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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# Visible-light-driven Photocatalytic H<sub>2</sub> Evolution from Aqueous Suspensions of Perylene Diimide Dye-sensitized Pt/TiO<sub>2</sub> Catalysts

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

TiO<sub>2</sub> is always among the most important semiconductor photocatalysts for solar light-driven H<sub>2</sub> production from photocatalytic water reduction. Commercialized mixed-phase Degussa P25 nanoparticle has been demonstrated as the most popular TiO<sub>2</sub>. However, its superiority can't be exerted in the visible-light region. In this work, molecular aggregates of perylene tetracarboxylic diimide (PTCDI, a kind of air-stable n-type organic semiconductor bearing electron-rich phenylamino moiety and dodecyl side-chain) were employed as a sensitizer to combine with Pt/TiO<sub>2</sub> nanoparticles via solution processing. The PTCDI/Pt/TiO<sub>2</sub> composites thus fabricated exhibit broad visible-light response and excellent photochemical stability. The initial intramolecular charge transfer of PTCDI and its energy level being well matched to TiO<sub>2</sub>, ensure effective charge transfer among the PTCDI/Pt/TiO<sub>2</sub> composite. When 25 mg of the composite powders are suspended into aqueous solution containing triethanolamine as a sacrificial electron donor, stable H<sub>2</sub> evolution with an activity of ~0.075 μmol h<sup>-1</sup> is achieved under visible-light (λ ≥ 420 nm) irradiation. Both intramolecular electron transfer from the electron rich 4-dimethylaminobenzyl group to the perylene core of PTCDI and the intermolecular charge transfer from PTCDI to TiO<sub>2</sub> are key to the effective visible-light photoactivity.

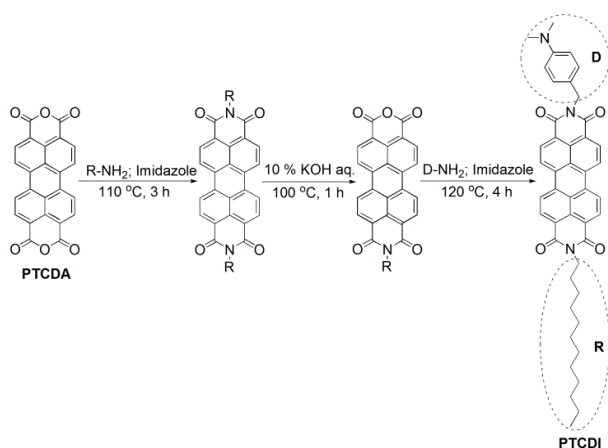
## Introduction

Photocatalytic water reduction over semiconductor nanoparticles utilizing solar light has been recognized as one of the most promising approaches to produce H<sub>2</sub>, an ideal clean and renewable energy source with high energy capacity.<sup>1-5</sup> The work initiated in 1970s with an inorganic semiconducting photocatalyst, titanium dioxide (TiO<sub>2</sub>).<sup>6</sup> In contrast to many other inorganic semiconductors (e.g., metal oxides and sulfides),<sup>2</sup> graphitic carbon nitride,<sup>7</sup> crystalline polyimides,<sup>8</sup> and carbon materials,<sup>9-12</sup> which have attracted intense interest in subsequent years, TiO<sub>2</sub> quite benefits from its cost-saving, effective and photochemically stable.<sup>13</sup> Much promising, high-activity, mixed-phase TiO<sub>2</sub> nanoparticles have been brought into market under the brand of Degussa P25. Despite its appealing features, low photoconversion efficiency still limits its use in practical applications.<sup>14</sup> The main obstacles are attributed to the following two aspects: its large bandgap (E<sub>g</sub> = ~3.2 eV), thus it can only be excited by ultraviolet light (only covering 4% of the solar spectra), and the rapid bulk and surface recombination of photoinduced electrons and holes.<sup>2,5</sup> Consequently, increasing research efforts have now been put into eliminating these drawbacks.<sup>15</sup> Normally, loading of Pt nanoparticles as cocatalyst on the surface of TiO<sub>2</sub> nanoparticles and adding sacrificial electron donors (e.g., triethanolamine and methanol) into the aqueous solutions are often necessary for photocatalytic H<sub>2</sub> production from water by inhibiting the fast charge recombination and the back reaction of H<sub>2</sub> and O<sub>2</sub> to water.<sup>6</sup> Additionally, adsorption of dye molecules on the surface of TiO<sub>2</sub>

