

Saket MATHUR, Benjamin ROGERS, Wei WEI

Organic conjugated polymers and polymer dots as photocatalysts for hydrogen production

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Abstract Owing to the outstanding characteristics of tailorable electronic and optical properties, semiconducting polymers have attracted considerable attention in recent years. Among them, organic polymer dots process large breadth of potential synthetic diversity are the representative of photocatalysts for hydrogen production, which presents both an opportunity and a challenge. In this mini-review, first, the organic polymer photocatalysts were introduced. Then, recent reports on polymer dots which showed a superior photocatalytic activity and a robust stability under visible-light irradiation, for hydrogen production were summarized. Finally, challenges and outlook on using organic polymer dots-based photocatalysts from hydrogen production were discussed.

Keywords polymer dots (Pdots), photocatalysis, hydrogen production

1 Introduction

With the increasing concern over the climate impact of non-renewable fossil fuels, it is necessary and important to develop promising approaches to convert solar energy into chemical energy for future energy production [1]. One sustainable alternative to fossil fuels is to use hydrogen as an energy carrier in the future [2]. Fujishima and Honda reported that hydrogen could be produced over TiO_2 photoelectrode via photocatalytic process for the first time in 1972 [3]. After that, tremendous reports have been

published exploring the performance of TiO_2 photocatalyst. However, the major bottleneck drawbacks, for example, the 3.2 eV wide band gap, with which the TiO_2 can absorb light only in the UV region impedes the applications of TiO_2 photocatalysts. Moreover, the recombination of photogenerated electrons and holes reduces the quantum efficiency of TiO_2 . Therefore, developing efficient visible-light-driven photocatalytic systems that generate hydrogen from water attracts great attention afterwards [4–7]. In other words, the development of semiconductors that possess visible-light responsive absorptions and suitable band structures for photocatalytic water splitting is among the most demanding and long-standing challenges [8–12]. Up to the present, many efforts have been made to improve the efficiency, such as heteroatom doping [13], multicomponent hybridization [14], fabrication of alternative one-dimensional nanostructures [15], and introducing heterojunction [16], etc. However, organic semiconductor photocatalysts which have an appropriate energy level for photocatalytic water splitting are still less explored compared with inorganic semiconductor photocatalyst, as the research on the inorganic semiconductor photocatalysts is started much earlier than organic semiconductor as photocatalysts [17–21]. Moreover, organic semiconductors which have some crucial advantages of being able to tune the structure and their properties, are easily accessible as well as cost effective while maintaining an efficient photoactivity.

One of the famous reported organic semiconductor photocatalysts that attracts significant attention is graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [22–30]. However, $\text{g-C}_3\text{N}_4$ and its derivatives can only offer limited chemical varieties, which restricts the fine-tuning of their structures and properties. Additionally, their relatively wide band gaps also limit the utilization of solar photons in visible light region. Thus, exploring other organic π -conjugated polymers with the molecular engineering flexibility and optoelectronic properties tunability attracts greater attention with the goal to enhance the performance of photocatalysts [31,32].

Polymer dots (Pdots) are one such application of

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Saket MATHUR, Benjamin ROGERS, Wei WEI (✉)
Mechanical Engineering Department, Wichita State University, Wichita
KS 67260, USA
E-mail: wei.wei@wichita.edu

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conjugated polymers, which range in size from 1 to 100 nm. Compared with traditional organic small molecules, semiconductor quantum dots, and inorganic nanomaterials, Pdots exhibit a higher extinction coefficient and a better photostability and chemical stability [33]. Additionally, Pdots surfaces often have different reactive functional groups that can provide a platform to construct multifunctional and hybrid nanomaterials when conjugated with different chemical and biological molecules [34].

This mini review will look at the advances in research by dividing them into three sections starting from a brief introduction of semiconducting polymers to an overview of the current trends in Pdots research, concluding with a section looking at possible future trends.

2 Semiconducting polymers

Most organic polymers without π -conjugated structures are insulators. However, when π -conjugated structures exist, the overlaps in π -electron clouds can allow the electrons to move along the polymer backbone through by hopping, tunneling, and related mechanisms [35,36]. In general, these π -conjugated polymers are so-called semiconducting polymers, since they are wide-band-gap semiconductors in their pristine states. In the 1970s, organic conjugated polymers and oligomers were discovered to be metallic upon heavy doping [37,38], a term derived from inorganic semiconductor chemistry, where the π electronic system was either oxidized (p-type doping) or reduced (n-type doping) [39]. Conjugated polymers became particularly attractive because they promised to achieve a new generation of polymeric materials which exhibited the tunable electrical and optical properties of metals or semiconductors while retaining the attractive mechanical properties and processing advantages of polymers. Moreover, the band gap could be tuned by altering the molecular structure of the polymer. Indeed, they were widely

demonstrated as active materials for a broad range of optoelectronic devices, including flat panel displays with organic light-emitting diodes [40–43], solar energy conversion photovoltaic devices [44,45], and thin-film transistors [46–48].

