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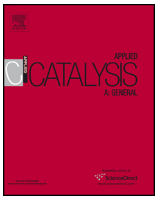

Enhancement of visible-light-driven photocatalytic H_2 evolution from water over g-C_3N_4 through combination with perylene diimide aggregates

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ABSTRACT

Graphitic carbon nitride (g-C_3N_4) is among the most promising metal-free photocatalysts for H_2 production from solar-driven water reduction. However, the photocatalytic efficiency of bulk g-C_3N_4 powders is limited. In this work, molecular aggregates of perylene tetracarboxylic diimides (PTCDIs, a robust class of air-stable n-type organic semiconductor) were loaded via solution processing on the surface of g-C_3N_4, which is pre-deposited with cocatalyst Pt nanoparticles. The PTCDIs/Pt/g-C_3N_4 composites thus fabricated exhibit broader visible-light response than Pt/g-C_3N_4, and possess excellent photochemical stability. The initial intramolecular charge transfer features of the PTCDIs, as well as their energy levels being matched to g-C_3N_4, ensure subsequent charge separation in the PTCDIs/Pt/g-C_3N_4 composites. When the composites are dispersed into aqueous solutions containing triethanolamine as a sacrificial electron donor, a tenfold enhancement of H_2 evolution activity ($\sim$0.375 μmol h^{-1}) is achieved compared to bare Pt/g-C_3N_4 under visible-light ($\lambda \geq 420$ nm) irradiation.

1. Introduction

Hydrogen (H_2) is an ideal green energy source to alleviate the impact of fossil fuel scarcity and environmental risk because it is renewable, energy dense, and environmentally friendly [1]. Splitting water using a photocatalytic reduction reaction on a semiconductor surface utilizing abundant solar energy has been demonstrated as a promising approach for clean, cost-effective production of H_2 [2–4]. In contrast to most inorganic semiconductor photocatalysts, metal-free polymeric graphitic carbon nitride, g-C_3N_4, is an inexpensive, effective, and photochemically stable organic semiconducting photocatalyst for H_2 generation from water reduction [5–7]. Related work originates from Wang's pioneering work in 2009 and has attracted intense interest in subsequent years, yielding a great deal of promising results [7,8]. However, despite its appealing features, the photocatalytic activity of bare g-C_3N_4 is relatively unsatisfied [9,10]. There are three main reasons for the unsatisfactory efficiency of as-prepared bulk g-C_3N_4 powders: (1) limited utilization of visible-light due to its moderate bandgap ($E_g = \sim$2.7 eV, corresponding to an optical wavelength of $\sim$460 nm); (2) rapid recombination of photoinduced electrons and holes due to the unavoidably disordered structure or defects; and (3) relatively small Brunauer–Emmett–Teller (BET) surface area (normally below 10 m^2 g^{-1}) [7,10]. Consequently, many attempts have been made to improve the photocatalytic performance. Combination of g-C_3N_4 with dye molecules may improve their visible-light response via sensitization process [7,8]. Normally, Pt nanoparticles are loaded onto the surface of g-C_3N_4 matrix to enhance their photocatalytic water reduction efficiency as cocatalyst [10]. Additionally, the presence of sacrificial electron donors, such as triethanolamine, methanol and ethylenediaminetetraacetic acid, is often necessary for photocatalytic H_2 production from water [7]. To enlarge the BET surface of g-C_3N_4, various micro/nanostructures (like nanoporous, nanosheet, etc.) have been constructed via different fabrication methods [7,10]. The morphologies are highly affected by factors such as precursors, condensation temperatures, and complex fabrication processes [7,10]. Thereby, bulk-phase g-C_3N_4 is still a representative good candidate to study the photosensitizing action of dyes.

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For visible-light-driven H_2 production, dyes with or without metals, such as ruthenium(II) complexes, nickel–thiourea–triethylamine complex, magnesium phthalocyanine, Eosin Y, and Erythrosin B, have been used as sensitizers for g-C_3N_4 [11–15]. These dyes suffer from disadvantages such as requiring expensive rare earth elements, poor stability under light irradiation or in water, limited visible-light response, complicated synthesis, or difficult functionalization. Therefore, their practical applications are limited [2–4]. In contrast, perylene tetracarboxylic diimides (PTCDIs), a robust class of air-stable n-type organic semiconductor molecules, exhibit high thermal and photostability, and strong light absorption (nearly covering the whole visible light spectrum) [16,17]. With suitable structural modification and the planar π-conjugate structure, PTCDIs can be fabricated into photoactive semiconductor heterostructures [17–20]. These features make PTCDIs strong candidates for light harvesting sensitizers in dye-sensitized photochemical systems. In fact, such applications have achieved enormous attention in organic photovoltaic fields, as well as TiO_2-based photo-degradation of pollutants [20–23]. On the other hand, PTCDIs solid owns an appropriate band structure, which encompasses the reduction and oxidation potentials of water [4,17]. However, the applicability of PTCDIs in photocatalytic H_2 production field is seldom reported. The main obstacles are considered to be their electron-deficient π-conjugated cores, rapid charge recombination, and inefficient charge transport in disorder molecular system [2,20,23].

