PFBT polymer still showed activity for light-driven hydrogen generation (Figure S5). These results indicate that PFBT Pdots are a robust photocatalyst for light-driven hydrogen generation. However, one future challenge is avoiding the aggregation during the catalysis, which may be addressed by 1) modifying the copolymer or introducing surfactant, and/or 2) introducing co-catalysts.

An apparent quantum yield of 0.5% was obtained at 445 nm (Figure S6). Increasing the concentration of Pdots should be a good strategy to further improve the quantum yield. Relevant work on this is undergoing. Another strategy is to accelerate the reaction rate for the proton reduction reaction by introducing co-catalysts. As shown in Figure S7, the quantum yield is expected to be enhanced by approximately 5-times just by simply adding Pt as co-catalyst to the system.

Notably, negligible hydrogen was detected by the pristine PFBT polymer suspensions under the same catalytic conditions (Figure S8). Thus the performance of hydrogen evolution was enhanced by 5-orders of magnitudes by transforming the polymer to the Pdots. This significant enhancement of activity should be attributable to the large surface area of the Pdots compared to that of the polymer powder. In this sense, we also speculate that the Pdots may also facilitate the charge separation and thus enhance the catalytic activity. To verify this assumption, electrochemical measurements were carried out to compare the catalytic activity of PFBT polymer suspension and the Pdots solution (Figure S9). This result indicates that the Pdots indeed exhibit more pronounced activity towards proton reduction than the pristine PFBT polymer solution, which is in good agreement with our hypothesis.

One advantage of using a hydrogen sensor instead of GC to measure the hydrogen generation is that the sensor can provide a full kinetic curve for the hydrogen generation; therefore, more kinetic information can be obtained. Interestingly, in our case, a 5 min induction time was observed in the light-driven hydrogen generation experiments (Figure 4). To understand this induction process, DLS measurements were first carried out to see if the particle size changes. As shown in Figure 4, the initial illumination resulted in slightly larger nanoparticles (from an average of 30 nm to 60 nm), thus, the induction time may due to the reorganization of the Pdots particles to form the active species which exhibit slightly larger particle sizes. In addition, transient UV/Vis spectra of the reaction mixture were recorded in-situ with simultaneous light illumination from LED during the induction time (Figure S10). Several interesting features were observed: 1) the stimulated emission at 540 nm is quenched around 40%, which may due to the structural reorganization of the nanoparticles as well as the productive quench;[20] 2) an isosbestic point appeared at 400 nm, indicating a possible structure change which happened during the illumination, which is in good agreement with the DLS measurement.

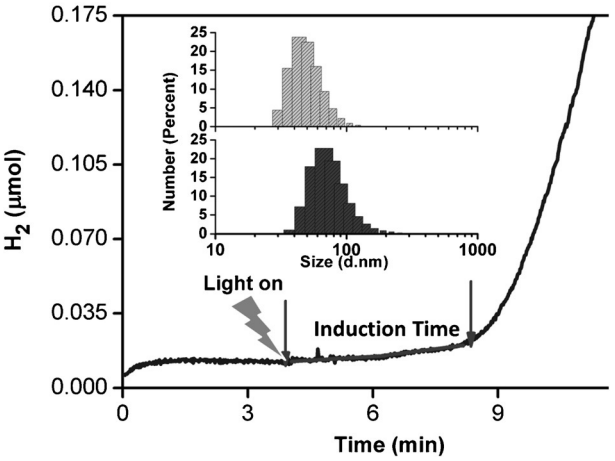

Figure 4. The initial state of the light-driven hydrogen generation experiment under the same catalytic conditions as above. Inset: Hydrodynamic diameter of PFBT Pdots measured by DLS before (top) and after (bottom) the induction time (ca. 5 min).

