Supporting information

1D Nanofiber Composites of Perylene Diimides for Visible-light-driven Hydrogen Evolution from Water

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Experimental Section

Chemicals and materials

PTCDA (high than 98.0%) was bought from TCI. N,N'-Dimethyl-*p*-phenylenediamine (97%) and dodecylamine (98%) were purchased from J&K Acros. All other chemicals including hexachloroplatinic acid hexahydrate (H_2PtCl_6•$6H_2O$) were obtained from Chemical Reagent Co. Ltd. (Shanghai, China). Titanium(Ⅳ) isopropoxide was purchased from Sigma–Aldrich. Commercial TiO_2 products P25 was supplied by Germany Degussa. All organic solvents were distilled from analytical reagent grade solvents before use. Pure water was prepared from Water Purifier. All organic synthesis reactions were carried out under a nitrogen atmosphere.

Characterization

Fourier Transform Infrared (FT-IR) spectra of sample-contained KBr pellets were recorded with a BIO-RAD FTS 165 Spectrometer. Optical properties were analyzed with a UV–vis spectrophotometer (SHIMADZU UV-1800). Fluorecence spectra were characterized by F-700FL (Hitachi High-Technologies Corporation). Thermogravimetry analysis (TGA) was performed on a NETZSCH STA 449F3 instrument. The samples were heated in an alumina crucible in the range from 10 ^{o}C to 800 ^{o}C with a heating rate of 10 ^{o}C min^{-1} under air atmosphere. Scanning electron microscopy (SEM) images were obtained on a ZEISS SUPRA55VP microscope.

General Synthesis of PDIs

Symmetric (PDI-1 and PDI-2) and asymmetrical (PDI-3) perylene diimide derivatives as well as perylene monoanhydride monoimide bearing side-group functionalization at the imide N- and/or N'- positions were synthesized starting by condensation of commercially available PTCDA with dodecanamine or N,N'-Dimethyl-*p*-phenylenediamine in molten imidazole following a typical Langals' procedure introduced with some modification.[1] All products were characterized and verified by FT-IR spectra.

Thermal analysis of PDIs

Thermal analysis of three PDI materials as shown in Fig. S1 highly demonstrates their good thermodynamic stability, that is, the degradation of the main structures appears at about 450 ^{o}C. On account of the difference in side-groups, phenylamino moieties attached molecules remain their weight *ca.* 40% when heated up to 800 ^{o}C, relatively stable than dodecyl-substituted ones, especially symmetric PDI-2.

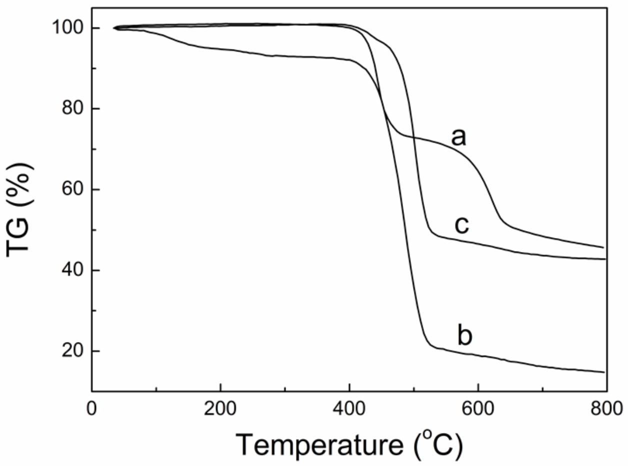

Fig. S1 TG analysis of PDI-1 (a), PDI-2 (b) and PDI-3 (c).

