

In-situ Prepared 2D Covalent Organic Framework as a Photocatalyst in the Photocatalytic-Biocatalytic Attached System for Highly Selective L-Glutamate Production under Solar Light

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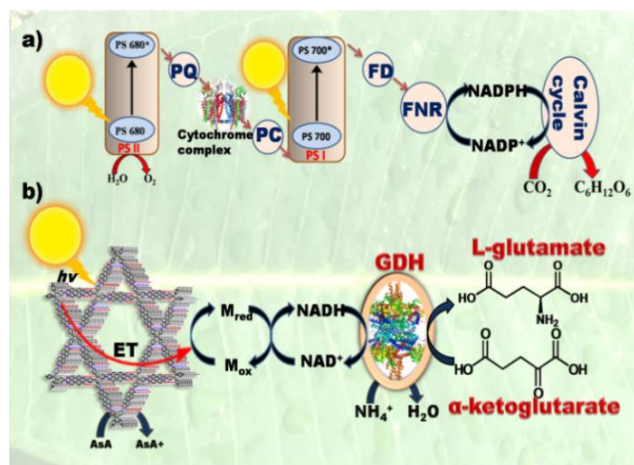
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Covalent organic frameworks (COFs) are a class of porous organic polymers with designable and predictable platform that may provide new opportunities to develop a metal-free in-situ prepared photocatalyst by condensation method. Currently, we have designed a new class of two dimensional covalent organic frameworks (2DCOFs), which is important for further growth in this promising field for boosting selective solar chemical productions under solar light. For this scientific research work, perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PDAH) and tetraaniline-4, 4', 4'', 4'''-(ethene-1, 1, 2, 2-tetrayl) (TAET) have been attached by a condensation method first time to the fabrication of in-situ 2DCOFs photocatalyst. The photocatalyst-biocatalyst attached system urbanized using 2DCOFs as photocatalyst functions in a highly selective manner, leading to high NADH regeneration (83.68%), followed by its consumption in L-glutamate production (89.95%) from α -ketoglutarate. In this article, in-situ prepared photocatalyst has an excellent solar light-harvesting ability, band gap suitability, and highly organized π -electron channels are very applicable for highly selective solar chemical (L-glutamate) production and expected to trigger further interest in developing flexible films for solar energy transformation applications.

Introduction

Covalent organic frameworks (COFs), which are a class of crystalline polymers with conventional fine structures [1,2], have drawn a big deal of significance because of their important applications in various field such as catalysis [2-4], gas adsorption, optoelectricity, and energy conversion [5-7]. In this environment, the synthesis of COFs usually gives thermodynamically utmost stable structures [8]. Distinct feature of one and two-dimensional covalent organic framework porosity is periodically scattering in only 2D sheets of COFs due to presence of pores, and these pores provide tremendous applications [2-8]. Additionally, the pores size and shape in a 2D COF can be well modified by changing the monomer units in the structures [9-12]. In this context, various kinds of pores size and shape into a COFs are still a big challenge. Therefore, formation of two pores COFs is very hard to control the shape and size simultaneously. In this context, here we report in-situ synthesized COF having two different kinds of pores [13], in which hexagonal and triangle are periodically arranged. Therefore, we developed 2DCOFs photocatalyst with excellent light-harvesting ability, band gap suitability, and favourably organized π -electron channels for highly selective solar

chemical production [14]. Herein, in our current research work [15,16] is interested in synthesizing PDAH containing TAET photocatalyst that may contribute as an excellent platform for selective solar light harvesting capabilities of PDAH with the desirable properties of 2DCOFs for mimicking natural photosynthesis. The synthesis of 2DCOFs is usually carried out by condensation polymerization methods [14-16]. However, in-situ synthesis of 2DCOFs photocatalyst by condensation method demonstrated a major synthetic challenge for this research work. To overcome this challenge, we wanted to build up a new synthetic route for synthesizing the desired 2DCOFs [17]. Thus, here we report a perylene dianhydride (PDAH) and tetraaniline-4,4',4'',4'''-(ethene-1,1,2,2-tetrayl) (TAET) attached photocatalyst, synthesised by the condensation method for the first time. As shown in **Scheme 1**, this latest framework constructed from PDAH and TAET building units proved to be an excellent solar light active photocatalyst for mimicking natural photosynthesis. To the best of our knowledge, solar light driven 2DCOFs photocatalyst-biocatalytic system for NADH regeneration (83.68%) and production of L-glutamate (89.95%) is reported first time (**Scheme 1**).