Figure 1(a) shows the processes of photocatalytic water splitting in semiconductor photocatalysts. Step (1) is to absorb the solar light and generate electron-hole pairs. In Step (2), those electrons and holes will separate and migrate to the reaction sites to produce H_2 or O_2 . However, some electrons and holes may recombine, as shown in Step (3). The working principle is demonstrated in Fig. 2(b). Under irradiation at an energy equal to or larger than the band gap of the semiconductor, valence band electrons are excited and jump into the conduction band. Holes are left in the valence band. These electrons and holes participate in reduction and oxidation reaction to achieve products, respectively. Furthermore, when comparing semiconducting polymers with inorganic semiconductors, one can see that organic polymers can be prepared over a continuous range of monomer compositions, by which the physical properties can be systematically controlled [49,50], while the crystalline inorganic semiconductors exist as discrete phases with specific physical properties [51].

In 1985, linear poly(*p*-phenylene)s were first reported being used as an organic photocatalyst for hydrogen production. An apparent quantum efficiency (AQE) of 0.006% under UV-light irradiation ($\lambda > 366$ nm) was reported [54]. Up to date, various organic semiconducting polymers have been investigated as potential photocatalysts for hydrogen production, such as polyazomethine [55], poly(*p*-phenylene) [54,56], polytriazine [57], poly(2,2'-bipyridine) [58,59], polypyrene [51], polyheptazine [60,61], polybenzothiadiazoles [62], polyhydrazine [63], and poly[(9H-carbazole-2,7-diyl)-1,4-phenylene] [18]. Since then, owing to their tailorable electronic and optical properties, conjugated organic polymer (COPs) with diverse synthetic modularity have been emerging as an

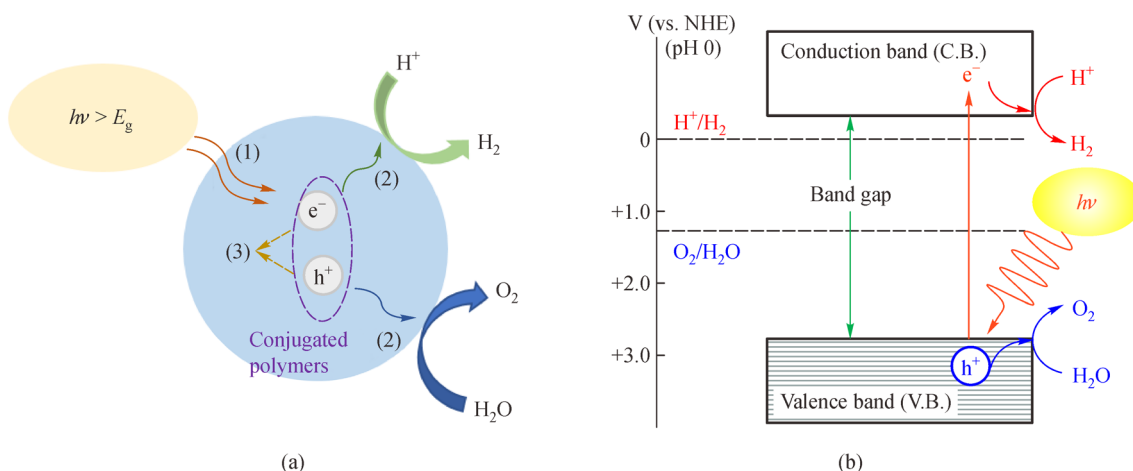


Fig. 1 Process and principle of photocatalytic H_2 production.

(a) Processes; (b) principle of photocatalytic water splitting in semiconductor photocatalysts (adapted with permission from Ref. [52]).

intriguing class of photocatalysts [64–68]. More and more attentions have been paid to COPs in the field of photocatalysis. For example, Kosco and coworkers used conjugated polymer photocatalysts F8BT as the model system to study the effect of palladium content (residues) on hydrogen production activity [53,69]. F8BT was synthesized by following Suzuki polymerization. Tris (dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) was used as the Pd catalyst (Fig. 2(a)). The residual Pd originally comes from the polymerization reactions when synthesizing PFBT or F8BT. Transient absorption spectroscopy (TAS) measurement were conducted to further investigate the influence of residual Pd. Figure 2(b) exhibits the emergence of a long-lived excited state absorption in the presence of DEA. Moreover, an increasing signal amplitude with a decreasing Pd content can be observed in Fig. 2(c). The resulting polymers exhibited the minimal amount of Pd under visible light and without Pt or Rh as a cocatalyst [70]. In addition, they had

important features such as solution processability, structural tunability, and high dispersion stability of nearly two months.

Very recently, Cooper and coworkers reported a series of tunable organic photocatalysts for visible light-driven hydrogen production that successfully avoided the use of platinum as a cocatalyst [51]. Fifteen polymer networks were synthesized using Pd(0)-catalyzed Suzuki–Miyaura polycondensation [71] of 1,4-benzene diboronic acid (1) and/or 1,3,6,8-tetraboronic pinacol ester of pyrene (3) and/or 1,2,4,5-tetrabromobenzene (2) and/or 1,3,6,8-tetrabromopyrene (4) (Fig. 3(a)). The optical properties of these 15 polymer networks can be fine-tuned over a broad range by adjusting the molar ratio of the monomers (Fig. 3(b)). The UV-visible reflectance spectra (Fig. 3(c)) manifest a redshift in the optical absorption onset from 420 to 640 nm with an increase of pyrene content. Similarly, the photoluminescence spectrum also shows a gradual redshift (Fig. 3(d)). Subsequent work investigated the much better