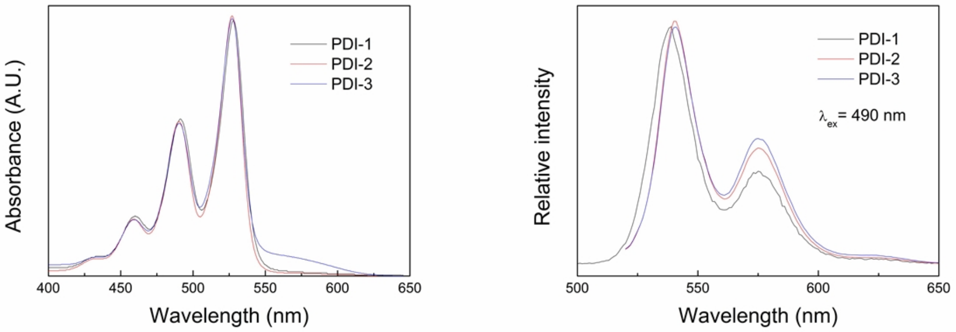

Fig. S2 UV-vis absorption and fluorescence spectra of monomeric PDIs in $CHCl_3$ solutions.

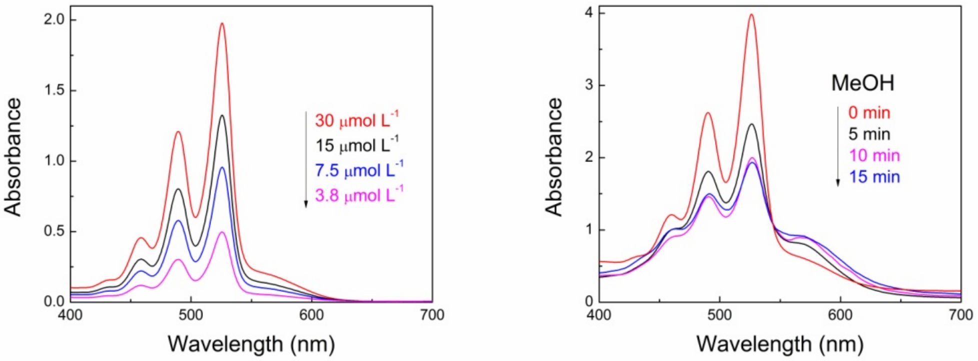

Fig. S3 UV-vis absorption spectra of PDI-3 in $CHCl_3$ solutions recorded under different concentrations, and at different time intervals following injection of CH_3OH.

Spectral characterization

As shown in Fig. S2, despite the different side-chains at their imide positions, monomeric PDIs exhibit quite similar UV-visible absorption and fluorescence spectra in $CHCl_3$ solutions. Furthermore, their aggregation behavior when increasing the concentrations or in self-assembling processes right after the injection of CH_3OH into $CHCl_3$ solutions resulting from their flat π-conjugated cores can be in-situ monitored by spectroscopic measurements, by taking PDI-3 as an example in Fig. S3. On the other hand, the strong fluorescence of monomeric PDI molecules almost disappears for crystalline 1D nanofibers, taking PDI-3 as examples in Fig. S4. Such fluorescence quenching is characteristic of the strong π-π stacking interaction within the molecular assembly.[2,3]

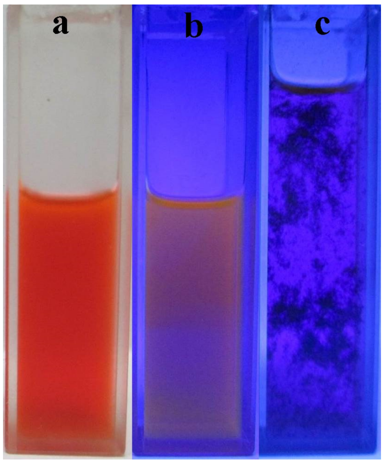

Fig. S4 Photo images of $CHCl_3$ solution (50 μmol L^{-1}) of PDI-3 under natural light (a), and UV-light (λ= 254 nm) before (b) and after injection of CH_3OH (c).

