Electronic Supplementary Information (ESI)

Graphene-BODIPY as a Photocatalyst in the Photocatalytic-Biocatalytic Coupled System for Solar Fuel Production from CO₂

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1. General remarks

Graphite powder (Lot. No. D12590-5) was purchased from Junsei Chemicals. Analytical grade NaNO₃, KMnO₄, 98% H₂SO₄ and 30% H₂O₂ aqueous solution were purchased from Samchun Pure Chemical, Korea, and were used directly without further purification. Picolylamine (CAS No. 1539-46-0), 2,4-Dimethyl-3-ethyl-pyrrol (~97%, CAS No. 512-22-6), Cyanuric chloride (CAS No. 9550-1), Boron trifluoride etherate [(C₂H₅)₂O. BF₃] (Cat. No. 17550-1), DDQ (~98% purity), DIEA (Cat No. D12590-5), Sodium phosphate buffer, Triethanolamine \geq 98% (Cas No. 102-71-6), Formate Dehydrogenase (Cas No. 9028-85-7), and NAD⁺ (99% purity, Cas No. 53-84-9) were purchased from Sigma-Aldrich. Aniline (Cat. No. 01384-01) was purchased from Kanto Chemicals, Korea. 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* = 5-C₅Me₅, bpy = 2,2-bipyridyl) was synthesized as described previously in literature.¹

2. Instruments and Measurements

¹H, and ¹³C spectra were recorded on a Bruker AVANCE II+ 500 MHz spectrometer with tetramethylsilane (TMS; $\delta = 0$) as internal standard. ¹¹B-NMR was recorded on a Bruker

AVANCE 300 MHz spectrometer. High resolution mass spectra (HRMS) were recorded on JEOL, MStation JMS-700 spectrometer operating in the EI⁺ mode. GC-MS data was recorded on Agilent 6890N gas chromatograph with 5973N mass selective detector. 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 $2\Theta = 5-70^{\circ}$ with Cu Ka radiation ($\lambda = 1.5406$ nm) at 40 kV and 100 mA. The thermal properties of the samples were characterized by a thermogravimeter (TGA, DSC, Model No. TA Instruments TGA Q5000, DSC Q-1000), and all the analysis were carried out under nitrogen over a range of 25-1000^oC with a ramp rate of 5^oC min⁻¹. XPS spectra were recorded on a Axis Nova photoelectron spectrometer (KRATOS). Raman spectra were recorded on SENTERA (Bruker) with a 50 x objective lens and 532 nm laser excitation. 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. 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. Synthetic Procedures

Synthesisof1-Picolylamine-2-Aminophenyl-3-Oxy-phenyl-4,4'-Difluoro-1,3,5,7-Tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene-Triazine (BODIPY)2

The synthesis was carried out by following a literature method in two steps as described below.

Step-I. To a stirred solution of 1-picolylamine-2-aminobenzene-3-oxy-benzaldehyde-triazine (0.59 g, 1.20 mmol) and 3-ethyl-2,4-dimethylpyrrole (0.24g, 2.56 mmol) in 60 ml of anhydrous THF was added a catalytic amount of trifluoroacetic acid under argon at ambient temperature. After stirring for 20 h, a solution of 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (0.23 g, 1.20 mmol) in anhydrous THF (30 ml) was added dropwise over a period of 10 min and the solution was allowed to stir for another 2 h at ambient temperature. The resultant mixture was then purified by passing over an aluminium oxide column (~40 g) using DCM/MeOH (97.5/2.5) as eluent to obtain a dark brown solution. After concentration, the product was dried under vacuum overnight and used for next step.

