Electronic Supplementary Information (ESI)

Highly Efficient Covalent Organic Framework Film Photocatalyst for Selective Solar Fuel Production from CO₂

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1. General remarks

Cyanuric chloride (CC), DIPEA, Formate dehydrogenase enzyme and β-nicotinamide adenine dinucleotide were purchased from Sigma-Aldrich. 3,4,9,10-Perylenetetracarboxylic diimide (PDI) was purchased from TCI. All the solvents were of HPLC grade and used without further purification. Ultra-pure water was obtained using a Millipore System (Tech Sinhan Science). The organometallic mediator (Rh), [Cp*Rh(bpy)Cl]Cl, (Cp* = pentamethylcyclopentadienyl, bpy = 2,2’-bipyridyl) was synthesized as described previously in literature.¹

2. Instruments and Measurements

CP-MAS ¹³C NMR spectra was recorded on a Bruker AVANCE II+ 500 MHz spectrometer. ES-MS spectrum was recorded on JEOL, MStation JMS-700 spectrometer operating in the positive ion mode. UV-Visible spectra were recorded on Shimadzu UV-1800 spectrophotometer. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Bruker ALPHA-T FT-IR spectrometer. The test specimens were prepared by the KBr-disk method. Wide-angle X-ray diffraction (XRD) analyses were carried out by using an X-ray diffractometer (D/MAX-2200, Rigaku Denki). The X-ray diffraction patterns were recorded in the range of 2θ = 5–40° with Cu Kα radiation (λ= 1.5406 nm) at 40 kV and 100 mA. The thermal properties of the samples were characterized by a thermogravimeter (TGA Model No.
TA Instruments TGA Q5000) and the analysis was carried out under nitrogen over a range of 25-900°C with a ramp rate of 5°C min⁻¹. XPS spectra were recorded on Axis Nova photoelectron spectrometer (KRATOS). A commercial atomic force microscope (Nanoscope; Digital Instruments, Veeco Metrology group), equipped with a J scanner was used to measure the morphology of the sample. Digital Instruments (Nanoscope) was used in the tapping mode. SEM analysis was carried out on JEOL-JSM 6700F instrument. High-resolution transmission electron microscope (HRTEM) images were obtained on a FET Phillips instrument [Model No. 200k VLAB6, (FEL TECNAI G2-20S-Twin)] operated at 200 kV.

3. Experimental Section

3.1 Synthesis of CTF

Cyanuric chloride (0.66 g, 3.6 mmol) was added to an Ar-filled 500-mL, two-neck, round bottom flask equipped with a magnetic stirring bar and a condenser. Perylene diimide (2.17 g, 5.16 mmol) was then added. A mixture of N, N-diisopropylethylamine (DIPEA) (3.185 g, 21.66 mmol) and THF (tetrahydrofuran, 150 mL, anhydrous), previously deaerated by Ar, was then transferred into the round-bottom flask. The flask was placed in an oil-bath at 90 °C for 18 hours. Within a few hours, precipitate started to form. The reaction mixture was further refluxed under Ar atmosphere for 2 days. The solid product thus obtained was separated by suction filtration, washed several times with DI water, methanol, dimethyl formamide and CH₂Cl₂, and dried in oven at 100°C to afford brown solid product (2.21 g, 80.55 % based on CC).
3.2 Synthesis of the Monomer

Similar steps as for polymer mentioned above, except that excess PDI was used in order to minimize polymerization. In this case CC (0.1418g, 0.76 mmol), PDI (1.1289g, 12.11 mmol), and N,N-diisopropylethylamine (DIPEA) (0.746g, 5.78 mmol) in THF (50 mL, anhydrous)
were used. Thereafter following identical procedure the solvent was removed on a rotary evaporator to yield a brown solid. The solid was washed several times with DI water, methanol, dimethyl formamide and CH$_2$Cl$_2$, and then further dried in oven at 100°C to afford brown solid product (0.33g, yield 46.77 % based on CC). Solid state CP-MAS $^{13}$C NMR (500 MHz): $\delta$ 211.86, 202.93, 178.90, 174.97, 145.88, 134.37, 108.66, 70.39. ES-MS (Positive-ion mode) $m/z$: 1246.26 [M + H]$^+$. 

3.3 Preparation of monomer and CTF films and their optimized coatings

The monomer and CTF films were prepared by dropcasting method. For a single coating on a 1 x 1 cm$^2$ polyimide support, 31μl of 1mM concentration of the photocatalyst solution (in DMF) was dropcasted and allowed to dry for 24 hours at 80°C. The procedure was repeated to obtain films with higher coatings. As shown in Table 1 below, the NADH regeneration activity of the films based on number of coatings was studied to obtain optimum results.

Table 1: NADH regeneration activity of the photocatalyst films based on number of coatings

<table>
<thead>
<tr>
<th>S.No.</th>
<th>No. of Coatings</th>
<th>NADH regeneration activity of monomer film (%)</th>
<th>NADH regeneration activity of CTF film (%)</th>
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<tr>
<td>1.</td>
<td>One</td>
<td>7.55</td>
<td>24.46</td>
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<tr>
<td>2.</td>
<td>Two</td>
<td>11.15</td>
<td>38.34</td>
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Optimum results were obtained for the films with three coatings. Therefore all further research work reported herein is with the triply coated photocatalyst film.