Cyclic voltammetry (CV) measurement

CV has been found as a highly successful method that can qualitatively reveal the reversibility of electron transfer during electrochemical reactions and also examine the electrical activity of organic materials by monitoring the oxidation and reduction in the form of a current–potential diagram. In this work, CV measurements were performed in a one-compartment cell containing a solution of PDI (10 mmol L^{-1}) in dry CH_3CN in the presence of tetra-n-butylammonium hexafluorophosphate (0.1 mmol L^{-1}) using a Model 263A potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control. For this, the working and counter electrodes were both Pt wires with a diameter of 1 mm, respectively. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode. Tests were carried out at a scan rate of 50 mV s^{-1} at room temperature under nitrogen.

Table S1 Forniter molecular orbital energies of PDIs estimated from electrochemical CV measurements.

Sample	E_{ox}/eV	E_{red}/eV	E_{HOMO}/eV	E_{LUMO}/eV
PDI-1	1.95	-0.75	-6.45	-3.75
PDI-2	2.0	-0.8	-6.5	-3.7
PDI-3	1.75	-0.65	-6.25	-3.85
		-0.67		-3.83

Note: HOMO and LUMO values were calculated using the equation.[4] E_{HOMO}= -4.5 eV - E_{ox}; E_{LUMO}= -4.5 eV - E_{red}.

Self-assembly of PDIs via Bulk Solvent-phase Transfer

1 D self-assembly of three PDI molecules were performed following Prof. Zang's previous work,[3] benefited to a balance between molecule solubility demonstrated by side-group functionization and the intrinsic π-π stacking interaction between perylene backbones. In general, a large amount of CH_3OH (400 mL) was injected into concentrated $CHCl_3$ (100 mL, 100 μmol L^{-1}) solutions of PDIs by dropwise addition,

and such bisolvent mixtures were sealed and standed for 24 h at room conditions. As a result, the original solutions were observed changing from clear phase to nanofibil suspensions, indicating effective molecular stacking of PDIs. For sequent tests, these dispersions were filtered using membrane filters (0.45 μm) and then dried at 100 °C under vacuum for 6 h. Alternatively, a quick injection and dispersion method was also employed. Specially, a concentrated $CHCl_3$ (100 mL, 100 μmol L^{-1}) solutions of PDI-3 was injected into CH_3OH (400 mL), and such bisolvent mixtures were stirred, sealed and standed for 24 h at room conditions. For sequent tests, this mixture was filtered using 0.45 μm membrane filters and then dried at 100 °C for 6 h.

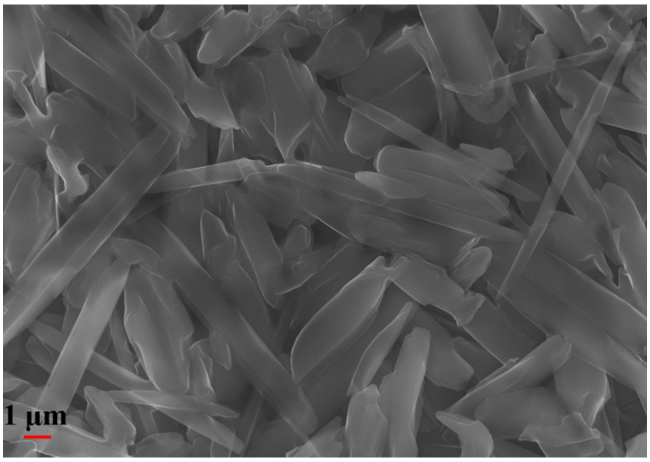

Fig. S5 SEM images of PDI-3 short nanorods fabricated from the quick injection and dispersion method.

In-situ deposition of Pt on TiO_2 or PDI nanofibers surfaces

For the preparation of Pt/TiO_2, a simple in-situ photo-reduction process was adopted. Typically, an aqueous solution of $H_2PtCl_6•6H_2O$ (3.3 mL, 0.1 g L^{-1}) was added to 100 mL of TiO_2 (P25) (0.025 g) aqueous methanol (Vwater:Vmethanol= 9:1) suspension. The reactant mixture was bath-sonicated for 5 min and stirred at 20 °C for 1 h under vacuum accompanied by irradiation under full arc light (λ> 300 nm; 500 W high-pressure mercury lamp) to facilitate the deposition of Pt, yielding a grey Pt(0.5 wt.%)/P25 powder after filtration, washing and finally drying at 100 °C for 12 h under vacuum.