Step-II. To a stirred solution of product obtained from step I and triethyamine (6.0 ml) in anhydrous THF (60 ml) under argon atmosphere at ambient temperature, boron trifluoridedietherate (6.92 g, 982 mmol) was added dropwise over a period of 20 min. The mixture was allowed to stir overnight and then passed over an aluminium oxide column (~40 g) using DCM/MeOH (98/2) as eluent. After removing the solvent under reduced pressure, the residue was re-dissolved in DCM (100 ml). The resultant solution was washed with 15 % aqueous K_2CO_3 (3 x 200 ml) followed by water (160 ml), dried over magnesium sulphate and concentrated under reduced pressure. The crude product thus obtained was purified by flash chromatography (DCM/MeOH: 98/2) to afford a dark green pure product. Yield: 0.29 g (30%). ¹H NMR (500 MHz, CDCl₃): δ 8.54 (d, 1H, *J* = 5 Hz), 8.47 (d, 1H, *J* = 5 Hz), 7.58 (m, 2H), 7.42 (m, 2H), 7.21-7.14 (m, 10H), 7.00 (m, 1H), 4.94 (s, 2H, -CH₂N-), 4.85 (s, 2H, -CH₂N-), 4.72 (br, 1H), 2.53 (m, 6H, CH₃ on BODIPY closest to N), 2.25 (q, 4H, *J* = 7.5 Hz, -CH₂- of ethyl group), 1.18 (s, 6H, CH₃ on BODIPY), 0.93 (t, 6H, *J* = 7.5 Hz, -CH₃ of ethyl group); ¹³C NMR (125.7 MHz, CDCl₃): δ 157.3, 149.7, 149.6, 138.9, 138.6, 136.9, 136.8, 129.4, 129.1, 123.1, 122.6, 122.5, 122, 121.7, 120.5, 46.4, 31.2, 17.3, 14.9, 12.7, 12, 9.7, 8.5; ¹¹B NMR (96.3 MHz, CDCl₃): -2.23 to -3.12 (br); HRMS (EI⁺): m/z 763.3748 [M+H]⁺.



Scheme 1. Synthesis of CCG-BODIPY photocatalyst

Synthesis of Chemically converted graphene from graphene oxide

The graphene oxide was prepared from natural graphite by the Hammers method.³ 5.0 g. of powdered flake graphite (325 mesh) and 2.5 g. of sodium nitrate was dissolved into 1.15 litres of sulphuric acid. The ingredients were placed in an ice-bath for safety. While maintaining vigorous agitation, 15.0 g of potassium permanganate was added to the suspension. The rate of addition was controlled carefully to prevent the temperature of the suspension from exceeding 20°C. The ice-bath was then removed and the temperature of the suspension brought to 35 °C for 30 minutes. As the reaction progressed, the mixture gradually thickened and effervescence ceased. At the end of 20 minutes, the mixture became brownish grey past with evolution of only a small amount of gas. After 30 minutes, 1.0 litres of water was slowly added with stirring, causing violent effervescence and an increase in temperature to 98 °C. The diluted suspension was maintained at this temperature for 15 minutes. The suspension was then further diluted further using approximately 2.0 litres of warm water and then treated with hydrogen peroxide to reduce the residual permanganate and manganese dioxide to colourless soluble manganese sulphate. Upon treatment with the peroxide, the suspension turned bright yellow. The suspension was filtered resulting in a yellow-brown cake. The filtration was conducted while the suspension was still warm to avoid precipitation of the slightly soluble salt of mellitic acid which forms as a side product. After washing the yellowish-brown filter cake three times with a total of 2.0 litres of warm water, the graphitic oxide residue was dispersed in 4.0 litres of water to approximately 0.0285 g solid. The remaining salt impurities were removed by treating with resinous anion and cation exchangers. The dry form of graphitic oxide was obtained by centrifugation followed by dehydration at 40°C over phosphorus pentoxide.³

CCG was synthesized as reported by Ajayan and co-workers.⁴ Dry graphene oxide (GO) was dispersed in deionized water to give a colloidal solution. The pH of this solution was adjusted to 9 - 10. Sodium borohydride was directly added into a stirred dispersion of GO, and the mixture was kept at 80°C for 1 h with constant stirring. The reduced product was filtered and washed with large amounts of water several times to remove most residual ions. This moderately reduced GO was vaccum dried over phosphorous pentoxide for two days and redispersed in concentrated sulphuric acid and then heated to 180°C with stirring for 12 h. After cooling down, the dispersion was diluted with deionised water. The final product was separated by filtration.⁴



Scheme 2. (a) Synthesis of chemically converted graphene (CCG) by the reduction of graphene oxide; (b) CCG imaged by tapping mode AFM in DMF; scale bar: 500nm.

