



# Highly efficient perylene-based polymer photocatalyst/biocatalyst systems for L-glutamate production under solar light

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**Abstract.** The selective production of fine chemicals using inexpensive solar light continues to be a challenge. As a means to achieve this we report herein the synthesis and development of a perylene-based solar-light-driven photocatalyst (PDA–DAA) obtained by the covalent bonding of perylene tetracarboxylic dianhydride (PDA) with a 2,6-diaminoanthraquinone (DAA) molecule. The photocatalyst/biocatalyst coupled system developed using PDA–DAA as a photocatalyst functions in a highly efficient manner, leading to high NADH regeneration (80.12%), followed by its consumption in exclusive production of L-glutamate (94.16%) from  $\alpha$ -ketoglutarate. The present research highlights the development and application of the PDA–DAA photocatalyst for direct formation of L-glutamate under solar light.

**Keywords.** PDA–DAA photocatalyst;  $\alpha$ -ketoglutarate; FTIR; NADH regeneration.

## 1. Introduction

Nature uses solar energy for the synthesis of various useful organic compounds from CO<sub>2</sub>. The development of an artificial analogue for this elegant system continues to be a big challenge in chemical sciences [1–6]. The current research therefore attempts the preparation of a photo-bioreactor system using a semiconductor photocatalyst through an integral bonding between photocatalytic and biocatalytic cycles for the selective formation of fine chemical using solar light.

It should be noted that 46 and 4% of total solar light available on the earth falls in the visible and UV ranges, respectively [7,8]. Therefore, a UV–visible-light-active photocatalyst is essentially required for solar fine chemical synthesis. Another important aspect to be noted is that in photocatalytic/biocatalytic systems, NADH-dependent enzymes are commonly used. However, the cost of NADH co-factors is too high for the industrial utilization of various promising enzymatic reactions [9,10]. Therefore, *in-situ*

regeneration of NAD<sup>+</sup>/NADH through a highly efficient route is the only way to make it industrially and economically feasible [11,12]. So far, for the *in-situ* regeneration of NADH, a number of approaches in particular photo-electrochemical routes has been explored [13], however still suffer from short comings [14]. On the contrary, photocatalytic regeneration of NAD<sup>+</sup> has shown promising results [15–17] but remains to be explored more systematically.

In the field of organic/inorganic photocatalysts, until recently, chemical fraternity has been focusing on graphene-based materials, and triazine nanocomposites for the production of hydrogen, formaldehyde, formic acid and methanol under solar light [8,18]. Perylene tetracarboxylic dianhydride (PDA) has been extensively used as a light harvester as a result of its high-photochemical/thermal stability, heat resistance and excellent chemical inertness exhibiting a high molar extinction coefficient, with good electron transport properties and strong fluorescence in the visible range [19–21]. In this study, a perylene-based solar-light-driven photocatalyst (PDA–DAA) has been designed

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and synthesized by the covalent bonding of PDA with a 2,6-diamino-anthraquinone (DAA) molecule for obtaining L-glutamate (solar fine chemical/aminoacid) from  $\alpha$ -ketoglutarate. A schematic illustration of natural and artificial photocatalytic/biocatalytic mechanistic cycles is shown in scheme 1. Upon visible light irradiation ( $\lambda \geq 420$  nm) of the PDA–DAA photocatalyst, an electron is excited from the highest-occupied molecular orbital to lowest-unoccupied molecular orbital. Thereafter, the excited electron gets transferred to methyl viologen (MV) thereby reducing it [22]. Consequently, a proton is abstracted from water by reduced MV which then transfers the hydride to  $\text{NAD}^+$ , thereby forming NADH (scheme 1). MV, thus, carries as an electron mediator between  $\text{NAD}^+$  and the PDA–DAA photocatalyst [23]. The NADH thus obtained is utilized by the biocatalyst glutamate dehydrogenase (GDH) to carry out exclusive production of L-glutamate from  $\alpha$ -ketoglutarate.

## 2. Experimental

### 2.1 Synthesis of PDA–DAA photocatalyst

The PDA–DAA photocatalyst was prepared by using a reported literature method [24]. PDA (0.5 g, 1.2 mmol) and DAA (0.3 g, 1.2 mmol) dissolved in DMF ( $\sim 10$  ml) were added to an  $\text{N}_2$ -filled 250-ml two-neck round-bottom flask

equipped with a magnetic stirring bar along with a condenser. The round-bottom flask was placed in an oil bath and refluxed at  $153^\circ\text{C}$  (see supplementary figure S1). After 24 h, the flask was removed from the oil bath, and the reaction mixture was filtered. The residue was stirred in 1% hot aqueous potassium hydroxide and filtered to remove impurities. The precipitate was added to water and the solution was acidified with 5% hydrochloric acid and then filtered. The product was washed with copious amount of water and dried to yield the PDA–DAA photocatalyst.