nanoparticles has been proven as one of the most facile approaches to utilize the visible-light (~43% of the solar spectra).<sup>14,16</sup> However, most reported photosensitizing dyes suffer from disadvantages such as expensive, thermally unstable, photobleaching, limited visible-light response, or difficult functionalization.<sup>6,14,17-20</sup> Therefore, it is highly desirable to develop novel dyes in this aspect.

Perylene diimides, a series of well-known n-type organic semiconductor molecules, exhibit unique photochemical and thermal stability under long-term light irradiation, and strong visible-light response.<sup>21-23</sup> In contrast to the extremely attractive applications of perylene diimide-based semiconductor systems for fabricating organic optoelectronic devices, such as organic photovoltaic cells, organic field effect transistors, organic light-emitting diodes, dye lasers, sensors, and so on,<sup>21-24</sup> very limited appealing results on photocatalysis field have been reported in the last decades. Recently, significant efforts have focused on the applicability of a series of hybrid photocatalyst composites, TiO<sub>2</sub> coated nanofibers of perylene diimides, for visible-light-driven H<sub>2</sub> generation from photocatalytic water reduction.<sup>25</sup> Although the fabrication of TiO<sub>2</sub> coatings from organic titanium complex precursors via in-situ hydrolytic processing was facile, the amorphous feature of TiO<sub>2</sub> limits their photoactivity compared to well crystallized Degussa P25.<sup>14,15</sup> Moreover, taking advantage of fine structural modification, perylene tetracarboxylic diimide (PTCDI; Scheme 1) modified with electron-donating 4-dimethylaminobenzyl group and inert dodecyl chain at the imide-position of the electron-deficient π-conjugated core has displayed

much more effective intramolecular charge separation than 4-dimethylaminophenyl group modification, and exhibits excellent charge transport along one-dimensional nanofibers (self-assembled from a bisolvent interfacial transfer process) under visible-light.<sup>25-28</sup> According to electrochemical cyclic voltammetry (CV) measurement, PTCDI has energy levels (vs. vacuum level) at the positions of -6.3 eV and -3.7 eV for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.<sup>26,27</sup> This ensures its visible-light absorption corresponding to a bandgap of 2.6 eV and its matched energy levels to TiO<sub>2</sub> (conduction band (CB): -4.2 eV; valance band (VB): -7.4 eV).<sup>6</sup> These features make PTCDI as a candidate for visible-light harvesting sensitizer in commercial TiO<sub>2</sub>-based photocatalytic water reduction system.



**Scheme 1** Synthesis route and chemical structure of PTCDI molecule.

In this work, to develop a facile and efficient solar water reduction H<sub>2</sub> generation system, a novel visible-light-driven composite photocatalyst employing commercial TiO<sub>2</sub> (P25; pre-deposited with cocatalyst Pt) as the main body and PTCDI assembles as the photosensitizer were fabricated. Asymmetric PTCDI was synthesized following a typical Langals' procedure reported before (Scheme 1).<sup>25-27</sup> After photo-deposition of

cocatalyst Pt on TiO<sub>2</sub>, a bisolvent-exchange triggered aggregation strategy was used to prepare PTCDI/Pt/TiO<sub>2</sub> composite. The weight ratio of PTCDI to Pt/TiO<sub>2</sub> was adjusted to tune the photocatalytic activity. Following that, the composite particles were suspended in aqueous solution containing triethanolamine (sacrificial electron donor) to sustain the photocatalytic reaction under visible-light illumination. In comparison, the photocatalytic activity of Pt/TiO<sub>2</sub> and another composite fabricated by mixing PTCDI solution and Pt/TiO<sub>2</sub> together were also explored to evaluate the photocatalytic activity of PTCDI/Pt/TiO<sub>2</sub> composites.