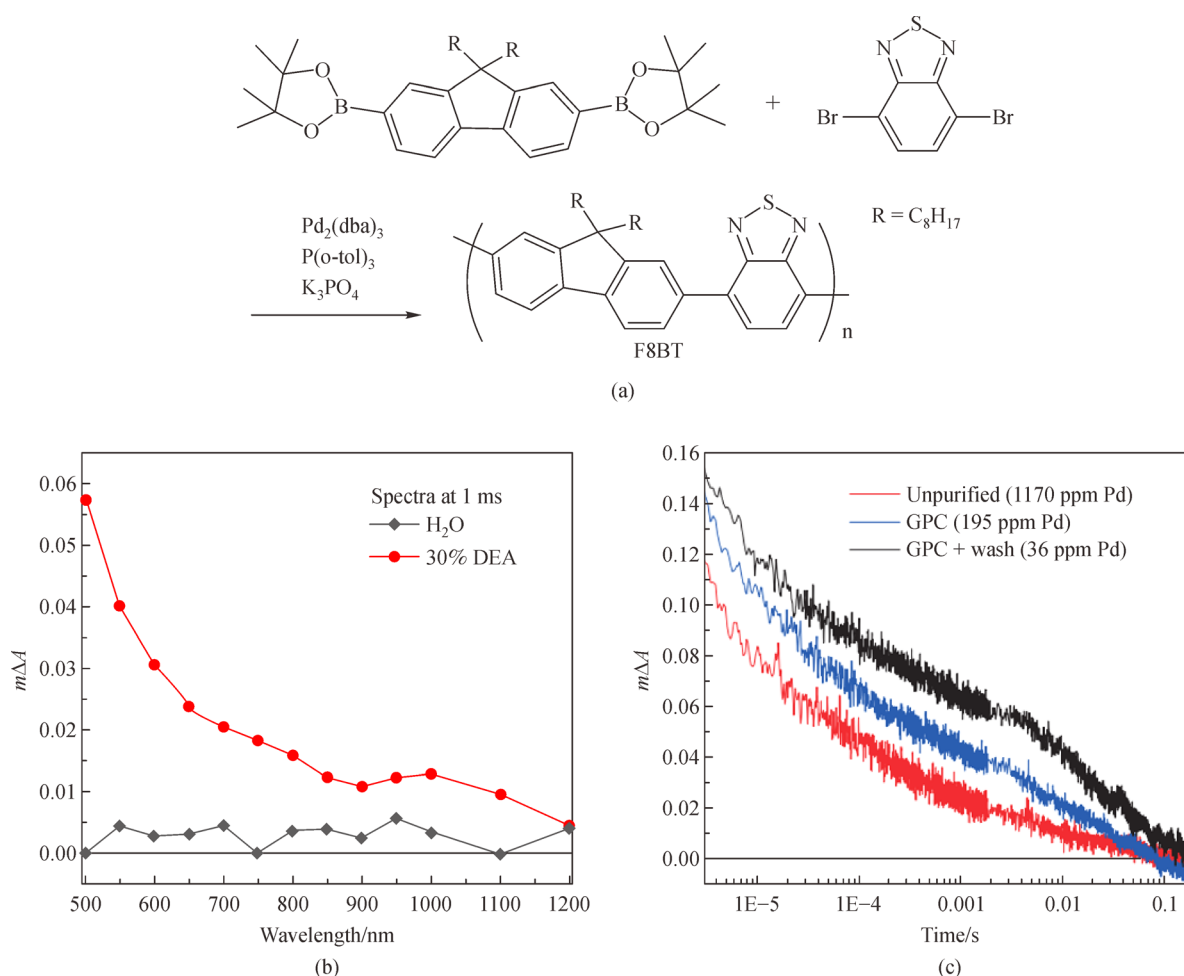


Fig. 2 Structure and transient absorption measurements of F8BT.

(a) Structure and synthesis method of F8BT via Suzuki polymerization; (b) transient spectrum of unpurified F8BT (1170 ppm Pd) at 1 ms, both in pure H_2O and in an aqueous suspension containing 30% diethylamine (DEA); (c) transient kinetics probed at 750 nm for different Pd concentrations in an aqueous suspension containing 30% DEA (adapted with permission from Ref. [53]).

