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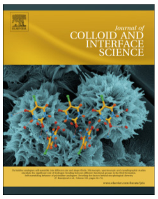


Regular Article

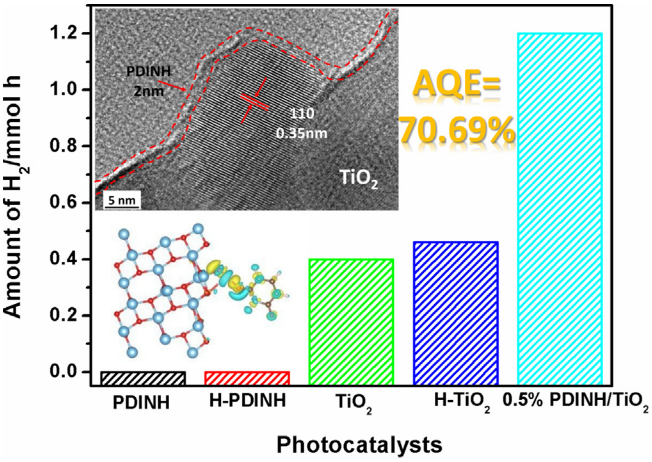
Self-assembled supramolecular system PDINH on TiO_2 surface enhances hydrogen production

Xin Li [a], Xingshuai Lv [b], Qianqian Zhang [a,*], Baibiao Huang [a,*], Peng Wang [a], Xiaoyan Qin [a], Xiaoyang Zhang [a], Ying Dai [b]

[a] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China
[b] School of Physics, Shandong University, Jinan 250100, PR China

GRAPHICAL ABSTRACT

$PDINH/TiO_2$ organic-inorganic hybrid displays a higher photocatalytic H_2 production activity and photocurrent intensity than pure PDINH and TiO_2, the apparent quantum efficiency for H_2 production over 0.5% $PDINH/TiO_2$ reaches as high as 70.69% using irradiation at 365 nm.



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ABSTRACT

Constructing organic-inorganic hybrids is one of the hopeful strategies to improve photocatalyst performance. In this study, perylene-3,4,9,10-tetracarboxylic diimide (PDINH) and commercial TiO_2 P25 are chosen as raw materials to construct a $PDINH/TiO_2$ organic-inorganic hybrid, which has higher photocatalytic H_2 production activity and photocurrent intensity than pure PDINH and TiO_2, respectively. The apparent quantum efficiency for H_2 production over 0.5%$PDINH/TiO_2$ reaches as high as 70.69% using irradiation at 365 nm. Moreover, XRD, DRS, HRTEM, FT-IR, and XPS are used to characterize the crystal structure, optical absorption, morphology, molecular structure, and chemical bonds, as well as the elemental and chemical states of $PDINH/TiO_2$ organic-inorganic hybrid. The interfaces between PDINH and TiO_2, which largely determine photocatalytic performance, is also analyzed systematically. Furthermore, charge density difference ($\Delta\rho$) is used to analyze the electron-ion interactions of PDINH and TiO_2, and reveals that substantial charge transfer occurs from PDINH to TiO_2.

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* Corresponding authors.
E-mail addresses: qianqianzhang@sdu.edu.cn (Q. Zhang), bbhuang@sdu.edu.cn (B. Huang).

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1. Introduction

In recent years, the photocatalytic water-splitting system has attracted enormous attention because it is a promising approach to gain hydrogen energy (H_2) by directly converting earth-abundant solar energy resources [1]. Compared with single-component photocatalysts, compound materials usually display better photocatalytic activities due to their high separation efficiencies of photogenerated electron-hole pairs [2]. Therefore, constructing organic-inorganic hybrids is a promising strategy to gain compound photocatalysts that can not only combine the advantages of organic and inorganic semiconductors but also bring forth new features that are different from those of single component [3,4].

Unlike common organic materials, such as polyaniline, polythiophene, polypyrrole, poly(*p*-phenylene), poly(3,4-ethylenedioxy thiophene), and their derivatives, PDINH is a typical *n*-type organic semiconductor with unique optical and electronic properties [5–7]. These special properties of PDIs have increased the research with regard to their applications in organic field-effect transistors (OFETs) [8], organic solar cells [9,10], fluorescence switches [11], sensors [12], photodynamic therapy (PDT) [13], and light-emitting diodes (LEDs) [14]. Moreover, self-assembled PDI supramolecular systems can be gained through $C{=}O\cdots H{-}N$ hydrogen bonding and π-π stacking between PDINH molecules, leading to improved photoinduced electron transfer along the π-π stacking direction and potential application in photocatalysis, such as Zn-PDI [15], Ni-PDI [16], and Ru-PDI [17]. Furthermore, PDIs can be used as organic components to construct organic-inorganic hybrid photocatalysts. For example, Zhu's group successfully fabricated PTCDI/P25 hybrid using 4-methoxylbenzylamino as a functional group of PDI [18]. Nagarajan's team revealed a new symmetrical *N,N′*-di(octadecyl)perylene-3,4,9,10-tetracarboxylic bisimide (DPBI) and loaded it on TiO_2 to enhance photocatalytic activity via degradation of Reactive Orange 4 [19]. Wang and his co-workers reported that PDI molecules, which were modified with electron-rich 4-dimethylaminobenzyl group highly improved the photocatalytic H_2 evolution of TiO_2 [20]. However, all the above studies mainly focused on PDI derivatives; moreover, the applications based on non-substituents at the parent skeleton (PDINH) in photocatalysis had been rarely investigated systematically. Recently, Zhu and his co-workers successfully fabricated a self-assembled PDINH supramolecular system photocatalyst for degradation of phenol and photocatalytic O_2 evolution via a rapid and simple solution dispersion [21]. However, to date, organic-inorganic hybrid photocatalysts combining PDINH with inorganic semiconductor have not been reported.