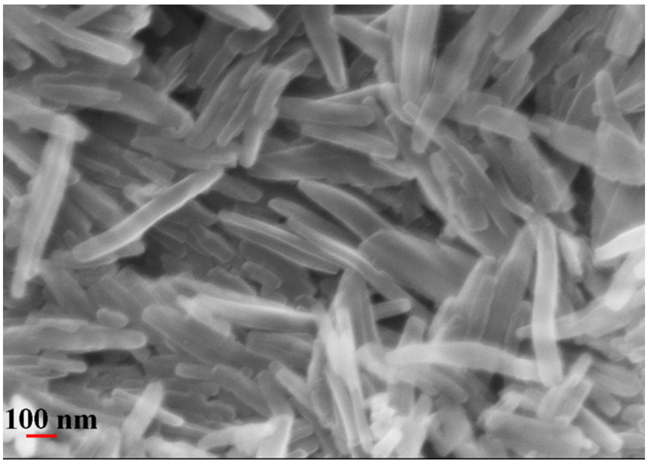

Fig. S6 SEM images of 0.5 wt.% Pt in-situ deposited PDI-1 nanorods.

Pt deposited PDI nanofibers (Pt/PDI) were prepared by the same method described above except the difference in the aqueous solution (Vwater:Vmethanol= 4:1). For photocatalytic tests, the system was evacuated three times prior to visible light irradiation, while canceling post-treatment, for example, filtration and drying.

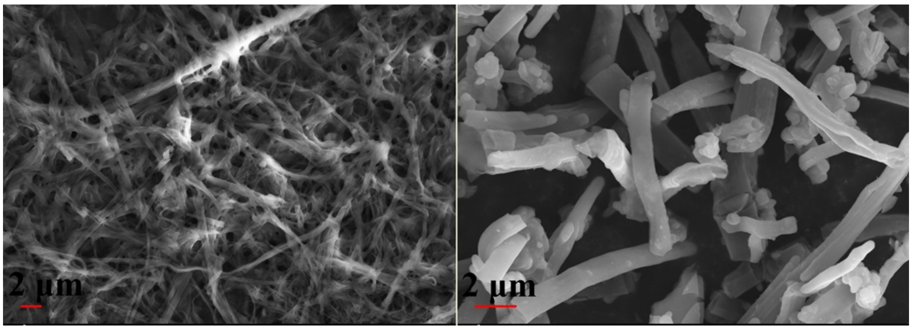

Fig. S7 SEM images of Pt(0.5 wt.%)/TiO_2(5 wt.%)/PDI-3 nanowires (left) and short nanorods (right) fabricated from the quick injection and dispersion method.

Dye-sensitized Pt/TiO_2 by PDI-based molecules

PDI (0.5 wt.% of the weight of Pt/P25) solution in $CHCl_3$ (100 μmol L^{-1}) was mixed with grinded Pt/P25 fine powders (0.025 g) in a mortar. The mixtures were grinded for 30 min, and then the powders were collected via evaporation for further analysis and photocatalysis.

