Journal of Catalysis 350 (2017) 64–71

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Synthesis of 1,4-diethynylbenzene-based conjugated polymer photocatalysts and their enhanced visible/near-infrared-light-driven hydrogen production activity

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ARTICLE INFO

Article history:
Received 17 January 2017
Revised 21 February 2017
Accepted 21 February 2017

Keywords:
Conjugated polymer
Hydrogen production
Photocatalysis
Extended light absorption
Stability

ABSTRACT

Some conjugated polymer organic semiconductors with linear or network structures and tunable band gaps are found to be efficient metal-free photocatalysts for H_2 production. In the present work, three 1,4-diethynylbenzene-based linear conjugated polymer organic semiconductors (named P7-E, B-BT-1,4-E, and P17-E) were synthesized by palladium-catalyzed Sonogashira–Hagihara cross-coupling polycondensation. Compared with three reported 1,4-benzene-based linear conjugated polymer organic semiconductors (P7, B-BT-1,4, and P17), the ethynyl group is introduced into their backbones and the absorption edge is extended by 150–190 nm to the red/NIR light region (up to ~750 nm). Importantly, a negative shift of LUMO levels and enhanced photocurrent intensity are also observed, and their visible-light-induced H_2 production activity is improved dramatically. P7-E exhibits the highest H_2 production rate of 180.7 μmol/h under $\lambda > 420$ nm irradiation even without Pt co-catalyst loaded. Moreover, the apparent quantum yield (AQY) value of P7-E is 4.2% at 420 nm, which is much higher than that reported so far for P7. The present result indicates that small changes in the chemical structure of conjugated polymers can significantly tune their optical and photocatalytic properties, which provides a new direction for attaining more efficient organic conjugated polymer photocatalysts.

1. Introduction

Water splitting for H_2 production using semiconducting photocatalysts and sunlight is still a key target in the field of photocatalytic technology [1–4]. Much effort is focused on exploiting and modifying inorganic semiconductors [5,6], but few organic semiconductors have been investigated [7–10]. Among them, the most representative is g-C_3N_4 [11–16], and other analogues are also reported, such as poly(azomethine)s [17], hydrazone-based covalent organic frameworks [18], triazine-based frameworks [19], and linear poly(p-phenylene) [20]. However, the low quantum efficiency and the limited visible light absorption region ($\lambda < 450$ nm) of pure g-C_3N_4 without modification do not make it an ideal photocatalyst. To achieve high H_2 production activity and quantum efficiency, a catalyst should have high absorption ability in the visible light region, possess a CB level more negative than 0 V vs. NHE, and attain rapid e^-/h^+ separation, migration, and reaction efficiency.

Recently, a series of conjugated microporous polymer networks (CP-CMP1-CP-CMP15), synthesized through facile Pd(0)-catalyzed Suzuki–Miyaura polycondensation of four different monomers, were investigated for H_2 production under $\lambda > 420$ nm irradiation by Cooper et al., and it turned out that the visible light absorption region and optical gap (1.94–2.95 eV) of the photocatalysts are easily tuned; especially, one polymer with specific monomer composition gives highest the H_2 production rate of ~17.4 μmol/h without any co-catalyst [21]. Unlike g-C_3N_4, which has a limited basic constitutional unit and elemental composition, the chemical structure and geometric configuration of conjugated polymers can easily be changed by varying the monomer with/without modification and polycondensation method, and then the optical

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http://dx.doi.org/10.1016/j.jcat.2017.02.026

absorption and gaps can be tuned, which will further influence the photoactivity of the polymers [7]. Indeed, Yu et al. found that combination of a weak electron acceptor and strong electron donor into a polymer network can develop efficient photocatalysts, and the as-prepared PCP4e exhibits the highest H_2 production rate of 164 μmol/h under full spectrum irradiation, and an AQY of 1.8% is achieved at 350 nm with 2.0 wt.% Pt as co-catalyst [22,23].

To further improve the H_2 production activity of polymer, planarized fluorene, carbazole, dibenzo[*b*,*d*]thiophene, or dibenzo[*b*,*d*]thiophene sulfone units were introduced into the linear poly(p-phenylene) structure, and the obtained planarized co-polymers (P2–P7) exhibited higher H_2 production activity than that of poly (p-phenylene) [24]. In particular, the introduction of dibenzo[*b*,*d*] thiophene sulfone (P7) resulted in the highest H_2 production rate of 92.0 μmol/h under $\lambda > 420$ nm with AQY of 2.7% at 420 nm in the absence of additional co-catalyst. The superiority of 1D linear polymers to 3D network analogues for H_2 production was also investigated by Wang's group using electron-donor–acceptor conjugated polybenzothiadiazoles as photocatalysts, and it was found that 1D linear B-BT-1,4 exhibited the largest absorption area and the highest H_2 production activity (116 μmol/h) under $\lambda > 420$ nm. Moreover, the AQY of the photocatalyst was 4.01% at 420 nm with 3.0 wt.% Pt loaded [25]. In addition, a linear polymer (P17) without heteroatoms, synthesized by polycondensation of 1,4-benzene diboronic acid and 1,6-substituted pyrene, also attained H_2 production of 5.0 μmol/h under $\lambda > 420$ nm [21].