Scheme 1. Diagrammatic illustration of (a) natural and (b) artificial photosynthetic system for NADH regeneration and selective solar chemical production.

Experimentals

Method and materials

Perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PDAH), tetraaniline-4,4',4'',4'''-(ethene-1,1,2,2-tetrayl) (TAET), dimethyl formamide (DMF), hydrochloric acid (HCl), 1% sodium hydroxide (NaOH), methyl viologen, NAD⁺ (Nicotinamide adenine dinucleotide), glutamate dehydrogenase (GDH), α-ketoglutarate, ammonium sulfate [(NH₄)₂SO₄], ascorbic acid, were purchased from Sigma-Aldrich.

Synthesis of 2DCOFs photocatalyst

2DCOFs photocatalyst (see in supporting information **Fig. S1**) was prepared by reported method [17]. TAET, 0.25g (0.6mmol) and PDAH, 0.5g (1.2mmol) were dissolved in a DMF (30mL) and added to 500 mL round bottom flask equipped with a magnetic stirring bar and a condenser. The flask was placed in an oil bath and suspension was refluxed at 140⁰ C for overnight after that solution was removed from the oil bath and filtered. The filtered was stirred in 1% hot aqueous sodium hydroxide solution and after that we removed unreacted PDAH material by filtration process. Afterward the filtrated was added to water along with dilute hydrochloric acid then again filtered. After that crude product was washed with huge amount of water and dried at 100⁰C in oven. Again solid product was purified by Soxhlet method [17].

2DCOFs photocatalytic system for NADH regeneration

The NADH regeneration was carried out under halogen light irradiation (450W) at room temperature on 450 nm cut-off filter. The mixing of 2DCOFs (0.1M) material at different concentrations with **M** (250μM), NAD⁺ (1mM), and AsA (0.01M) solution is prepared for the light reaction. Here **M** and AsA act as reaction mediator, and sacrificial electron donor. Before we mixed them, 2DCOFs stock solution was dispersed in AsA solution for half an hours in presence of nitrogen. After that we used

UV-visible spectrophotometer for percentage (%) of NADH regeneration at 340 nm [18-19].

2DCOFs photocatalytic system for solar chemical production

The enzymatic production of L-glutamate in presence of GDH was conducted upon solar light irradiation (λ > 420 nm) by using the reaction medium consisting of 2DCOFs (1 mg ml⁻¹), **M** (124 μM), NAD⁺ (240 μM), α-ketoglutarate (10 mM), (NH₄)₂SO₄ (100 mM), AsA (310 μM), and GDH (30 U) dispersed in 2.3 ml of buffer solution (pH 7.0). L-glutamate was analyzed by liquid chromatography (Agilent Technologies, USA). By the use of phosphoric acid solution (0.05%) at the flow rate of 1.0 ml/min samples were eluted and detected at 214 nm [19].

Result and discussion

2DCOFs photocatalyst–biocatalyst attached system for highly selective L-glutamate production from α-ketoglutarate

In-situ prepared 2DCOFs photocatalyst–biocatalyst attached system for solar chemical production via NADH regeneration (**Scheme 1**). Under solar light irradiation, yield of NADH regeneration is 83.68% (**Fig. 1a**) in presence of in-situ prepared 2DCOFs photocatalyst in two hours, where as in presence of PDAH yield of NADH regeneration is very less (16.16%). Consequently, regenerated NADH consumed by GDH enzyme, which is NADH dependent enzyme and converting the α-ketoglutarate into L-glutamate. The yield of L-glutamate is 89.95% (**Fig. 1b**) in presence of in-situ prepared photocatalyst. The NADH regeneration in absence of 2DCOFs photocatalyst and with different types of light sources (in the above mentioned same experimental conditions) is found to be negligible [19-21].