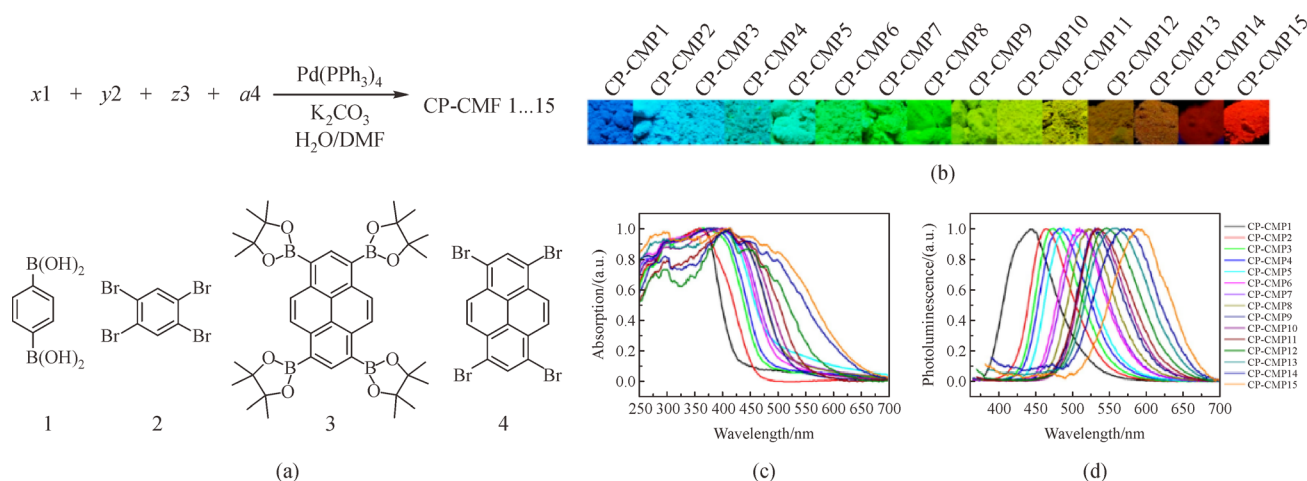


Fig. 3 Structure and optical properties of conjugated copolymer photocatalysts.

(a) Synthesis of conjugated copolymer photocatalysts; (b) photographs of the 15 copolymers (CP-CMP1–15), imaged under irradiation with UV light ($\lambda_{\text{excitation}} = 365 \text{ nm}$); (c) UV–visible absorption spectra of the copolymers measured in the solid state (intensities normalized); (d) photoluminescence spectra of the copolymers (adapted with permission from Ref. [51]).

photocatalysts for hydrogen evolution, i.e., the planarized conjugated polymers [72]. However, it is more challenging to process these materials into functional composites due to the insolubility of organic polymers. Moreover, the photocatalytic activity may be lost due to the sedimentation, that is the reason for the fact that the photocatalysts are typically kept in suspension by stirring [73]. The same group reported a solution-processable organic polymer (in powder or thin film) as a good photocatalyst for hydrogen production from water (Fig. 4) [18]. Furthermore, copolymerisation for a family of 1,4-phenylene/2,5-thiophene [74] and the introduction of nitrogen into poly(*p*-phenylene) type materials could also affect their ability to be used as hydrogen production photocatalysts [75]. As a short conclusion, under visible-light irradiation, the COPs can catalyze the photocatalytic hydrogen production efficiently without using any cocatalysts. The future directions in developing organic semiconductors for hydrogen production are to improve the performance, remove the organic solvent phase, increase surface areas and dispersibility in water, etc [74–78].

3 Conjugated Pdots

3.1 Properties of Pdots

Compared with traditional organic small molecules, semiconductor quantum dots, and inorganic nanomaterials, Pdots exhibit a higher extinction coefficient, a better photostability, and a chemical stability [33]. Additionally, Pdots surfaces often have different reactive functional groups that can provide a platform to construct multifunctional and hybrid nanomaterials when conjugated with

different chemical and biological molecules [34]. Importantly, due to the hydrophobic π -conjugate backbone and amphiphilic polymer matrixes, Pdots are biocompatible compared with inorganic nanoparticles of heavy metals and semiconductors [34,79]. Other features of Pdots include tunable optical gaps by molecular dopants, relatively long excited state lifetimes, effective synthetic methods, and tunable particle size and surface hydrophilicity [80]. As a result, Pdots show a great potential in various applications such as sensing [81,82], phototherapy [83,84], labeling [85], bioimaging [86], drug delivery and theranostics [87], and excellent biocompatibility and flexibility in surface modification [85]. Thus far, several reviews have been published discussing different aspects of Pdots, i.e., biology and medicine [39], and imaging of microvasculature [88]. Furthermore, Pdots possess an excellent water dispersibility that eliminates the organic solvent, highly efficient hydrogen production rates, tunable semiconductor properties that is suitable for visible-light driven processes, and facile structural modification, which are considered to be particularly attractive as photocatalysts [89,90]. Thus, Pdots have been reported as an alternative to inorganic semiconductors (TiO_2 , etc.) photocatalysts for hydrogen production [70,91–93]. However, there is no systematic report that reviews and summarizes the recent advances in π -conjugated Pdots for hydrogen production.

