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Rational design of donor-π-acceptor conjugated microporous polymers for photocatalytic hydrogen production

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ABSTRACT

Developing highly efficient catalysts for photocatalytic hydrogen generation from water splitting is one of the grand challenges in solar energy conversion. Herein, we report the design and synthesis of a library of donor-π-acceptor (D-π-A) conjugated microporous polymer (CMP) photocatalysts using pyrene, benzothiadiazole, and benzene (biphenyl) as donor, acceptor, and π crosslinker units, respectively. By adjusting the ratio of pyrene to benzothiadiazole units, a range of CMPs with various polymeric structures and components was synthesized and the influence of the molecular structures on the photocatalytic performance was comparatively investigated. Photocatalytic hydrogen evolution rate (HER) up to 106 μmol h^{-1} was achieved on PyBT-2 with a ratio of 9:2 of pyrene to benzothiadiazole under UV–vis light irradiation ($\lambda > 300$ nm). The structure-performance relationships revealed in this work offer a fundamental understanding in the rational design of CMPs for high performance organic photocatalysts.

1. Introduction

Hydrogen energy, as a green and sustainable energy system, has attracted much attention due to the higher calorific value and carbon-free emission upon combustion of hydrogen [1,2]. Photocatalytic hydrogen evolution from water splitting has been considered as a promising technology to address the energy crisis and environmental pollution [3–5]. In the past decades, most studies were mainly focused on inorganic metal-based semiconducting photocatalysts [6–9], which could absorb UV or visible light to generate electrons and holes. Particularly, significant advance has been achieved in carbon dots based semiconductor photocatalysts [10,11]. However, most inorganic photocatalytic materials suffer from low photocatalytic activity under visible-light, harsh preparation conditions, and rare elements [6]. Organic polymeric photocatalysts have been the subject of intense recent interest due to their diverse synthetic modularity, which allows the fine synthetic control over their chemical structures and electronic properties [12–16]. The linear conjugated polymers (*e.g.* poly(*p*-phenylene)s [17,18], poly(pyridine-2,5-diyl) [19,20]) showed moderate photocatalytic activity for hydrogen evolution from water under UV light irradiation [21]. Graphitic carbon nitride (g-C_3N_4), as the state-of-the-art organic photocatalyst, has been widely studied for hydrogen evolution from water splitting [22–26], and various synthetic strategies have been developed to improve the photocatalytic performance of g-C_3N_4 [27–29]. However, the synthesis of most g-C_3N_4 photocatalysts involves harsh preparation conditions and the real chemical structure is unknown, which limit the scope for fine-tuning chemical structure and electronic property [30–32].

Conjugated microporous polymers (CMPs) feature extended π-conjugation, high specific surface area, excellent physicochemical and thermal stability, tunable chemical structure and electronic property, making them attractive photocatalysts for hydrogen evolution [14,33–36]. Indeed, more recent studies revealed that CMPs are emerging as a novel class of photocatalysts for hydrogen production from water splitting and the photocatalytic activity could be improved by rational design of the polymer structure [13,14]. For example, Cooper et al. synthesized a series of pyrene-based CMPs photocatalysts with tunable optical gap, the obtained bare CMPs show highly photocatalytic activity for hydrogen evolution from water under visible-light irradiation [33]. They also developed the spirobifluorene-based CMPs with enhanced photocatalytic activity for hydrogen evolution under visible-light irradiation [37,38]. Yu et al. reported a series of bipyridyl-containing porous conjugated polymer photocatalysts and found that the photocatalytic activity could be greatly enhanced by improving

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charge separation processes and broadening light absorption because of the incorporation of bipyridyl unit [34,39]. Wang et al. developed a molecular structural design principle of conjugated polybenzodiazoles as organic photocatalysts for visible-light-promoted hydrogen evolution, and revealed that the linear conjugated polymer with an alternating phenyl-benzothidiazole polymer structure exhibited superior photocatalytic activity in H_2 evolution, compared to its three-dimensional polymer network counterparts [35]. We explored the influence of porosity, bandgap and charge transport on the photocatalytic performance of the perylene-containing CMPs photocatalysts [40,41]. Tian et al. prepared benzothiadiazole-based polymer dots organic photocatalysts, which also exhibited excellent photocatalytic activity for H_2 evolution from water splitting [42]. Beyond this, some other kinds of organic porous polymers with extended π-conjugation along the skeleton have also been developed for hydrogen evolution. For instance, the covalent triazine-based framework of CTF-T1 with π-stacked aromatic units showed excellent photocatalytic activity for hydrogen evolution under visible light irradiation [43]. The 2D imine-linked covalent organic framework of TFPT-COF with strong light harvesting capability also exhibited great potential for photocatalytic hydrogen generation under visible light irradiation [44]. Considering the synthetic diversity, flexible design ability and the variety of structural variations of CMPs, one could expect to develop more efficient CMPs photocatalysts for hydrogen evolution by the rational molecular design.

In this work, we constructed a library of donor-π-acceptor (D-π-A) CMPs photocatalysts and demonstrated their high photocatalytic performance for hydrogen evolution. Pyrene with planar structure and extended π-conjugation was employed as donor unit, the electron-withdrawing benzothiadiazole was selected as acceptor unit, and benzene or biphenyl was used as π crosslinker unit, respectively. The influences of molecular structure and the ratio of donor to acceptor on the photocatalytic performance of the resulting CMPs were comparatively studied. It was found that the photocatalytic performance of the D-π-A polymers is much better than that of the D-A alternatively polymers without π crosslinker unit and the D-π-D polymers without acceptor unit. Additionally, the ratio of donor to acceptor has a large influence on the photocatalytic performance of the resulting CMPs photocatalysts. This work highlights that the construction of D-π-A is crucial for the rational design of efficient CMPs photocatalysts.