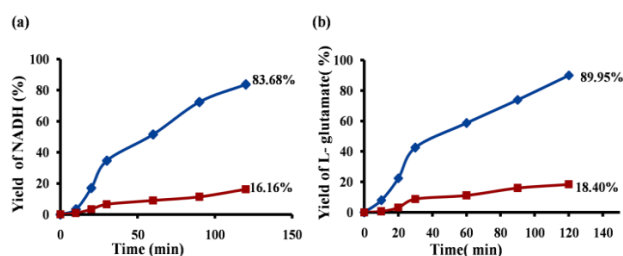


Fig. 1. Photocatalytic activities of PDAH (red colour line) and 2DCOFs (blue colour line) (a) NADH regeneration and (b) L-glutamate production from α-ketoglutarate.

A schematic illustration (**Scheme 1b**) of the in-situ prepared PDAH based two pore covalent organic framework i.e. 2DCOFs photocatalyst involved in the production of L-glutamate from α-ketoglutarate in presence of solar light. The light-harvesting 2DCOFs collect the incident solar light for electronic transition between valence bands and conduction band for the reduction of methyl viologen (**M**) [20-21]. The solar light active 2DCOFs reduces the methyl viologen (**M**). After reduction of methyl viologen (**M**), electrons are

transferred to NAD^+ via methyl viologen (M) to generate enzymically active 1,4-NADH. In this manner, methyl viologen act as an electron mediator between 2DCOFs photocatalyst and NAD^+ which is important for exclusive regeneration of 1,4-NADH cofactor. Subsequently, 1,4-NADH is utilized by the enzyme glutamate dehydrogenase (GDH) in presence of buffer solution for production of L-glutamate from α -ketoglutarate as a solar chemical. The NAD^+ released persistently acts as a substrate for the photocatalytic cycle, which leads to NADH regeneration under solar light irradiation[22]. Hence, in-situ prepared 2DCOFs photocatalyst exclusively take part in NADH regeneration and produce L-glutamate as solar chemical, which is the final product.

The study of UV-visible absorption spectra of PDAH and 2DCOFs has been conducted in DMF solution [23]. The UV-visible spectra of PDAH and 2DCOFs is shown in **Fig. 2a**. It is clearly shown that 2DCOFs show higher absorption in comparison with PDAH which may allocated to strong $\pi-\pi^*$ transition [24] which is also supported by fluorescence spectra (**Fig. 2b**).

The 2DCOFs photocatalyst is more efficient due to presence of light harvester PDAH and stacking [14-24]. The prominent UV-visible spectra of 2DCOFs is near about 580 nm corresponding to optical band gap energy 2.14 eV. The observed optical band gap appear to significantly solar light active for reduction of methyl viologen complex (M) which lead to NADH regeneration (83.68%) and production of L-glutamate (89.95%).

Additionally, to the best of our finding from the literature this is the first recorded fluorescent spectra (**Fig. 2b**) of 2DCOFs photocatalyst. After that we checked the excitations of 2DCOFs photocatalyst in DMF solution at 520 nm, which emitted a band at 580nm corresponding to optical band gap value of 2.14eV. This analysis is entirely different from the still reported non-fluorescent two pores COF materials [25]. We believe the fluorescence of 2DCOFs most likely originated from PDAH after attached TAET monomer[26].

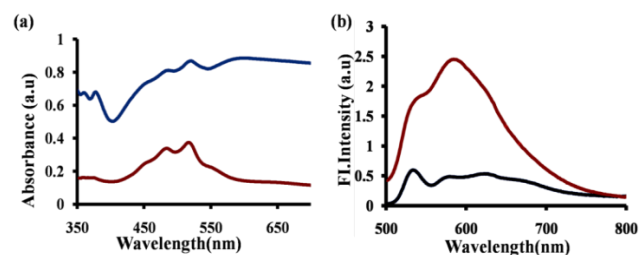


Fig. 2. (a) UV-visible absorption spectra of 2DCOFs (blue colour line) and PDAH (red colour line) (b) fluorescence spectra of PDAH (red colour line) and 2DCOFs (blue colour line). UV-visible absorption and fluorescence spectra of 2DCOFs and PDAH (1×10^{-4} M in DMF).

The Fourier transform infrared spectroscopy was carried out by the Bruker, ALPHA-T FT-IR spectrometer. In FT-IR spectra (**Fig. 3**) of PDAH the peaks are obtained at 1771.9cm^{-1} , 1021cm^{-1} , 1595cm^{-1} and 3120cm^{-1} correspond to C=O, C-O, C=C and C-H respectively.