3.2 Preparation of Pdots

There are various methods to synthesize Pdots, including nanoprecipitation, mini-emulsion, and self-assembly [85]. The nanoprecipitation method uses miscible organic solvents, whereas the mini-emulsion method employs

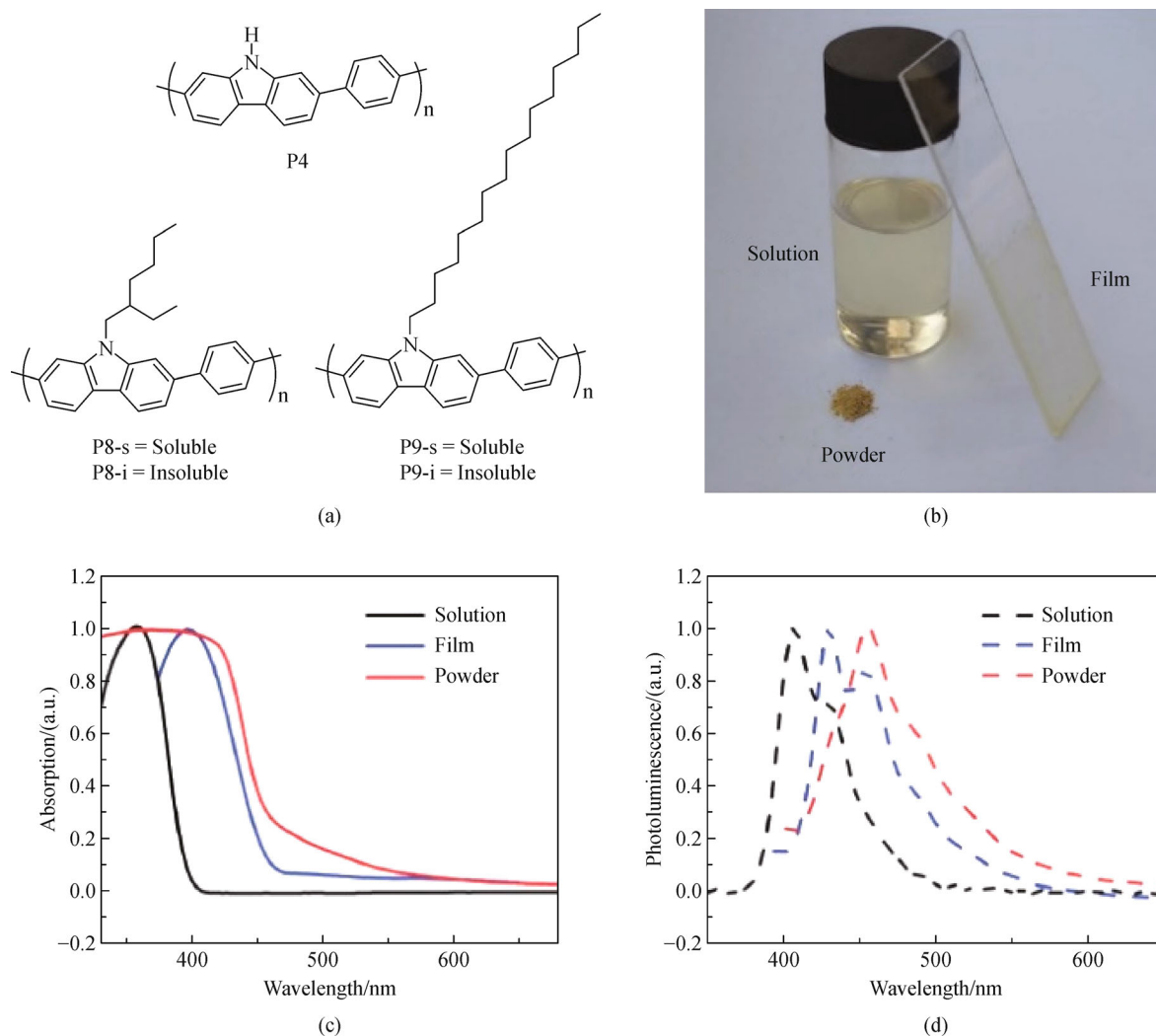


Fig. 4 Structure and properties of semiconducting polymers.

(a) Structures of P4, P8, and P9; (b) photograph of P8-s as a powder and as a thin film; (c) UV-vis absorption; (d) photoluminescence ($\lambda_{\text{exc}} = 360$ nm) spectra of P8-s (adapted with permission from Ref. [18]).

immiscible organic solvents. Notably, the physical size of Pdots depends on the methods used to prepare them [36].

3.3 Pdots as photocatalysts

Because pristine organic semiconducting polymers are generally insoluble in water, in order to increase their dispersibility in the reaction phase, organic solvents are usually used. This problem can be solved by incorporating Pdots. In 2016, the first application of Pdot-based photocatalysts for enhanced H_2 production using visible light in an ascorbic acid (0.2 mol/L) solution under metal-free conditions was reported made by Tian and coworkers (Fig. 5(a)) [92]. As shown in Fig. 5(b), the team reported a significant improvement over pristine polymers poly[(9,9'-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-2,1',3' thiadiazole)] (PFBT) Pdots without using any noble metal cocatalysts. The results showed a high HER of

8.3 mmol/(h·g) at $\lambda > 420$ nm [92]. Oxygen is an inhibitor to proton reduction reaction [94]. Thus, oxygen is an inevitable byproduct in the hydrogen production from photocatalytic water splitting process. Therefore, one of the key features for a good photocatalyst is the oxygen-resistance. One thing to note is that PFBT Pdots process a good resistant to oxygen. Subsequently, the same group synthesized the PFODTBT Pdots and explored their photocatalytic activity. An impressive HER of 50.0 mmol/(h·g) (six times higher than that of the previously reported PFBT Pdots) was reported [93]. However, these Pdots can only be stable for a maximum of 4 h with a high roll-off efficiency. Two years later, the group prepared the hollow structured Pdots by using copolymers of PFODTBT and 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HTPS) for hydrogen production [95]. The results suggest that the reduced particle size (from 90 to 50 nm) is the main reason for the