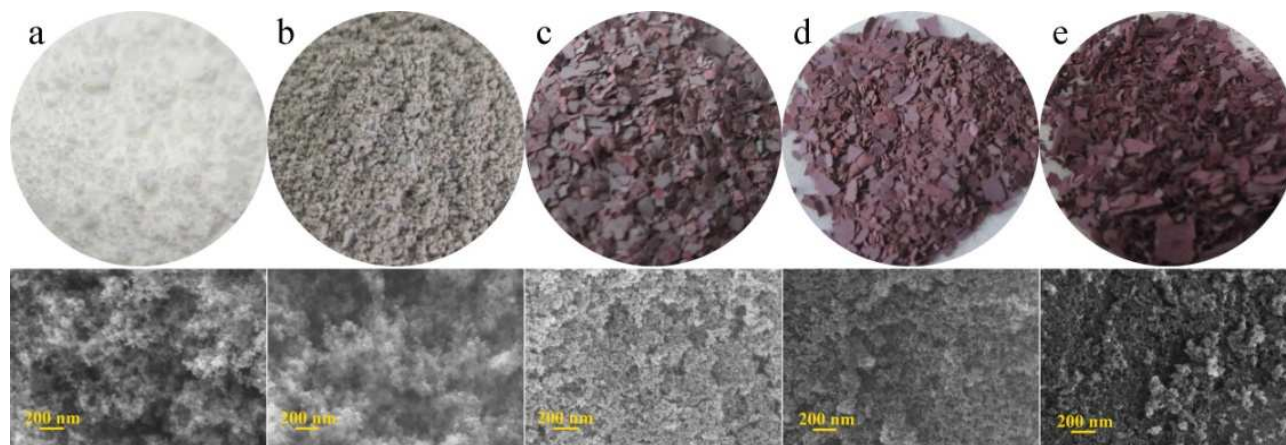
## Experimental section

### Chemicals and Materials

TiO<sub>2</sub> nanoparticles, P25 (Fig. 1a), was supplied by Degussa, Germany. Perylene 3,4,9,10-tetracarboxylic dianhydride (PTCDA; Scheme 1), 4-(dimethylamino)benzylamine, dodecylamine and hexachloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O) were purchased from J&K Acros. All other chemicals were obtained from Chemical Reagent Co. Ltd. (Shanghai, China) in analytical grade and used without any purification.

### Preparation of PTCDI/Pt/TiO<sub>2</sub> Composites

10 mL of PTCDI solution in CHCl<sub>3</sub> (12.5, 25 or 50 mg L<sup>-1</sup>) was mixed with Pt/TiO<sub>2</sub> powders (25 mg; weight ratio of Pt to TiO<sub>2</sub> is 1:200; Fig. 1b) in a 50 mL round-bottom flask. The mixture was stirred at 25 °C for 6 h in the dark, and then for another 2 h after the dropwise injection of 40 mL of CH<sub>3</sub>OH. The precipitate was collected by vacuum suction filtration using 0.45 μm membrane filter and then dried at 80 °C for 6 h to give composites, denoting as 0.5%, 1% or 2% PTCDI/Pt/TiO<sub>2</sub> (Fig. 1c-e). For comparison, 5 mL of CHCl<sub>3</sub> solution of PDI (1 % of the weight of Pt/P25) was mixed with grinded Pt/TiO<sub>2</sub> fine powder (0.025 g) in a mortar. The mixture was grinded for 5 min, and then the powder was collected via evaporation for comparative photocatalytic experiment.



**Fig. 1** Photo and SEM images of a) TiO<sub>2</sub>, b) Pt/TiO<sub>2</sub>, and PTCDI/Pt/TiO<sub>2</sub> composites containing PTCDI with different weight ratios of c) 0.5%, d) 1% and e) 2%.