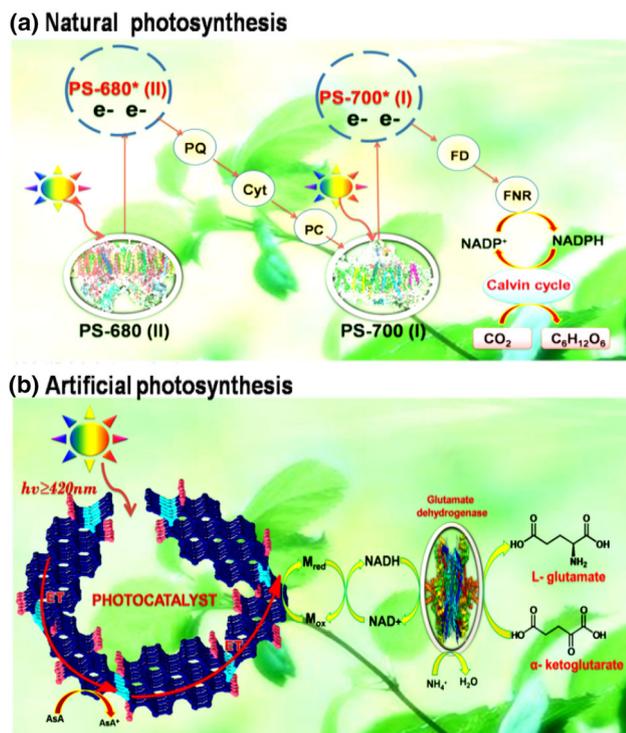
### 2.2 Photocatalytic studies

The PDA–DAA photocatalyst ( $1 \text{ mg ml}^{-1}$ ), M ( $250 \mu\text{M}$ ),  $\text{NAD}^+$  ( $1 \text{ mM}$ ) and  $0.01 \text{ M}$  ascorbic acid (AsA) solution was prepared in a quartz tube at neutral pH; next the materials were homogenized under nitrogen atmosphere for 30 min for better dispersion. The percentage of NADH co-factor was calculated by using a UV–visible spectrometer at  $340 \text{ nm}$  [25]. For the reusability test, the PDA–DAA photocatalyst was washed with distilled water, after that it was collected through centrifugation before re-use. The solar fine chemical (L-glutamate) was synthesized in the presence of GDH enzyme under solar light ( $\lambda > 420 \text{ nm}$ ). The reaction medium consists of PDA–DAA photocatalyst ( $1 \text{ mg ml}^{-1}$ ), AsA ( $310 \mu\text{M}$ ),  $\alpha$ -ketoglutarate ( $0.01 \text{ M}$ ), M ( $124 \mu\text{M}$ ),  $(\text{NH}_4)_2\text{SO}_4$  ( $0.1 \text{ M}$ ),  $\text{NAD}^+$  ( $240 \mu\text{M}$ ) and GDH ( $30 \text{ U}$ ) dispersed in  $2.3 \text{ ml}$  of buffer solution at  $\text{pH} = 7.0$ . The analysis of L-glutamate was estimated by high-performance liquid chromatography [26]. Furthermore, all solutions were eluted with a  $0.05\%$  phosphoric acid solution at  $1.0 \text{ ml min}^{-1}$  and it was detected at  $214 \text{ nm}$ .