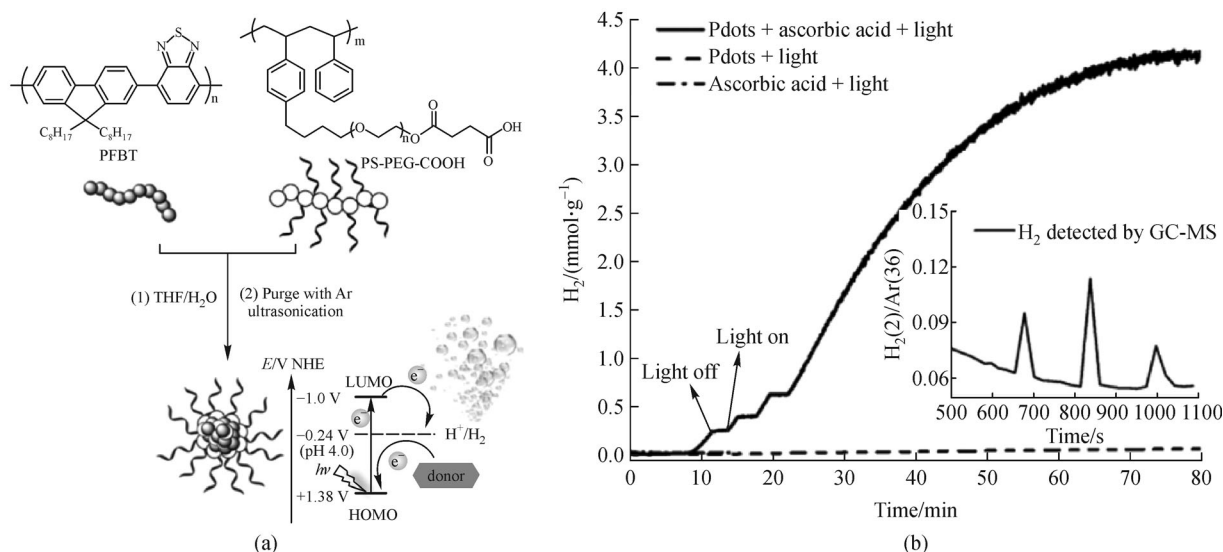


Fig. 5 Preparation and performance of Pdts.

(a) Preparation process of PFBT Pdts and light-driven hydrogen generation diagram; (b) visible-light-driven hydrogen generation from water at room temperature (adapted with permission from Ref. [92]).

performance enhancement. The authors concluded that the nature-mimicking hollow Pdts with porous shells can be used as alternative photocatalysts in solar energy conversion and storage applications.

A few other Pdts have been recently reported for photocatalytic hydrogen evolution. Although there is not much progress noticed in terms of quantum yield of hydrogen, Pdts are an important inclusion in the family of metal-free photocatalyst with much promise. One common feature of all these reported Pdts is their effective extended absorption edge beyond 500 nm. This is highly desirable for harvesting low energy photons. Some Pdts are even active in harvesting photons up to 700 nm [96], and can produce hydrogen in the absence of any organic solvent or co-catalyst.

In 2018, Chou and coworkers developed new types of Pdot-based platforms to enhance their efficiency and long photocatalytic function [91]. In their report, a Pt complex was introduced into the semiconducting polymer backbone through covalent bonding. The cycloplatinated Pdts (Fig. 6(a)) were then obtained by transforming these Pt-based semiconducting polymers. The obtained cycloplatinated Pdts after optimizing the Pt complexes ratio, had an impressive hydrogen production rate compared with the pristine PFTFQ Pdts and the Pt-complex-blended-counterpart Pdts, which were prepared under otherwise identical conditions (Fig. 6(b)). The enhanced performance was mainly caused by the molecular design strategy. The reported Pdts also had an excellent stability of 12 h with a low roll-off efficiency (Fig. 6(c)). Figure 6(d) indicates that the PtPy-blended counterpart PFTFQ Pdts have a higher HER than that of the PFTFQ Pdts alone. Figure 6(e) shows the time-resolved transient photoluminescence

decay spectra, in which the lifetime is shown for the cycloplatinated complex units containing Pdts. This suggests that the cycloplatinated complex units can be used as a cocatalyst to enhance the process of charge transfer. Very recently, a library of polymers was created by the same group. In the report, the importance of acceptor comonomers of pristine Pdts and cycloplatinated Pdts was also investigated for the first time [97]. The results show that in a solution without methanol and under visible light irradiation, the PFTBTA-PtPy Pdts provide the very good hydrogen production rates of 7.34 ± 0.82 mmol/(h·g). The authors also employed the MTT assay experiments to confirm that the cycloplatinated Pdts can minimize the toxicity compared with the conventional approach that directly adding Pt into a solution system.