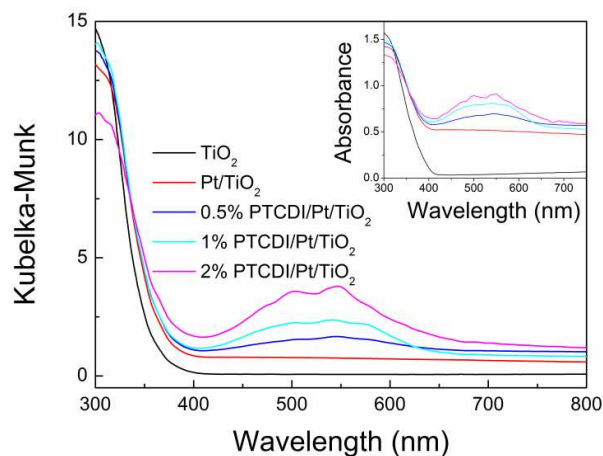
### Photocatalytic Tests

H<sub>2</sub> generation experiments were carried out in a top-irradiation

type reactor connected to a closed gas circulation and evacuation system (Labsolar-H<sub>2</sub> photocatalytic water-splitting H<sub>2</sub> production system, Bofeilai, Beijing). Generally, 25 mg of sample photocatalyst powder was suspended using a magnetic stirrer in 100 mL aqueous solution containing triethanolamine (10% by volume) as sacrificial electron donor. Before photo-irradiation, the system was evacuated to remove oxygen, and the reaction temperature was maintained at 25 °C by a flow of water during the entire experiment. A 400W Xenon lamp (CEL-S500, Beijing AULTT) attaching with a 420 nm cutoff optical filter, which blocked the light with wavelengths of below 420 nm, was used as the light source. The intensity of the incident light ( $\geq 420$  nm) was measured to be  $\sim 150$  mW cm<sup>-2</sup> with a optical power meter (NEWPORT 1916-C). The effective irradiation surface area is 19.6 cm<sup>2</sup>. The amount of evolved H<sub>2</sub> was detected and analyzed by an inline gas chromatography (GC-system 7890A; Agilent Technologies) with N<sub>2</sub> as carrier gas. The photocatalytic test under monochromatic light irradiation was also conducted under the same photocatalytic reaction condition by using relevant band-pass filter (with wavelength of 365, 380, 420, 450, 500, 550 and 610 nm possessing full width at half maxima of 15 nm). The apparent quantum efficiency (AQE) of H<sub>2</sub> evolution was calculated over 0.25 g of optimal PTCDI/Pt/TiO<sub>2</sub> catalyst according to the typical formula,  $AQE = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% = \frac{2 \times \text{number of evolved H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100\% = \frac{(2 \cdot n \cdot t \cdot N)}{(E \cdot A \cdot t \cdot \lambda/h/c)} \times 100\%$ , where n is the amount of H<sub>2</sub> evolution under the light with the wavelength  $\lambda$ , t is the illumination time, N is Avogadro constant, E is the irradiated light intensity, A is the effective irradiation surface area, h is the Planck constant, and c is the speed of light.

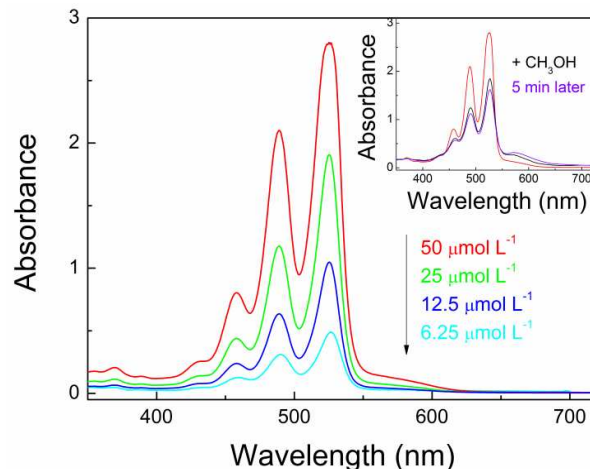
### Characterization

Optical properties were analyzed with a UV-vis spectrophotometer (SHIMADZU UV-1800). UV-vis Diffused Reflectance Spectra (DRS) of the samples were recorded at room temperature on an EVOLUTION 220 UV-visible spectrophotometer equipped with an integrating sphere assembly. Scanning electron microscopy (SEM) images were obtained on a ZEISS SUPRA55VP microscope.