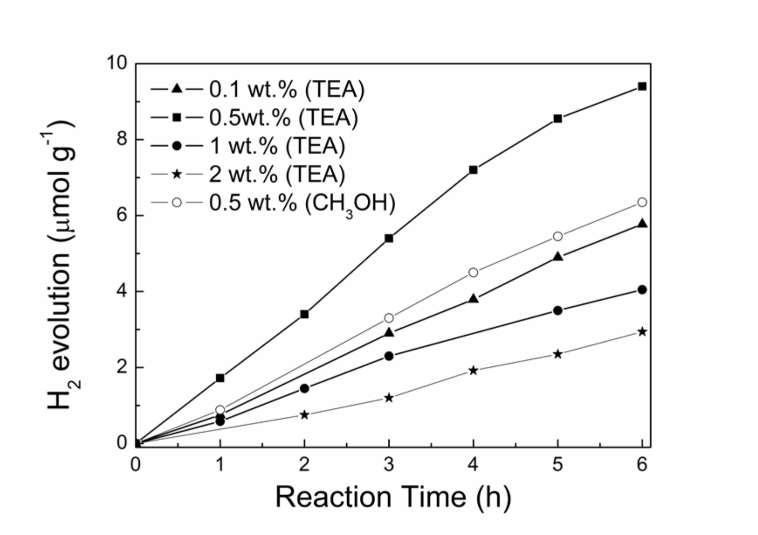

Fig. S8 The time courses of H_2 evolution over various ratio of Pt deposited PDI-1 nanorods with 10 vol.% CH_3OH or TEA as sacrificial reagents.

Preparation of Pt/TiO_2/PDI nanofiber composites

Under the conditions of stirring, 1 mL of dilute $CHCl_3$ solution containing 0.463 μL of Titanium(Ⅳ) isopropoxide was dropwise added into $CHCl_3$/CH_3OH mixtures of PDIs nanofibers (0.025 g; directly using after self-assembly process) within 1 h. After keeping stir for 2 h under N_2 production, 20 mL of aqueous solution (Vwater:Vmethanol= 1:9) was added drop by drop into this dispersion more than 2 h, further stirring for another 12 h. The resultant products were filtered and dried at 100 °C for half an hour. Finally, Pt nanoparticles were deposited on TiO_2 coated PDI nanofibers following above described in-situ photodeposition process.

Photocatalytic tests

In this study, the photocatalytic reaction was carried out in a Labsolar-H_2 photocatalytic water-splitting hydrogen production system (Bofeilaii, Beijing) using an outer-irradiation type reactor. The photocatalyst powder (50 mg) was pre-dispersed by ultrasonic treatment for 5 min, and then dispersed using a magnetic stirrer in aqueous solution (100 mL) containing 10 mL of CH_3OH or TEA as the sacrificial agent. A 400W Xenon lamp (CEL-S500, Beijing AULTT) equipped with a 420 nm cutoff filter, namely, effectively shelving light with wavelengths below 420 nm, was used as the light source (light power ca. 0.15 W cm^{-2} onto the aqueous solution surface) for photocatalytic irradiation, while a high-pressure mercury lamp (CHF-XM-500W, Beijing Trusttech Technology) for photo-chemical deposition of Pt. Before photo irradiation, the reactor was purged with nitrogen for about 30 min to remove oxygen, and the reaction temperature was kept at 20 ± 2 ^{o}C during the entire experiment. The evolved H_2 was detected and analyzed by an online gas chromatography (GC-system 7890A; Agilent Technologies) with N_2 as the carrier gas.

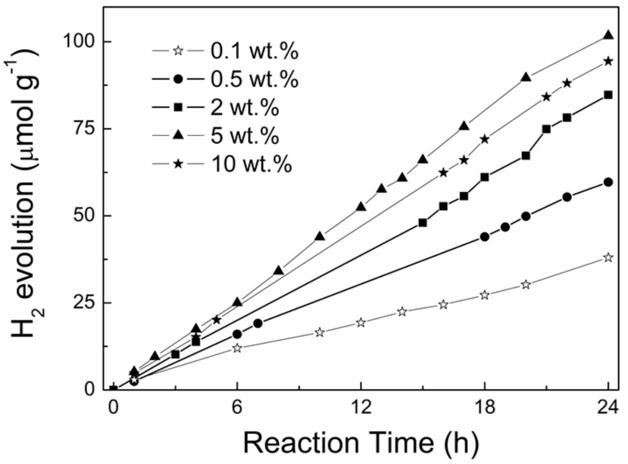

Fig. S9 The time courses of H_2 evolution over Pt(0.5 wt.%)/TiO_2/PDI-3 nanofibers varying from different amount of TiO_2 using 10 vol.% TEA as the sacrificial reagent.

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