In 2DCOFs photocatalyst additional peaks observed at 1376cm^{-1} , 1750cm^{-1} and 1646cm^{-1} which is assigned to C-N, C=O and imide bonds, respectively which confirm the formation of bond between PDAH and TAET [23-30] and also confirmed imide bonds by zeta potential analysis (See supporting information **Fig. S3**). Zeta-potential (ξ) of 2DCOFs photocatalyst is more negative (-4.89mV) than PDAH (-4.04mV). It show the covalent attachment of PDAH with TAET molecule [31].

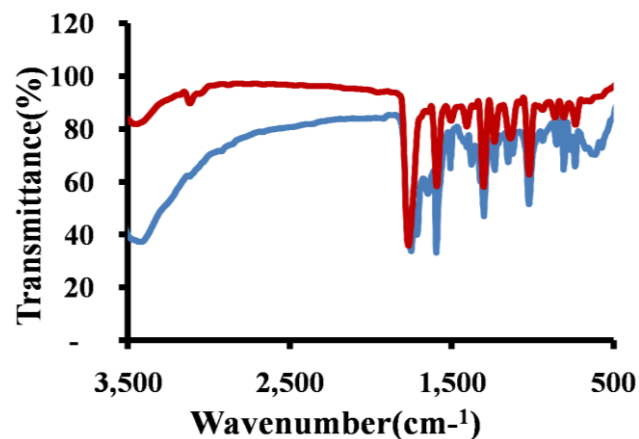


Fig. 3. FT-IR spectra of PDAH (red colour line) and 2DCOFs (blue colour line).

The in-situ prepared 2DCOFs material is crystalline as per reported paper [14-31] as pointed out by powder X-ray diffraction (PXRD) measurements (**Fig. S4**). The 001 diffraction peak at $2\theta=28.24$ corresponds to d-spacing 3.2 nm, suggesting a typical van der Waals contact between the layers of 2DCOFs materials. The average crystal domain size of 2DCOFs was calculated to be 27 nm from the line broadening of reflection through Scherrer equation.

Morphological studies of PDAH and in-situ prepared covalently bonded 2DCOFs sample were investigated by field emission scanning electron microscope (FE-SEM) which are shown in **Fig. 4**. Rod shape morphology of PDAH (**Fig. 4a**) is entirely changed after attaching the TAET (**Fig. 4b**). Moreover, FE-SEM images of PDAH and 2DCOFs photocatalyst show that the 2DCOFs consists of stacked 2D sheet (see in supporting information **Fig. S2**), which confirms the highly ordered arrangement [24-32].

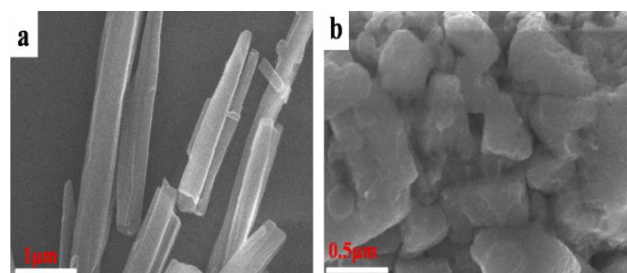


Fig. 4. Field emission scanning electron microscope (FE-SEM) studies of (a) PDAH and (b) 2DCOFs photocatalyst respectively.

Conclusions

In-situ prepared 2DCOFs is mesoporous in nature, having two types of pores one is hexagonal and other is triangle. 2DCOFs is highly efficient solar light active photocatalyst for solar chemical production. Here we first time successfully synthesized a perlyne based two pore covalent organic framework 2DCOFs by condensation polymerization between PDAH and TAET. The polymeric structure improved its light harvesting capacity, suitable band gap highly ordered π -electron channel system facilitates charge carrier transport. Its excellent solar light absorption properties accelerate electron transfer which enhances its photocatalytic performance. In the presence of solar light active in-situ prepared 2DCOFs the yield of NADH regeneration is 83.68%. Furthermore, production of L-glutamate is 89.95% in presence of glutamate dehydrogenase (GDH) enzyme. Certainly this work will set an innovative approach in the area of in-situ preparations of 2DCOFs and their subsequent application in the field of artificial photosynthesis.

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Conflicts of interest

No conflict of interest.

Keywords

2DCOFs photocatalyst, NADH regeneration, GDH enzyme, L-Glutamate.

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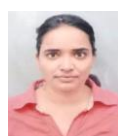
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Authors biography



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