**Fig. 2** DRS Kubelka-Munk and absorption (inset) spectra of TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, and PTCDI/Pt/TiO<sub>2</sub> with different weight ratio of

PTCDI to Pt/TiO<sub>2</sub>.



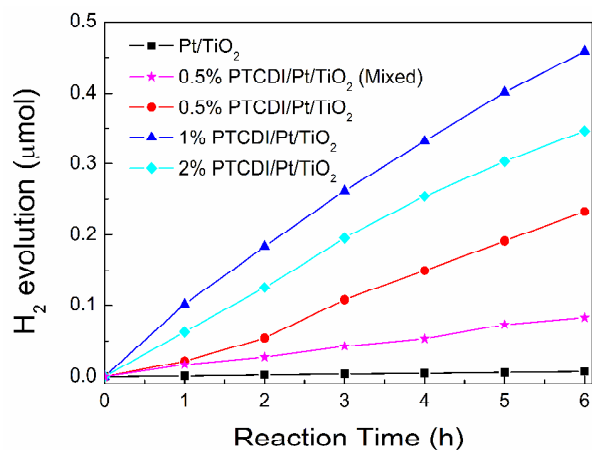
**Fig. 3** UV-vis absorption spectra of PTCDI in CHCl<sub>3</sub> solutions with different concentrations, and recorded by adding 50 vol.% CH<sub>3</sub>OH (inset).

## Results and discussion

### Materials and Characterization

Commercial TiO<sub>2</sub> nanoparticles (Fig. 1a) were loaded with traces of cocatalyst Pt via a simple *in situ* photo-deposition procedure, resulting in a color change varying from white to grayish (Fig. 1b) and a red-shift of the absorption band edge to some extent according to the Kubelka–Munk function but still lies within 400 nm (Fig. 2). Thus, to develop a functional visible-light-driven photocatalytic system, PTCDI is implemented to photosensitize TiO<sub>2</sub> forming a kind of composite PTCDI/Pt/TiO<sub>2</sub> (Fig. 1c-e). It is known that the organization of PTCDI molecules into aggregates can provide continuous pathway for charge transport.<sup>24</sup> Therefore, a solution processing approach derived from the reported self-assembly strategies of perylene diimides is initially introduced to prepare PTCDI/Pt/TiO<sub>2</sub> composite as stated in the Experimental Section.<sup>24,26</sup> For balancing the aggregation behavior and solubility, PTCDI quite benefits to its asymmetric structure modified with 4-dimethylaminobenzyl group and long dodecyl chain at N,N'-positions. It is facily soluble in CHCl<sub>3</sub> while not in CH<sub>3</sub>OH. Stacking of PTCDI molecules surround Pt/TiO<sub>2</sub> nanoparticles (in suspending state) occurs as their solubility decreases when injecting a fourfold volume of CH<sub>3</sub>OH into their CHCl<sub>3</sub> solution, which is mainly driven by their strong intrinsic co-facial  $\pi$ - $\pi$  stacking of the flat aromatic core (stacking along the long axis) in conjunction with the association between the side chains (aggregating along the short axis).<sup>24,25</sup> This method bears the advantages of low-cost, low power consumption, easy scaling, and simplicity. The robust visible-light harvesting property of PTCDI and the aggregation process can be followed by UV-vis absorption spectra in Fig. 3, where a novel absorption peak among 550-600 nm appears accompanied by the transformation of monomeric molecules to aggregates.<sup>24</sup> As can be seen from the DRS measurements (Fig. 2), the absorption range of Pt/TiO<sub>2</sub> (below 400 nm) extends to the visible range (400-700 nm) after combining with PTCDI aggregates, which makes the PTCDI/Pt/TiO<sub>2</sub> composite as a good candidate