For insights into the induction time as well as the electron transfer kinetics during the light-driven catalytic reaction, time-correlated single photon counting (TCSPC) measurements were carried out. As shown in Figure 5, the photoluminescence lifetimes of the Pdots were measured at different stages of the catalytic reaction. The lifetimes at each stage were obtained by fitting the curves to bi-exponential decays. It can be seen that the longer photoluminescence lifetime is quenched gradually, causing the shorter one to rise in amplitude over time. The average lifetimes are: 2.11 ns, 1.53 ns, and 1.25 ns, at 0 min, 5 min, and 30 min illumination time, respectively. Thus, the charge transfer efficiency could

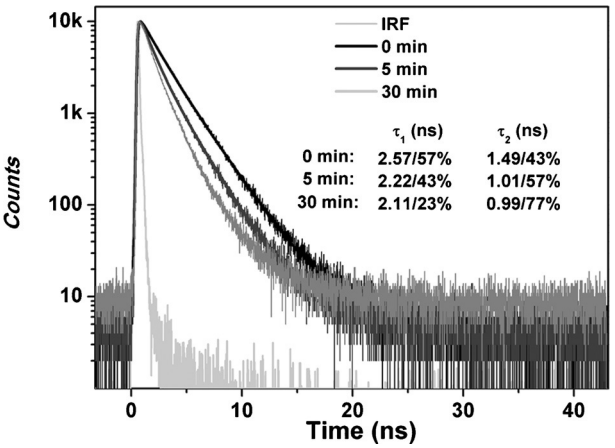

Figure 5. The TCSPC curves and fitting data of Pdots with different illumination times under the catalytic conditions.

be calculated as 28% and 41% at 5 min and 30 min, respectively. As expected, the charge transfer between the Pdots and donor becomes more efficient after light illumination; this again is in good agreement with the observed induction time. The reorganization product after the induction time should have an optimized structure that can facilitate the charge separated state of the photocatalyst. Unfortunately, we have not been able to directly observe or measure the intermediates. To further investigate the dynamics of the system in the shorter timescales, time-resolved fluorescence (streak camera) measurements were also performed. The results (see details in the Supporting Information, Figure S11) further support the rearrangements of the Pdots nanoparticles during the induction time.

Oxygen is an inevitable byproduct when generating hydrogen from complete water splitting, and oxygen is also abundant in the atmosphere. Therefore, oxygen will inevitably exist in the system. Unfortunately, it is usually an inhibitor of proton reduction, especially for light-driven reactions. Thus, a catalyst with oxygen-resistant properties is the key to develop a really robust system for hydrogen production. Unfortunately, very few studies have touched on oxygen-resistant systems.[21] To address this issue, the oxygen-resistance of the PFBT Pdots was also studied (Figure S12). The results indicated that the Pdots are a relatively stable material in the presence of oxygen even under photo-catalytic conditions.

Previous work indicated that the planarization of the fluorene unit is important for the activity of the catalyst.[16] In this work, the PFBT also contains a fluorene unit, and the PFBT Pdots can work as efficient photocatalysts for hydrogen generation. A control experiment (Figure S13) showed that P3HT Pdots (P3HT = poly(3-hexylthiophene-2,5-diyl, without fluorene unit) exhibit very little activity as compared to the PFBT Pdots under the same conditions. This is in good agreement with the suggestion that the planarization of the fluorene unit should be crucial for the activity of the catalyst.[16]

In summary, polymer dots based on PFBT were adapted as photocatalysts for visible-light-driven hydrogen generation for the first time and showed impressive activity in an absolute aqueous solution in the presence of a sacrificial electron donor. The Pdots afford an initial light-driven hydrogen generation rate of $8.3 \pm 0.2\ \mathrm{mmol\,h^{-1}\,g^{-1}}$ without the assistance of any co-catalysts. Compared to the pristine PFBT polymer, the activity of the Pdots nanoparticles is enhanced by 5-orders of magnitude. An induction time of a few minutes was observed during the catalysis, which was tentatively assigned to a reorganization of the nanoparticles to facilitate the charge transfer. The Pdots also exhibited activity during catalysis in the presence of oxygen. Furthermore, most of the starting materials can be recycled without any decomposition. Future work will focus on investigating other semiconducting Pdots, as well as increasing the quantum yield by using an efficient proton reduction co-catalyst. Because of the facile surface modification, catalysts can also be easily linked to the Pdots. This work may pave a way for developing a new type of robust and environmentally friendly hydrogen generation photo-catalysts with broad light absorption. Furthermore, the unexpected oxygen resistance of PFBT Pdots and its suitable HOMO provide a possibility to pursue photochemical water oxidation with this kind of material, with the goal of making a complete water-splitting system based on all-organic semiconductors.

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