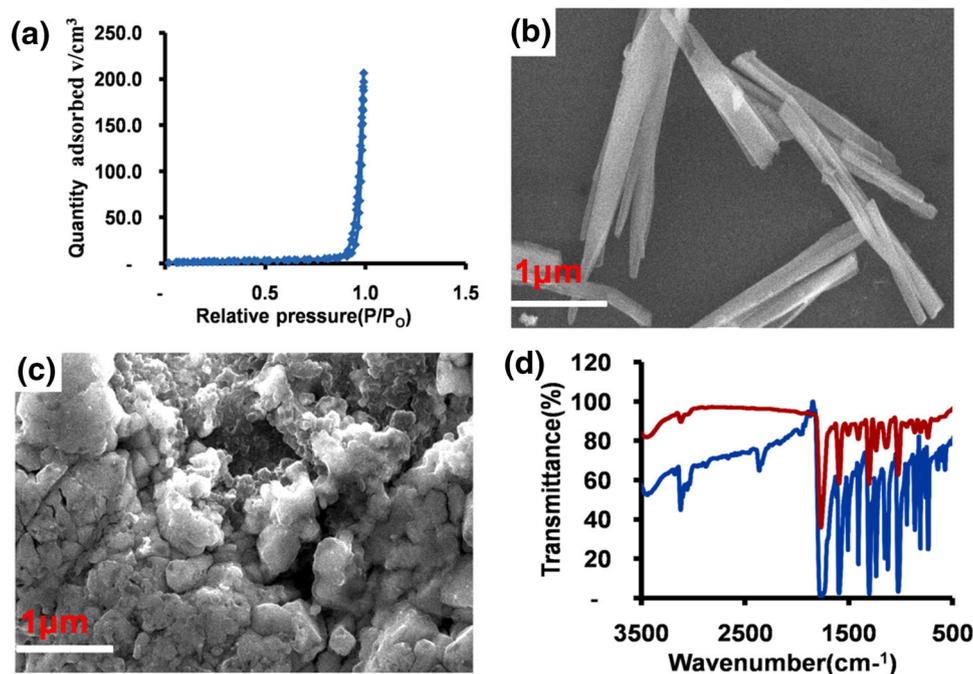
## 3. Results and discussion

### 3.1 Characterization

The field emission-scanning electron microscopic (FE-SEM) studies were performed to gain insight into the morphology of PDA and PDA–DAA (figure 1b and c). From the FE-SEM images, it could be clearly observed that the morphology of PDA was totally different from that of PDA–DAA (figure 1c). Although DAA does not show porosity, the PDA–DAA exhibited a porous structure. The PDA–DAA photocatalyst was therefore further characterized using  $\text{N}_2$  adsorption/desorption studies at  $77 \text{ K}$  (figure 1a). PDA–DAA displays the curve and a high-adsorption capacity in a low pressure region, which further supported the intrinsic microporosity properties of the PDA–DAA photocatalyst. The Brunauer–Emmett–Teller (BET) surface area was found to be  $9.78 \text{ m}^2 \text{ g}^{-1}$ , in agreement with the previous reported paper [27]. The microporosity is formed by the inefficient packing of polymer chains due to a rigid structure [28].



**Scheme 1.** Schematic illustration of (a) natural photosynthesis in which two photosystems participate in production of glucose and oxygen and (b) perylene-based photocatalyst–biocatalyst system for NADH regeneration and selective solar chemical production.

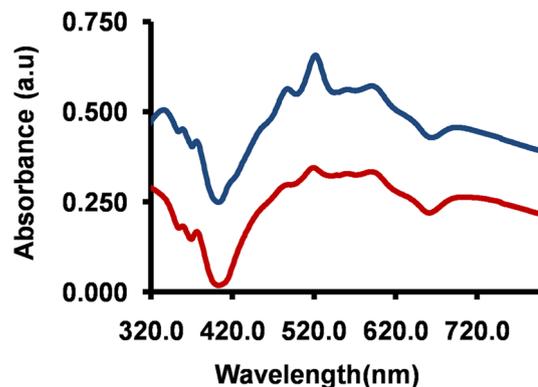


**Figure 1.** (a) Nitrogen adsorption–desorption isotherm curve of PDA–DAA photocatalyst, (b) FE-SEM studies of PDA and (c) PDA–DAA photocatalyst, (d) FTIR spectra of PDA (red line) and PDA–DAA photocatalyst (blue line), respectively.

The Fourier-transform infrared (FT-IR) spectroscopic studies were carried out for DAA and the PDA–DAA photocatalyst (figure 1d). The PDA–DAA photocatalyst exhibited characteristic bands at  $1771\text{--}1614\text{ cm}^{-1}$ , which is attributed to the symmetric and asymmetric vibrations of the C=O groups along with the C–N stretching vibration near about  $1301\text{--}1235\text{ cm}^{-1}$  which was different from that observed in the case of DAA. This indicated the covalent attachment of PDA with DAA. Additionally, peaks in the range of  $1595\text{--}1407\text{ cm}^{-1}$  were observed due to the C=C stretching peaks of the PDA–DAA photocatalyst skeleton [29].