for visible-light-driven photocatalyst. In view of the weight ratio difference between PTCDI and Pt/TiO<sub>2</sub>, more PTCDI components in the composites lead to stronger visible-light absorption (Fig. 2) as evidenced by their much darker color (Fig. 1). However, it should be pointed that the contact of PTCDI with Pt/TiO<sub>2</sub> is still not so strong as chemically bonding (e.g., via covalent bond),<sup>14</sup> thus, the effect of PTCDI on the absorption edge of Pt/TiO<sub>2</sub> is not so obvious. As a result, in the composite, PTCDI acted only as the photosensitizer to utilize the photos of light above 420 nm. Further, the photocatalytic activity may be tuned due to the strong electron-donor feature of 4-dimethylaminobenzyl group to electron-deficient PTCDI unit, constructing fast intramolecular charge transfer among donor-acceptor type PTCDI.<sup>25-27</sup> Under visible-light illumination, photoexcitation of PTCDI promotes electron transition from the HOMO to the LUMO, while TiO<sub>2</sub> works as electron transfer relay that accepts electron from PTCDI and transfers it to Pt, which provides active sites for reduction of water to H<sub>2</sub>. However, it is speculated that more PTCDI didn't give rise to better photocatalytic activity because the contact area between PTCDI and Pt/TiO<sub>2</sub> is confined and excess amount of PTCDI aggregates may deteriorate the dispersity of the composite in aqueous solution. This is supported by SEM measurements (Fig. 1) where in the presence of 2% PTCDI, the composite shows a kind of clump-like morphology.

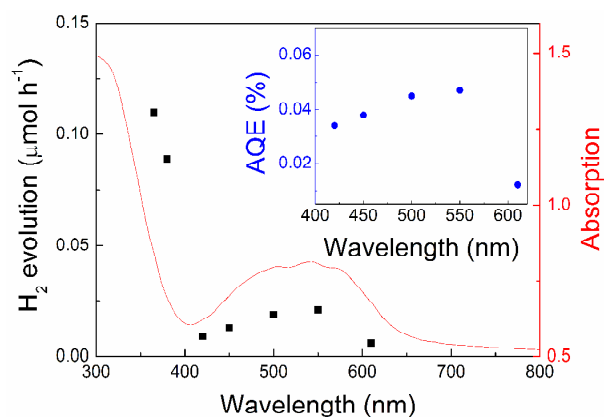


**Fig. 4** The time courses of H<sub>2</sub> evolution from water over Pt/TiO<sub>2</sub> and various PTCDI/Pt/TiO<sub>2</sub> composites with assistance of visible-light irradiation.

### Photocatalytic H<sub>2</sub> production

As shown in Fig. 4, H<sub>2</sub> evolution from PTCDI/Pt/TiO<sub>2</sub> composite system is stable and proceeds at a rate up to 0.075 μmol h<sup>-1</sup> in contrast to nearly inactive Pt/TiO<sub>2</sub> under visible-light (λ ≥ 420 nm) illumination. The weight ratio of PTCDI component to Pt/TiO<sub>2</sub> was optimized at 1% to balance the surface coverage and dispensability, resulting into the highest performance followed by 2% and 0.5%. It has been found that excess (2%) aggregates of PTCDI on the surface of Pt/TiO<sub>2</sub> nanoparticles can obstruct their active cores for H<sub>2</sub> generation and limited the dispersity of the constructed composite in aqueous solution, while fewer amounts of PTCDI aggregates (0.5%) may lead to uncovered Pt/TiO<sub>2</sub>. The ratio of 1% is the appropriate choice to maintain good