Synthesis of chemically converted Graphene coupled BODIPY (CCG-BODIPY)

Finally, the photocatalyst was synthesized by a modified literature method.^{4,5,6}

Chemically converted graphene (CCG, 50mg) was reacted with excess of SOCl₂ in presence of catalytic amount of DMF at 70 °C for 24 h to obtain the acyl-chloride of CCG. The unreacted SOCl₂ was removed under reduced pressure and subsequently by washing with toluene. The residue thus obtained was allowed to react with BODIPY (150mg) dissolved in DCM (50ml) in presence of catalytic amount of triethylamine at 130 °C for 72 h under argon atmosphere. The completion of reaction was monitored by thin layer chromatography (TLC). The solution was then poured into acetone. The resultant suspension was filtered through membrane filter of 0.1µm pore size. The crude product thus obtained was washed repeatedly with DCM until TLC and UV-vis spectroscopy indicated absence of BODIPY in the final washing. The CCG-BODIPY was then washed with a small amount of H₂O to remove acid-amine impurities, and eventually dried under vacuum to yield the hybrid CCG-BODIPY (40mg). The photocatalyst CCG-BODIPY was analyzed by AFM, TEM, UV, FTIR, TGA, DSC, XRD, Raman, XPS, CV, LSV and time-correlated single-photon counting control technique.

Synthesis of 5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (TPP).

5-(4-Aminophenyl)-10,15,20-triphenylporphyrin was prepared by the method reported by W. J. Kruper, Jr. and co-workers.⁷ The (Nitrophenyl)triphenylporphyin (1.25 g) was dissolved in concentrated hydrochloric acid under argon atmosphere. Excess amount of $SnCl_2.2H_2O$ was added to the solution, and the reaction was heated to $65^{0}C$ for an hour. The reaction was then allowed to cool. Upon cooling, 200 ml of cold water was added and pH of the solution was adjusted to 8 using concentrated ammonium hydroxide. The aqueous phase was extracted with 6 x 200 ml portions of chloroform, which were then combined and dried over MgSO₄. The NH₂-TPP (aminophenyl)triphenylporphyrin (0.85 g) was then purified by passing over an aluminium

oxide column (~40 g) using DCM as eluent affording 71% of pure product. $R_f = 0.48$ in chloroform: ¹H NMR (CDC1₃,) **δ** 8.95 (d, 2 H, J = 5.0 Hz, β-position of pyrrole), 8.84 (d, 2 H, J = 5.0 Hz, β-position of pyrrole), 8.83 (s, 2 H, β-position of pyrrole), 8.22 (m, 6 H), 8.00 (d, 2 H, J = 8.2Hz, 4-aminophenyl), 7.76 (m, 9 H), 7.06 (d, 2 H, J = 8.3 Hz, 4-aminophenyl), 4.02 (s, 2 H, amino), -2.73 (s,2 H, central position of NH of pyrrole).

Synthesis of Chemically converted Graphene coupled TPP (CCG-NH-TPP).

CCG-NH-TPP was synthesised by reported method.⁸ Chemically converted graphene (CCG, 50mg) was reacted with SOCl₂ (25ml) in presence of catalytic amount of DMF at 70^oC for 24 h to obtain the acyl-chloride of CCG. The unreacted SOCl₂ was removed under reduced pressure and subsequently by washing with toluene. Then TPP (250mg) was stirred in DCM (50ml) in presence of catalytic amount of triethylamine (1ml) at 130 ^oC for 3 days under argon with the above residue. After completion of the reaction, the solution was poured into acetone. The resultant suspension was filtered through membrane filter. The crude product was washed repeatedly with CHCl₃/CH₂Cl₂. UV spectroscopy and thin-layer chromatography were used to determine whether filtrate contained any TPP. The CCG-NH-TPP was then washed with a small amount of H₂O to remove acid-amine impurities, and eventually dried under vacuum to yield the hybrid CCG-NH-TPP. The FTIR and HR-TEM results are identical to that reported earlier (Fig.S7a and b).

4. Quantum Yield determination of CCG-BODIPY photocatalyst.

The Quantum yield determination (Φ_Y) of CCG-BODIPY for photocatalytic NADH regeneration was carried out in a quartz cuvette reactor (3 mL) under an argon atmosphere at

room temperature. A 450-watt Newport Xenon Lamp (Oriel Instruments, USA) equipped with a 20 nm bandpass filter at 500 nm was used as a light source. The photochemical regeneration of NADH was conducted by illuminating the quartz reactor containing NAD⁺ of conc. 0.4 mM, organometallic compound [Cp*Rh(bpy)Cl]Cl of conc. 0.2 mM, TEOA of conc. 0.4 M and CCG-BODIPY (0.5 mg) in 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.