2. Experimental section

2.1. Chemical and materials

Pyrene, bromine, 1,4-benzenediboronic acid, 4,7-dibromobenzothiadiazole, bis(pinacolato)diboron, [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$), potassium acetate and potassium carbonate were purchased from TCI. Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), dioxane, tetrahydrofuran (THF), nitrobenzene and *N*,*N*-dimethylformamide (DMF) were purchased from J&K Scientific Ltd. All chemicals were used as received without further purification. 1,3,6,8-Tetrabromopyrene, 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) and 3,5,3′,5′-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl were synthesized according to the reported methods [45–47].

2.2. Synthesis of the polymers

All the polymers were synthesized *via* Pd(0)-catalyzed Suzuki－Miyaura coupling reaction. A typical experimental procedure for PyBT-0 is given as an example. To a mixture of 1,4-benzenediboronic acid (322 mg, 2.0 mmol) and 1,3,6,8-tetrabromopyrene (518 mg, 1.0 mmol) in DMF (25 mL), an aqueous solution of K_2CO_3 (2.0 M, 5 mL) and $Pd(PPh_3)_4$ (10 mg, 8.6 μmol) were added. The mixture was degassed under freeze–pump–thaw, purged with N_2, and stirred at 150 °C for 48 h. Then, the mixture was cooled to room temperature and poured into water. The precipitate was collected by filtration, and washed with water, chloroform, tetrahydrofuran and methanol, respectively. Further purification of the polymer was carried out by Soxhlet extraction with tetrahydrofuran for 72 h. The product was dried in vacuum for 24 h at 70 °C and obtained as a green-yellow powder (Yield: 345 mg, 98%). Elemental combustion analysis (%) Calcd for $(C_{28}H_{14})_n$: C, 96%; H, 4%; Found C, 93.36%; H, 4.88%; Pd 0.000154% from ICP-MS. The detail of the synthesis for the other polymers is given in the Supporting Information.

2.3. Characterization

FT-IR spectrum was measured on a Tensor 27 FT-IR spectrometer (Bruker) in transmission mode at room temperature. Solid state magic angle spinning ^{13}C CP/MAS NMR measurement was carried out on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 10 kHz. Thermal properties of the polymer networks were evaluated using thermogravimetric analysis (TGA) with a differential thermal analysis instrument (Q1000DSC + LNCS + FACS Q600SDT) over the temperature range from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Morphology of the polymer networks was obtained using a field emission scanning electron microscope (SEM, JSM-6700F, JEOL, Japan). Powder X-ray diffraction measurement was carried out on an X-ray Diffractometer (D/Max-3c). Elemental analysis was performed on a EURO EA3000 Elemental Analyzer. Pd content was determined by inductively coupled plasma mass spectrometry (ICP-MS), where the sample (25 mg) was firstly digested in HNO_3/H_2O_2 (0.8 mL/0.2 mL) at 60 °C for 12 h, then cooled to room temperature and diluted with HNO_3 (4 mL). Surface areas and pore size distributions were measured by N_2 adsorption and desorption at 77.3 K using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer. Surface area was calculated in the relative pressure (P/P_0) ranging from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the N_2 adsorption branch using non-local density functional theory (NL–DFT). Sample was degassed at 120 °C for 12 h under vacuum (10^{-5} bar) before analysis. UV–vis diffuse reflection spectrum was obtained for the dry-pressed disk samples using a scanning UV–vis spectrophotometer (UV-Lambda 950, PerkinElmer, US) equipped with an integrating sphere assembly, using $BaSO_4$ as a reflectance sample. Fluorescent spectrum of the polymers was measured with a Shimadzu F-7000 PC fluorescence spectrometer by using excitation wavelength of 400 nm at room temperature. Time-resolved fluorescence spectroscopy was performed on Edinburgh Instruments FLS 920 fluorescence spectrometer.

2.4. Electrochemical measurements

Cyclic voltammetry (CV) measurement was carried out on a CHI660E (Chenhua, Shanghai) electrochemical workstation in a three-electrode-cell system: glassy carbon electrode as the working electrode, $Hg/HgCl_2$ electrode as the reference electrode, platinum wire as the counter electrode. The sample was prepared by first mixing ground polymer with 5 wt% Nafion, the mixture was dropped cast on top of a glassy carbon working electrode and let the solvent evaporate in a vacuum chamber for 60 min. The measurement was carried out in a solution of tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in acetonitrile with a scan rate of 100 mV s^{-1} in the range of –1.6 V to 1.2 V. For the conversion from $Hg/HgCl_2$ redox couple to the Normal Hydrogen Electrode (NHE), the equation of $E_{NHE} = E_{SCE} - 0.241$ V was applied. Three times were carried out for each sample to get an average value. The photocurrent of the polymer was measured on CHI660E electrochemical workstation with a bias voltage of 0.02 V under UV–vis light irradiation with 20 s light on-off cycles. The working electrode prepared from the polymer catalyst and 5 wt% Nafion was immersed in 0.1 M Na_2SO_4 aqueous solution.