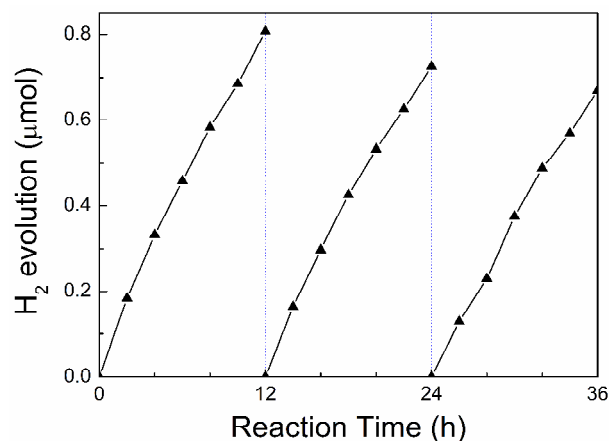
dispensability and avoid clumping of the composite during the construction process. The above statements are supported by the images as shown in Fig. 1. For mixed PTCDI/Pt/TiO<sub>2</sub> system, much poor photocatalytic efficiency is achieved probably due to the unsatisfied interfacial action between PTCDI and Pt/TiO<sub>2</sub>. In other words, the weak contract between them results in inferior interfacial charge transfer.<sup>25</sup> Conversely, the good photocatalytic performance of the sample via solution processing method is largely due to the bisolvent triggered aggregation of PTCDI molecules. The PTCDI assemblies thus fabricated may play a role as glue to sticking Pt/TiO<sub>2</sub> nanoparticles together via forces such as hydrogen bonding and π-π stacking. This structure in combination with π-π stacking morphology of PTCDI enables efficient interfacial charge transfer and separation to enhance photocatalytic activity.<sup>25</sup> In addition, it has been demonstrated that nanofiber composite of Pt/PTCDI without TiO<sub>2</sub> shows poor activity (ca. 0.025 μmol h<sup>-1</sup>) under the same conditions, which is attributed to the competition between intrinsic inefficient photoactivity of organic dyes without a semiconductor matrix to act as an efficient charge separator and the well-defined 1D nanofiber morphology for enhanced charge transfer.<sup>25,27</sup> Therefore, a synergetic role is involved in the system of PTCDI (photosensitizer) to Pt (photoreduction reaction core) deposited TiO<sub>2</sub> (photocatalyst). This conclusion is also supported by the photocatalytic test under monochromatic light illumination. In general, a wavelength dependence feature of the incident light on the rate of H<sub>2</sub> evolution over optimal 1% PTCDI/Pt/TiO<sub>2</sub> catalyst has been demonstrated. As seen in Fig. 5, the AQE data are quite consistent with the H<sub>2</sub> evolution rate in accordance with the absorption spectrum of 1% PTCDI/Pt/TiO<sub>2</sub>. Thus, it can be speculated that under the irradiation of light with the wavelength above 420 nm, it is PTCDI molecules who act as the light-absorber. Especially, an AQE as high as 0.47% is achieved under the irradiation of 550 nm monochromatic light.



**Fig. 5** Absorption spectrum and the photocatalytic activity of 1% PTCDI/Pt/TiO<sub>2</sub> for H<sub>2</sub> evolution under monowavelength light irradiation. The inset figure shows the dependence of the AQE on the wavelength of monochromatic visible-light.

Further, the stability of the photocatalytic activity of 1% PTCDI/Pt/TiO<sub>2</sub> for H<sub>2</sub> evolution under visible-light illumination was observed in Fig. 6. As both PTCDI and TiO<sub>2</sub> are stable under light irradiation in aqueous triethanolamine solution, the photocatalytic reaction results in a stable H<sub>2</sub> evolution rate, although there is still a decrease by ~10% during 36 h probably

due to the interface separation between PTCDI and TiO<sub>2</sub> during stirring process. Furthermore, PTCDI molecules are stable enough to inhibit photobleaching. They can be regenerated by dissolving the reacted composite powders into CHCl<sub>3</sub>.

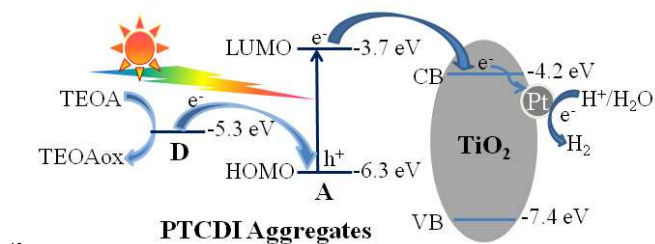


**Fig. 6** Stable H<sub>2</sub> evolution from water over 1% PTCDI/Pt/TiO<sub>2</sub>. The reaction was continued for 36 h, and reset every 12 h.