In this study, we chose commercial PDINH and TiO_2 P25 as raw materials to construct PDINH/TiO_2 organic-inorganic hybrid, which has higher photocatalytic H_2 production activity and photocurrent intensity than pure PDINH and TiO_2. The interfaces between PDINH and TiO_2, which largely determine photocatalytic performance, were also analyzed systematically. The $-C{=}O\cdots H$ hydrogen bond in the interfaces between the $-OH$ of TiO_2 and $-C{=}O$ of PDINH, which acted as a short and fast channel for migrating the photogenerated charge carriers from PDINH to TiO_2, was proposed to explain the reduced photoinduced charge carrier recombination and increased photocatalytic H_2 production activity.

2. Experimental section

2.1. Preparation of catalysts

All chemical materials were purchased from commercial sources and used without further purification unless particularly pointed out. The TiO_2 P25 powder, which was purchased from Degussa, had a specific surface area of about 50 m^2/g and average particle size of about 25 nm, and the ratio between anatase and rutile was 80:20. In a typical experiment, initially, 300 mg TiO_2 P25 powder was dispersed in 10 mL concentrated sulfuric acid (Sinopharm Chemical Reagent Co., Ltd, 95–98%) for 12 h. Afterward, a certain amount of perylene-3,4,9,10-tetracarboxylic diimide (PDINH, J&K, 95%) was dissolved in the TiO_2 solution under ultrasonic treatment for 10 min, and 100 mL deionized water (DI) was added slowly to the above dispersion solution under constant stirring for 120 min. The nanoparticles were centrifuged, washed with DI water and ethanol thrice, and air dried at 60 °C for 12 h. Loading concentrations of PDINH were changed from 0.1 wt% to 2.0 wt%, and the corresponding photocatalysts were denoted as 0.1% PDINH/TiO_2, 0.3% PDINH/TiO_2, 0.5% PDINH/TiO_2, 1.0% PDINH/TiO_2, and 2.0% PDINH/TiO_2.

For comparison, pure H-PDINH was also prepared using the above method without TiO_2. Furthermore, to analyze the effect of sulfuric acid on TiO_2, pure TiO_2 was treated with concentrated sulfuric acid for 12 h, and the H_2SO_4-treated TiO_2 powder that was gained after centrifugation was washed and dried at 60 °C for 12 h in air, and the photocatalyst that was gained was denoted as H-TiO_2.

To study the effect of the ratio between anatase and rutile phases of TiO_2 on the final properties of PDINH/TiO_2 systems, different ratios of anatase and rutile phases in TiO_2 and corresponding 0.5% PDINH/TiO_2 samples were prepared. The anatase phase TiO_2 was prepared by a simple hydrothermal method [22], and 25 mL tetrabutyl titanate ($Ti(OBu)_4$, Sinopharm Chemical Reagent Co., Ltd, 98%) and 3 mL hydrofluoric acid (HF, Sinopharm Chemical Reagent Co., Ltd, 47%) were mixed thoroughly in a 100-mL Teflon autoclave and kept at 180 °C for 24 h. The pure anatase phase TiO_2 powder (A-TiO_2) was collected, washed, naturally cooled to room temperature, and then dried. Moreover, a series of mixed phases of TiO_2 with different ratios of anatase and rutile phase was gained by annealing Degussa P25 powder at different temperatures (600 °C and 700 °C) in air, and the corresponding samples were denoted as P25-600 and P25-700. Pure rutile phase TiO_2 powder (R-TiO_2) was gained when the annealing temperature increased to 800 °C [23] in this work.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) patterns were used to characterize the structures of samples on a Bruker AXS D8 Advance powder diffractometer with a Cu Kα X-ray tube ($\lambda = 0.154056$ nm) at room temperature. The morphology and crystallinity of the products were analyzed by using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) on a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. UV–VIS diffuse reflectance spectra (DRS) were analyzed using a Shimadzu UV 2500 recording spectrophotometer equipped with an integrating sphere, and $BaSO_4$ was used as a reference. FT-IR spectra were recorded by using a FTLA2000-104 spectrometer with the standard KBr pellet method. X-ray photoelectron spectroscopy (XPS) spectra were characterized by using a Thermo Fisher Scientific Escalab 250 spectrometer and calibrated the peak position of C 1s at 284.6 eV. Photoluminescence (PL) measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer with 257 nm excitation wavelength at room temperature.

2.3. Hydrogen evolution measurements

To evaluate the photocatalytic hydrogen evolution of PDINH/TiO_2 samples, a top irradiation vessel connected to a glass-