4.1. Photoelectrochemical measurements: Photoelectrochemical measurements were carried out in a three-armed cell consisting of reference (Ag/AgCl, BASI, MF-2063 RE-5), working (GFPC 1 electrode) and Platinum wire (Part Number: CHI115) counter electrodes using a Electrochemical analyzer (CHI Instruments 1100A). 0.1 M NaCl solution containing 0.1 M ascorbic acid was used as a redox couple/electrolyte. Newport solar simulator (69911) was used as a light source for photocurrent studies. Light intensity was measured by VSLI standard incorporated Oriel P/N 91150V.

For CV studies- Potential scanned at 100 mVs⁻¹ scan rate.

For photocurrent studies- 50 mVs⁻¹ scan rate; bias potential: 0 to 0.1 V (vs. Ag/AgCl).

4.2. Photocatalytic NADH Regeneration: The photochemical regeneration of NADH was performed within a quartz reactor under an inert atmosphere at room temperature, using a 450W Xenon lamp (Newport 66921) with a 420 nm cut-off-filter as light source (100 mW/cm²). The photocatalytic regeneration of NADH was carried out as follows. The reaction was performed in a quartz reactor. The reaction consisted of β–NAD⁺ (1.24 μmol), rhodium complex Rh (0.62 μmol), Ascorbic acid (0.1 mmol) and 1 x 1 cm² photocatalyst film in 3.1 mL of sodium phosphate buffer (100 mM, pH 7.0). The regeneration of NADH was monitored by UV-vis spectrophotometer (UV-1800, Shimadzu).

4.3. The artificial photosynthesis of formic acid from CO₂: The artificial photosynthesis of formic acid from CO₂ was also performed within a quartz reactor at room temperature, using

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<tbody>
<tr>
<td>3.</td>
<td>Three</td>
<td>20.57</td>
<td>75.88</td>
</tr>
<tr>
<td>4.</td>
<td>Four</td>
<td>20.84</td>
<td>78.97</td>
</tr>
</tbody>
</table>
a 450W Xenon lamp with a 420 nm cut-off-filter as light source (100 mW/cm²). The reaction consisted of 1 x 1 cm² photocatalyst film, β–NAD⁺ (1.24 µmol), rhodium complex Rh (0.62 µmol) and formate dehydrogenase enzyme (3 units) in 3.1 mL of sodium phosphate buffer (100 mM, pH 7.0) with Ascorbic acid (0.1 mmol) in the presence of CO₂ (flow rate: 0.5 mL/min). The amount of formic acid was estimated by GC (7890A, Agilent Technologies).

4.4. Quantum Efficiency determination: The Quantum efficiency determination of CTF for photocatalytic NADH regeneration was carried out in a quartz cuvette reactor (3.5 mL) at room temperature. A 450-watt Newport Xenon Lamp (Oriel) attached to an IR filter (Oriel), and a 20 nm bandpass filter at 420 nm was used as a light source (100 mW/cm²). The number of incident photons was measured using a silicon photodiode with integrating sphere (Oriel).

The photochemical regeneration of NADH was conducted by illuminating the quartz reactor containing β–NAD⁺ (1.24 µmol), rhodium complex Rh (0.62 µmol), Ascorbic acid (0.1 mmol) and 1 x 1 cm² photocatalyst film in 3.1 ml of 0.1 M sodium phosphate (NaH₂PO₄-Na₂HPO₄) buffer (pH ~ 7.0). The concentration of NADH was spectrophotometrically measured through the change in absorbance of NADH at 340 nm in UV-visible spectrum. The quantum efficiency was calculated using the equation below:

\[
\text{Quantum efficiency (\%)} = 2 \times \frac{\text{Moles of NADH produced}}{\text{Moles of incident photons}} \times 100
\]

The quantum efficiency was calculated to be 13.5 % for the photocatalytic NADH regeneration process.
Figures

Fig. S1 Photograph of the film photocatalyst along with illustrative image of stacked 2D sheets of CTF and detailed chemical structure (Gray = C; Blue = N; Red = O).

Fig. S2 (a) AFM roughness image of polyimide sheet. (b) AFM 3D image of polyimide sheet.

Fig. S3 HRTEM image of CTF after photodeposition of platinum particles which clearly depicts the electron channel structure of CTF.
**Fig. S4** Powder XRD pattern of CTF.

**Fig. S5** C1s and deconvoluted X-ray photoelectron spectrum (XPS) of CTF.

**Fig. S6** N1s and deconvoluted X-ray photoelectron spectrum (XPS) of CTF.
Fig S7 Photocatalytic 1,4-NADH regeneration upon repetitive use (3 cycles) of CTF photocatalyst [β-NAD$^+$ (1.24 μmol), Rh (0.62 μmol), TEOA (1.24 mmol) and 1 x 1 cm$^2$ photocatalyst film in 3.1 mL of sodium phosphate buffer (100 mM, pH 7.0)].

Fig. S8 Cyclic voltammogram (CV) of CTF.

Fig S9 GC-MS data of (a) HCOOH obtained from CO$_2$. (b) H$^{13}$COOH obtained from $^{13}$CO$_2$.

References