The zeta potential values of PDA and the PDA–DAA photocatalyst were found to be  $-4.04$  and  $-9.71$  mV, respectively (supplementary figure S3a and b). The lower negative zeta potential ( $\zeta$ ) value indicated a lower stability of PDA compared to the PDA–DAA photocatalyst, and also confirmed the covalent attachment of PDA with DAA [30].

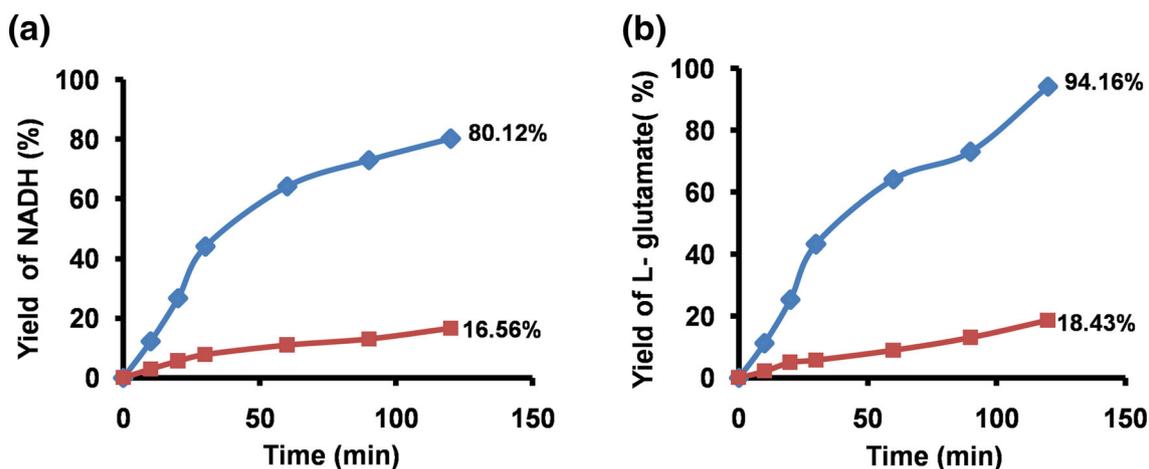
The UV–visible spectra of DAA and PDA–DAA photocatalyst are shown in figure 2. They exhibited a broad absorption peak for the PDA–DAA photocatalyst with maxima at 522 nm. They showed an optical band gap of 2.38 eV which indicated that it could function as a visible-light-active photocatalyst [31]. The experimental optical band gap of PDA–DAA appeared to be enough to carry out solar-light-driven reduction of MV which consequently led to NADH regeneration and production of L-glutamate from  $\alpha$ -ketoglutarate.



**Figure 2.** UV–visible absorption spectra of PDA–DAA photocatalyst (blue line) and DAA (red line), respectively.

### 3.2 Photocatalytic studies

The light-driven photocatalytic performances of PDA and PDA–DAA were evaluated. The regeneration of NADH was performed under halogen light irradiation at ambient temperature. As shown in figure 3a, 16.56 and 80.12% of NADH regeneration were achieved in 2 h upon using PDA and the PDA–DAA photocatalyst, respectively. Upon coupling with a biocatalyst GDH, 18.43 and 94.16% L-glutamate from  $\alpha$ -ketoglutarate in 2 h were obtained using PDA and the PDA–DAA photocatalyst, respectively (figure 3b). These results undoubtedly showed the highly efficient and selective solar light photocatalytic activity of the PDA–DAA photocatalyst.



**Figure 3.** (a) NADH regeneration through PDA (red line) and PDA–DAA photocatalyst (blue line), respectively. (b) L-Glutamate production through PDA (red line) and PDA–DAA photocatalyst (blue line), respectively.

#### 4. Conclusions

In summary, we successfully synthesized a perylene-based photocatalyst (PDA–DAA) for solar fine chemical under solar light. The PDA–DAA photocatalyst has been characterized by FE-SEM, FT-IR, BET, UV–visible spectroscopy and zeta potential. The PDA–DAA photocatalyst is a highly efficient solar-light-active photocatalyst of the photocatalyst/biocatalyst-integrated system for the NADH (80.12%) regeneration and production of L-glutamate (94.16%) from  $\alpha$ -ketoglutarate. The current study represents a new instance of utilization of solar energy by photocatalyst/biocatalyst-incorporated systems for NADH regeneration and solar fine chemical production in a low cost, efficient, selective and eco-friendly manner.

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