Till now, conjugated polymers have been synthesized by different polycondensation routes, such as the Suzuki cross-coupling reaction, Schiff-base reaction, Sonogashira–Hagihara reaction, Yamamoto reaction, Friedel–Crafts reaction, oxidative coupling reaction, phenazine ring fusion reaction, and cyclotrimerization reaction [7,26]. As can be seen, all the above polymers reported for H_2 production are synthesized by the Suzuki cross-coupling reaction, but Vilela et al. synthesized conjugated microporous poly(benzothiadiazole) networks (CMP_0-CMP_60) on SiO_2 NPs by palladium-catalyzed Sonogashira–Hagihara cross-coupling polycondensation for photocatalytic conversion of a-terpinene into ascaridole [27]. In contrast to B-BT-1,3,5 (conjugated polybenzothiadiazoles attained through the Suzuki cross-coupling reaction by Wang et al.), the CMP_0 exhibits at least a 100 nm red shift in the visible light absorption edge, which should be caused by the introduction of ethynyl groups into the backbone of B-BT-1,3,5 through Sonogashira–Hagihara cross-coupling polycondensation, and the conjugated system is then extended [25,27]. Moreover, we have recently introduced BBT onto the surfaces of TiO_2 [28] and Bi_2MoO_6 [29] by the in situ method, and the BBT–TiO_2 composite exhibited good activity for visible-light-driven hydrogen evolution [28]. Thus, one can expect to improve the H_2 production activity of the linear polymers that have been reported in the broader visible light region by introduction of ethynyl groups.

Herein, ethynyl groups are introduced into three reported linear polymer structures, P7, B-BT-1,4, and P17 (refer to Fig. 1) by palladium-catalyzed Sonogashira–Hagihara cross-coupling polycondensation to form new linear polymers, and named P7-E, B-BT-1,4-E, and P17-E, respectively. Indeed, the introduction of ethynyl groups causes a more than 150 nm red shift on the absorption edge, a negative shift of LUMO levels of the corresponding polymers, and enhanced photocurrent behavior, and thus the visible-light-driven H_2 production activities and AQY values at 420 nm of the new polymers are significantly improved. Especially, P7-E exhibits the highest H_2 production rate of 180.7 μmol/h under $\lambda > 420$ nm with an AQY of 4.2% at 420 nm in the absence of additional Pt-cocatalyst, and the AQY at 420 nm can be further improved to be 7.2% when 3.0 wt.% Pt is loaded.

2. Experimental

2.1. Materials

N,*N*-dimethylformamide (DMF), triethylamine (TEA), dichloromethane (CH_2Cl_2), triethanolamine (TEOA), copper(I) iodide (CuI), and methanol were purchased from Sinopharm Chemical Reagent. Bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) was obtained from Energy Chemical. 1,6-Dibromopyrene and 1,4-diethynylbenzene were supplied by Shanghai Bepharm Corporation. All of the reagents were analytically pure level and used directly without further purification. B-BT-1,4, P7, P17, and 3,7-dibromodibenzo[*b*,*d*]thiophene 5,5-dioxide were synthesized according to the reported procedure [21,24,25]. All chemicals and solvents were used as received unless otherwise specified.

2.2. Characterization

The functional groups were measured by Fourier transform infrared spectroscopy (FT-IR, Nicolet Inc., USA) on a pressed pellet with KBr. Solid state NMR experiments were carried out using a

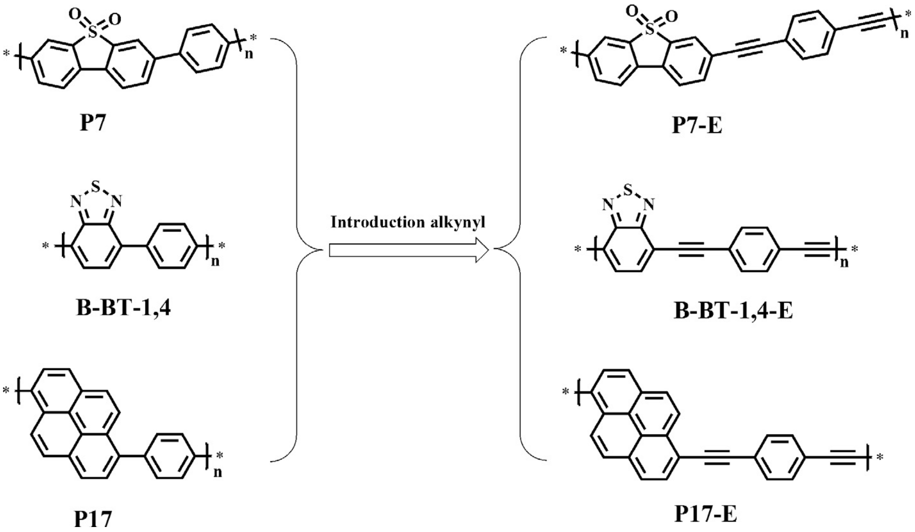

Fig. 1. Structures of two series of conjugated polymers.