Conjugated polymers are unique and promising photocatalysts for visible-light-driven hydrogen production, but understanding their photocatalytic efficiencies in aqueous solutions is still very challenging. Recently, Hu et al. first demonstrated a highly efficient strategy to boost the photocatalytic hydrogen evolution of conjugated polymers by functionalizing conjugated backbones with hydrophilic oligo (ethylene glycol) monomethyl ether (OEG) side chains [98]. Figure 7 displays the chemical structures and basic properties of conjugated polymers. The OEG side-chain-functionalized conjugated polymers can render a 90-fold improvement compared with alkyl-functionalized conjugated polymers as photocatalysts. Due to the robust interaction between the OEG side chains with the Pt co-catalysts, the charge transfer from the polymer to the Pt co-catalysts has been improved. Recently, the same group also prepared the novel conjugated polyelectrolytes (CPEs)

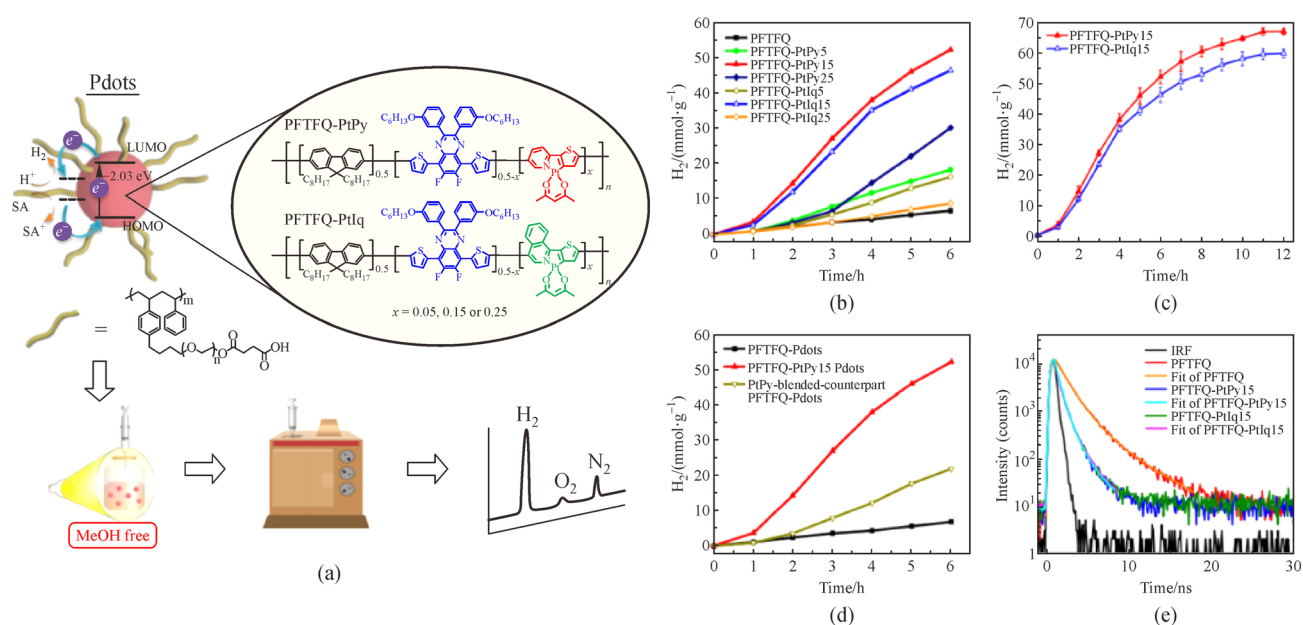


Fig. 6 Structure and performance of Pdots.

(a) Structure and preparation process of PFTFQ-PtPy- and PFTFQ-PtIq-based Pdots and visible light-driven hydrogen production diagram; (b) time course of produced H₂ for PFTFQ Pdots, and the cycloplatinated Pdots; (c) time course of produced H₂ for PFTFQ-PtPy15 and PFTFQ-PtIq15 Pdots for 12 h; (d) comparison of hydrogen generation of chemically linked PFTFQ-PtPy15 pdots and physically PtPy-blended-counterpart PFTFQ Pdots; (e) time-resolved fluorescence decay of IRF (black solid line), the PFTFQ Pdots and cycloplatinated Pdots (adapted with permission from Ref. [91]).

coordinating with a metal cocatalyst for hydrogen production under visible light [99,100]. Similar to the previous report, the counterions and the interaction of the CPE side chains with Pt cocatalysts are the determining factors for the photocatalytic performance. As a result of the robust interactions with Pt, the cationic CPE (PFN-Br) exhibited a higher hydrogen production rate than that of the anionic CPE (PFS-Na). Table 1 summarizes the state-of-the-art progress in Pdots as photocatalysts for hydrogen production.