However, large exciton diffusion lengths and high electron mobility of PTCDIs can be achieved through the extended π–π electronic interaction enabled by the cofacial molecular stacking [17]. Significant efforts have focused on designing intramolecular electron donor–acceptor structures and constructing orderly, one-dimensional (1D) nanostructures of PTCDIs (e.g., nanofiber) via self-assembly driven by strong π–π stacking of their large planar aromatic cores [21,22,24]. In 2010, Zang's group reported that an electron-rich dimethylaminobenzyl group attached to the imide-position of the PTCDIs molecule can facilitate intramolecular charge separation under visible-light irradiation. Meanwhile, efficient charge transport was achieved along long axis of nanofibers under white light [19]. Inspired by this, we have recently demonstrated the applicability of a series of PTCDI nanofiber composites for photocatalytic H_2 production from water reduction [25]. Meanwhile, a similar photocatalytic concept was also proven for the nanofibers of perylene monoimides [26].

In this work, we reported on a novel visible-light-driven composite photocatalyst employing g-C_3N_4 as the matrix and PTCDIs assembles as the adjuncts (Fig. 1). g-C_3N_4 was prepared from one-step thermal condensation of a cheap and abundant precursor, melamine. Symmetric PTCDI-1 and asymmetric PTCDI-2 molecules modified with 4-dimethylaminobenzyl and/or dodecyl side groups were synthesized to explore the effect of side-chain modification on aggregation behaviour, nanostructure morphology and photocatalytic activity. After photo-deposition of Pt on g-C_3N_4, a bisolvent-exchange triggered aggregation method [27] was used to prepare PTCDI/Pt/g-C_3N_4 composites. Then, the composite particles were suspended in aqueous solutions containing triethanolamine (sacrificial electron donor) to sustain the photocatalytic reaction under visible-light illumination. For comparison, the photocatalytic activity of Pt/g-C_3N_4 as well as Pt/PTCDIs nanofiber composites was also investigated to help understand the improved photocatalytic activity of PTCDI/Pt/g-C_3N_4 composites.

2. Experimental

2.1. Preparation of materials

Bulk g-C_3N_4 powders (Fig. 2a) used in this study were prepared using simple pyrolysis technique through thermal polycondensation of melamine at 600 °C for 4 h under ambient pressure in air [7,8,28]. g-C_3N_4 thus prepared contains structural defects such as =NH, —NH_2, and —OH groups which can be attributed to imperfect condensation and adsorbed H_2O [10,29,30]. The resultant brown–yellow powder was collected, ground and used as the photocatalyst matrix without any further treatment. Pt as a cocatalyst for photocatalytic H_2 evolution was loaded onto the g-C_3N_4 powders via a typical and simple in situ photoreduction procedure from an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ [25]. The greyish yellow powder Pt/g-C_3N_4 (Fig. 2b) was ground and used as sensitization matrix for the following test without further treatment. The synthesis of symmetric PTCDI-1 (Fig. 2c) and asymmetric PTCDI-2 (Fig. 2d) was performed following a typical Langals' procedure with yields of ca. 80% and 45%, respectively, that is, by condensation of commercially available perylene 3,4,9,10-tetracarboxylic dianhydride (PTCDA) with 4-(dimethylamino)benzylamine and/or dodecylamine in molten imidazole under a N_2 protection [17,19].

2.2. Preparation of PTCDIs/Pt/g-C_3N_4 composites

10 mL of PTCDIs solution in $CHCl_3$ (125 mg L^{-1}) was mixed with ground Pt/g-C_3N_4 fine powders (25 mg) in a 100 mL round-bottom flask. The mixtures were ultrasonicated and stirred at 25 °C for 6 h in the dark, and then another 2 h after the injection of 40 mL of CH_3OH dropwise. The precipitates were collected by vacuum suction filtration using 0.45 μm membrane filter and then dried at 80 °C for 6 h to give PTCDI-1/Pt/C_3N_4 (Fig. 2e) and PTCDI-2/Pt/C_3N_4 powders (Fig. 2f). Comparatively, 1D self-assembly of PTCDIs nanofibers were performed via feasible bisolvent phase-transfer process by injecting a large amount of CH_3OH (400 mL) into concentrated $CHCl_3$ (100 mL; 400 μmol L^{-1}) solutions of PTCDIs [19,25]. Then, Pt (0.5 wt.%) was deposited on PTCDIs nanofibers (denoted as Pt/PTCDIs) following the same in situ photo-reduction process just as above described to prepare Pt/g-C_3N_4.

2.3. Characterization

Thermogravimetry analysis (TGA) of PTCDIs was performed on a NETZSCH STA 449F3 instrument. The samples were heated in an

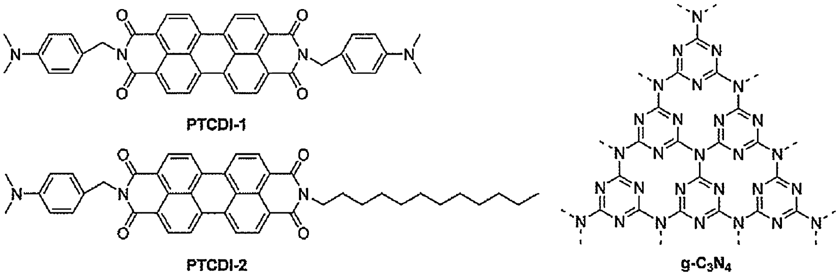

Fig. 1. Chemical structures of PTCDI-1 and PTCDI-2 molecules, and g-C_3N_4.