### Mechanism speculation

To explain the visible-light-driven photocatalytic H<sub>2</sub> generation performance of PTCDI/Pt/TiO<sub>2</sub> from aqueous solution in the presence of sacrificial reagent triethanolamine, both the intramolecular electron transfer from the electron rich 4-dimethylaminobenzyl group (donor part) to the perylene core (acceptor part) of PTCDI and the intermolecular charge transfer from PTCDI to TiO<sub>2</sub> due to the energy level difference are taken into consideration. As illustrated in Scheme 2, under visible-light illumination, only PTCDI can be excited by absorbing photons with the light wavelengths above 420 nm. On one hand, an ultra-fast intramolecular charge transfer process occurs, that is, after the excitation of PTCDI, the electrons can be transferred from the 4-(dimethylamino)benzyl moiety to the HOMO orbital of the photoexcited PTCDI core to quench the photogenerated holes. Due to the presence of large amount of sacrificial reagent triethanolamine (electron donor), the oxidized (dimethylamino)benzyl is easily reduced to its ground state. These processes highly inhibit the recombination of photo-generated electron-hole pairs among PTCDI. Consequently, residual excited photogenerated electrons are left on the LUMO of PTCDI. On the other hand, due to the energy level fall from the LUMO of PTCDI to the CB of TiO<sub>2</sub>, the rich excited electrons of PTCDI move to the CB of TiO<sub>2</sub> via interface charge transfer. These electrons are captured by the loaded Pt nanoparticles (electron traps) on TiO<sub>2</sub>, thus promoting the reduction of water to H<sub>2</sub> by providing active sites and suppressing the back charge recombination.<sup>6</sup> The electrons are consumed by water to proceed the reduction reaction process for H<sub>2</sub> production. Such TiO<sub>2</sub> mediated electron transfer from PTCDI to Pt helps suppress the electron-hole recombination of PTCDI. Further, the  $\pi$ - $\pi$  stacking morphology of PTCDI in the composite is also good for its photocatalytic performance by providing large electron mobilized terrace for PTCDI and TiO<sub>2</sub> nanoparticles, which can enhance the intra-/inter-molecular charge transfer among the composite.<sup>25</sup> As a result, PTCDI can be identified as an efficient

visible-light-responsive sensitizer for TiO<sub>2</sub>.



**Scheme 2** Proposed mechanism for photocatalytic H<sub>2</sub> evolution over PTCDI/Pt/TiO<sub>2</sub> under visible-light ( $\lambda \geq 420$  nm). D: 4-dimethylaminobenzyl moiety of PTCDI; A: perylene core of PTCDI; TEOA: triethanolamine. Energy values (vs. vacuum level) are taken from references.<sup>25-27</sup>

### Conclusions

To sum up, PTCDI/Pt/TiO<sub>2</sub> composite is demonstrated as an efficient photocatalyst for visible-light-driven H<sub>2</sub> evolution from photocatalytic water reduction. Two key design criteria for the application of PTCDI are involved: one is the electron donor-acceptor feature of PTCDI resulting from the presence of electron-rich 4-dimethylaminobenzyl moiety; and the other is bisolvent-induced  $\pi$ - $\pi$  stacking morphology with the assistance of dodecyl modification. Although the present photocatalytic activity of this composite is still unsatisfied, perylene diimide sensitized commercial TiO<sub>2</sub> nanoparticles hold great potential for practical photocatalytic water reduction processes due to their excellent solar light harvesting ability, good photochemical and thermal stability, and flexible structural design of perylene diimides.<sup>28</sup> Moreover, the simple solution-induced processing method demonstrates a new strategy to develop economical organic-inorganic composite photocatalysts. More efforts are needed in tuning the structures of perylene diimide molecules (e.g., introducing functional side-groups to improve their binding ability with TiO<sub>2</sub>) and tunable composite fabrication.<sup>29</sup>

### Acknowledgements

Financial support by the National Natural Science Foundation of China (Grant No. 21173261), the "One Hundred Talents" program of Chinese Academy of Sciences (Grant No. 1029471301), and the "Cross Cooperation Program for Creative Research Teams" of Chinese Academy of Sciences (Grant No. Y251821601) is gratefully acknowledged.

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