Quantum Yield
$$(\Phi_{Y}) = 2 \times \frac{\text{moles of NADH produced}}{\text{moles of incident photon}} \times 100 (\%)$$

The quantum yield of CCG-BODIPY was calculated to be 9.6 % for the photocatalytic NADH regeneration process.

5. Fluorescence decay time profile calculations

The charge separation (k_{CS}) and charge recombination (k_{CR}) rate constants were calculated from the data obtained from decay time profile studies using the equations given below. These equations were adapted from literature.⁹

$$k_{CS} = \tau_{(CCG-BODIPY)}^{-1} - \tau_{(BODIPY)}^{-1}$$
$$k_{CR} = \tau_{(CCG-BODIPY + BODIPY)}^{-1}$$

6. Density Functional Theory calculations of electronic structures

All density functional theory (DFT) calculations was performed using the plane-wave approach as implemented in the VASP code¹⁰ within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation function.¹¹ Frozen-core projector augmented wave pseudopotentials¹² were used. The Monkhorst-Pack scheme **k**-points grid sampling was done only with Γ -point for the integration of the irreducible Brillouin zone. The Kohn–Sham wave functions of the valence electrons were expanded using a plane wave basis set within a specified energy cutoff that was chosen as 400 eV. The positions of the nuclei in the initial structures were first relaxed by the conjugate-gradient algorithm, until the Hellman-Feynman forces on each nucleus were less than 0.01 eV/Å. After the relaxation a spin-polarized total energy of the electronic structure was calculated using a self-consistent field method that terminated when change in total energy between two subsequent steps was less than 10^{-6} eV. In VASP modeling of the molecular properties, the dipole correction, proposed by Neugabeauer and Scheffler,^{13,14} was used. The correction removes the artificial filed arising in the empty space from the use of Periodic Boundary Conditions (PBC) in solution of Poisson equation by Fast Fourier Transform (FFT) method.

A series of DFT calculations using Projector-Augemented Wave (PAW) atomic pseudopotentials and PBE exchange-correlation functional for GGA calculations¹⁰ support the directional electron transfer on excitation form BODIPY to Graphene. The Fermi level of CCG lies in the forbidden gap, about 1.10 eV lower than the lowest unoccupied molecular orbital (LUMO) level of BODIPY. The calculated bandgap of BODIPY is ~1.85 eV with DFT and ~2.73 eV with ZINDO calculation.

The huge surface area and the extremely high carrier mobility of graphene raise the probability for electrons to be transferred into rhodium complex, eventually accelerate the chemical reactions of NADH generation. Furthermore, the graphene also acts as an electron reservoir to transport multiple electrons. In most molecular systems, the energy cost of electron addition is very high because of large Coulomb repulsion between localized electrons. In graphene, the multi-electron addition or removal can be possible because of the delocalized nature of wavefunctions over the whole graphene surface (extending several µm).



Fig. S1 XRD patterns of CCG, BODIPY, and CCG-BODIPY.



Fig. S2 AFM height profile images of (a) CCG and (b) CCG-BODIPY.



Fig. S3 Raman spectra of GO, CCG and CCG-BODIPY recorded at different locations using 532 nm laser excitation.



Fig. S4 (a, b) C1s and O1s X-ray photoelectron (XPS) spectra of CCG and (c, d, e, f) C1s, O1s, N1s, F1s X-ray photoelectron spectra of CCG-BODIPY.





Fig. S5 (a) 1 H NMR, (b) 13 C[1 H] NMR, and (c) 11 B NMR spectra of BODIPY.



Fig. S6 (a) FTIR spectra of GO, CCG-NH-TPP, and NH_2 -TPP, and (b) HR-TEM image of CCG-NH-TPP.



Fig. S7 Linear sweep voltammograms (LSV) of **Rh**, CCG-BODIPY and CCG-BODIPY in presence of **Rh**.



Fig. S8 GC-MS data of (a) formic acid from CO_2 obtained experimentally, (b) formic acid from CO_2 calculated theoretically and (c) formic acid (H¹³COOH) from ¹³CO₂ obtained experimentally.

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