4 Outlook

Although Pdots have several advantages to be used as photocatalysts for hydrogen production, such as a high

extinction coefficient, a good photostability and chemical stability, the tunability in optical gaps, a tunable particle size and a surface hydrophilicity, and a relatively long excited state lifetime, there are challenges need to be overcome. It is believed that the challenges include the further enhancement of its performance and a better understanding of its mechanism. It is expected that the research in the Pdots field will continue to inspire the chemistry community make new discoveries and resolve challenges. It is envisioned that the exploration of new Pdots species with improved performance and stability and well-controlled surface properties will be the main focus of the field in the future. Through the optimization of photophysical properties, including visible region light harvesting, alignment of band gap, and photogenerated charge generation and transportation, etc., the Pdot

Table 1 Recent progress in Pdots for hydrogen production under visible light irradiation

Pdots	HER/(mmol·(g·h) ⁻¹) at > 420 nm	AQE/%	Ref.
Hyperbranched	0.84	0.9 at 500 nm	[70]
Cycloplatinized	12.7	0.4 at 515 nm	[91]
PFBT	8.3	0.5 at 445 nm	[92]
PFODTBT	50.0	0.6 at 550 nm	[93]
PFODTBT/HTPS	22.6	—	[95]
F8T2/g-C ₃ N ₄	0.93	5.7	[101]
PBDTBT-7EO	18.03	0.3 (600nm)	[98]
PFNDPP-Br	11.16	0.4 (600nm)	[100]
HD-Br	1.08	—	[99]

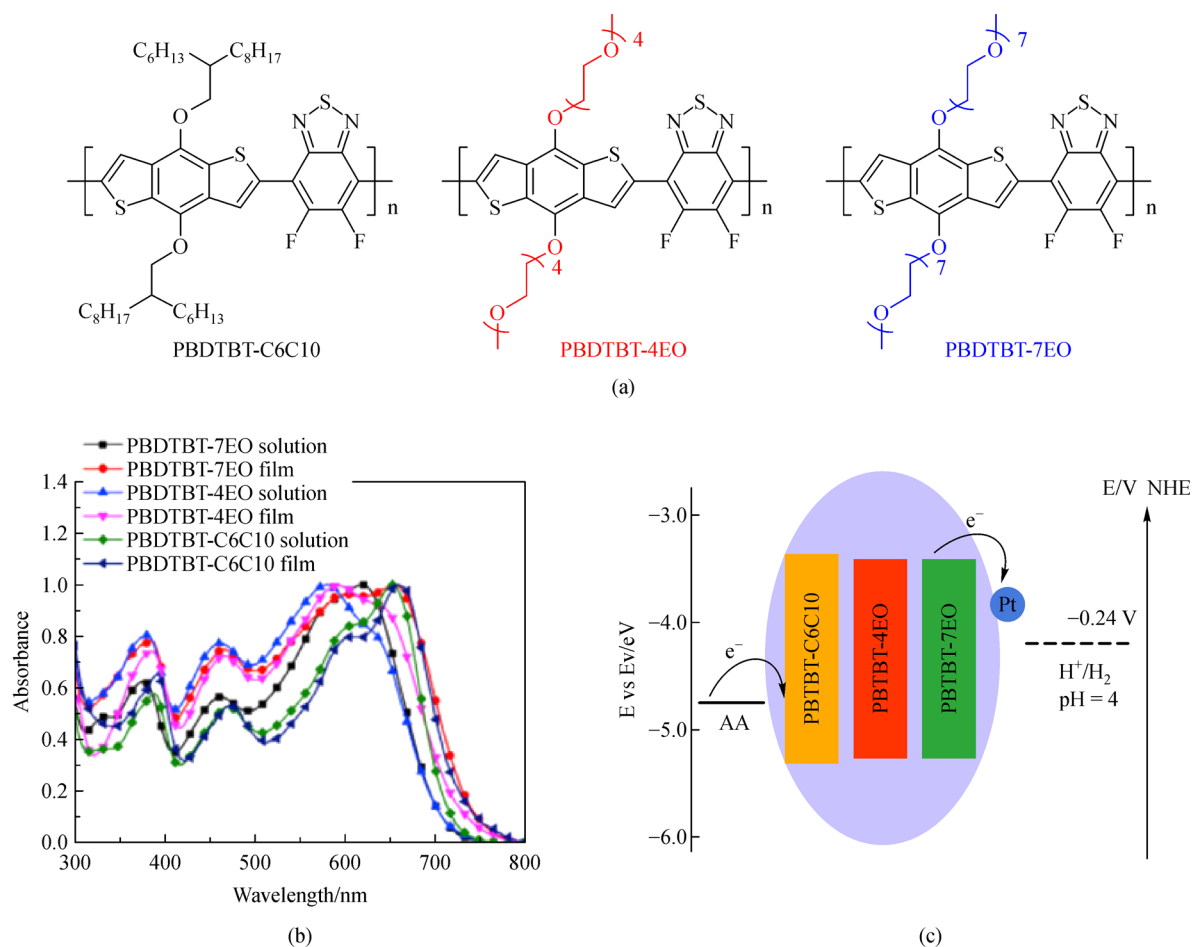


Fig. 7 Structures and properties of conjugated polymers.

(a) Chemical structures; (b) UV-vis-NIR absorption spectra; (c) energy levels of conjugated polymers and energy transfers among photocatalysts, co-catalysts, sacrifying agent, and water (adapted with permission from Ref. [98]).

technology is expected to have a broad and lasting impact on photocatalysis. Moreover, linear conjugated polymers, 2D covalent organic frameworks, and 3D conjugated porous polymers will be of great interests. Furthermore, through multiple modification strategies, including doping (S-doped, P-doped), hybridization, and copolymerization, highlight efficient organic photocatalysts can be realized.

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