A Bio-proton Coupled Semiconductor/Metal-complex Hybrid Photoelectrocatalytic interface for Efficient CO$_2$ Reduction

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1. The Synthesis Scheme for Ru-BNAH and Ru-PLA

Scheme S1 The Synthesis Scheme for Ru-BNAH and Ru-PLA
2. The Preparation for Ru-BNAH and Ru-PLA

1-Benzyl-3-carboxypyridinium bromide (2): Nicotinic acid (12.3 g, 100 mmol) was dissolved in acetonitrile (200 mL) and benzyl bromide (17.1 g, 100 mmol) was added. The reaction mixture was refluxed at 100 °C for 15 h, after which time a precipitate was observed. The solution was cooled and diethyl ether (100 mL) was added to further precipitate the final product. After filtering and washing with diethyl ether (3 x 50 mL), the bromide salt was obtained as a white powder. $^1$H NMR (D$_2$O 400 M), $\delta$ (ppm) = 9.32 (s, 1H), 8.95 (d, $J$ = 8.0 Hz, 1H), 8.88 (d, $j$ = 8.0 Hz, 1H), 8.00-8.10 (m, 1H), 7.30-7.40 (m, 5H), 5.76 (s, 2H).

1-benzyl-1,4-dihydropyridine-3-carboxylic acid (3): The procedure for the synthesis of 1-benzyl-1,4-dihydropyridine-3-carboxylic acid refer to the reference reported$^{1-3}$. Under nitrogen atmosphere, 1-benzyl-3-carboxypyridinium bromide (14.5 g, 50.0 mmol) was dissolved in distilled H$_2$O (500 mL) and CH$_2$Cl$_2$ (100 mL) at 0 °C and NaHCO$_3$ (25.5 g, 300 mmol) was added. Sodium dithionite (34.8 g, 200 mmol) was then added in small portions over a period of 10 min and the reaction mixture was stirred at 0 °C for 1 h in the dark. The organic phase was separated, washed with cold water (3 x 200 mL), dried over MgSO$_4$, and the solvent was evaporated under reduced pressure to afford product 3a as a white powder, which was recrystallized from MeOH-H$_2$O. $^1$H NMR (400 MHz, DMSO-d6) $\delta$7.38-7.29 (m, 5H), 7.15 (s, 1H), 5.93 (dd, $j$ = 8.0 Hz, 1H), 4.69 (q, $j$ = 8.0 Hz, 1H), 4.37 (s, 2H), 2.86 (dd, $j$ = 3.0 Hz, 2H).

Ruthenium(II) 4-(2,6-di(pyridin-2-yl)pyridin-4-yl)benzoic acid complex: To a solution of RuCl$_3$·xH$_2$O (1 g) in anhydrous DMF (8 mL) was added 4-(2,6-di(pyridin-2-yl)pyridin-4-yl)benzoic acid (1.75 g, 5 mmol g) and activated anhydrous anhydrous lithium chloride (0.143 g). The resulting mixture was stirred at 120 °C for 5 h under the protection of nitrogen. The reaction mixture was cooled to room temperature and diluted with acetone (20 mL). The mixture was laid up under -25 °C for 12 h to give the black solid which was collected by filtration. The title compound was obtained by washed with cold water, cold acetone and dried in vacuum at 40°C.

Tert-butyl 2-(picolinamido)ethylcarbamate (7): To a solution of Picolinic acid
(615 mg, 5 mmol) in SOCl₂ (7 mL) was added 2 drops of DMF. The mixture stirred at 80 °C for 5 h. The solvent was removed in vacuum and then dichloromethane (10 mL) was added to give a solution A. To a solution of tert-butyl 2-aminoethylcarbamate (810 mg, 5 mmol) in dichloromethane (10 mL) was added trimethylamine (1.55 g, 15 mmol) at 0 °C. Then solution A was added dropwise. The mixture was stirred at room temperature for 3 h. The mixture was washed with water (60 mL), brine (60 mL), dried over MgSO₄, filtered and concentrated in vacuum to give a yellow solid. The title compound was obtained by silica gel chromatography (EtOAC: Petroleum ether = 10:1-1:1) to give the title compound as a white solid. ¹H NMR (400 MHz, DMSO-d₆) δ8.64 (d, j = 8.0 Hz, 1H), 7.95-8.10 (m, 2H), 7.60 (t, j = 8.0 Hz, 1H), 6.95 (s, 1H), 3.30-3.40 (m, 2H), 3.09-3.20 (m, 2H), 1.36 (s, 9H).

N-(2-aminoethyl)picolinamide (8): To a solution of tert-butyl 2-(picolinamido)ethylcarbamate (1.05 g) in dichloromethane (10 mL) was added 2,2,2-trifluoroacetic acid (10 mL) at 0 °C. The mixture was stirred at room temperature for 1 h and then concentrated in vacuum to give the title compound (0.653 g, 100%). ¹H NMR (400 MHz, DMSO-d₆) δ8.71 (d, J = 4.0 Hz, 1H), 8.49 (t, J = 8.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 4.0 Hz, 1H), 3.61 (t, J = 8.0 Hz, 1H).

N-(2-(1-benzyl-1,4-dihydropyridine-3-carboxamido)ethyl)picolinamide (9): To a solution of 1-benzyl-1,4-dihydropyridine-3-carboxylic acid (215 mg, 1 mmol) in SOCl₂ (2 mL) was added 1 drops of DMF. The mixture stirred at 80 °C for 2 h. The solvent was removed in vacuum and then dichloromethane (10 mL) was added to give a solution B. To a solution of N-(2-aminoethyl)picolinamide (165 mg, 1mmol) in dichloromethane (10 mL) was added trimethylamine (500 mg, 5mmol) at 0 °C. Then solution B was added dropwise. The mixture was stirred at room temperature for 3 h. The mixture was washed with water (10 mL), brine (10 mL), dried over MgSO₄, filtered and concentrated in vacuum to give a yellow solid. The title compound was obtained by silica gel chromatography (EtOAC: Petroleum ether = 10:1-1:1) to give the title compound. ¹H NMR (400 MHz, DMSO-d₆) δ9.40 (s, 1H), 9.12 (d, J = 8.0 Hz, 1H), 8.81 (d, J = 8.0 Hz, 1H), 8.05-8.20 (m, 1H), 7.70-7.80 (m, 1H), 7.40-7.60 (m, 7H).
7.20-7.25 (m, 1H), 4.61 (s, 1H), 3.78 (s, 1H), 2.90-3.10 (m, 4H).

**Ru-BNAH:** To a solution of Ruthenium(II) 4-(2,6-di(pyridin-2-yl)pyridin-4-yl)benzoic acid complex (56 mg, 0.1 mmol) in 10 mL EtOH/H₂O (9:1) was added N-(2-(1-benzyl-1,4-dihydropyridine-3-carboxamido)ethyl)nicotinamide (36 mg, 1 mmol). The mixture was stirred at 120 °C under N₂ protection for 8 h. The solvent was removed in vacuum and the residue was purified by silica gel chromatography (EtOAC: Petroleum ether = 1:1 to dichloromethane: methanol = 10:1) to give Ru-BNAH. ¹H NMR (400 MHz, DMSO-d6) δ 9.65-9.76 (m, 2H), 9.20-9.40 (m, 3H), 8.90 (d, J = 8.0 Hz, 1H), 8.67 (d, J = 8.0 Hz, 2H), 8.05-8.30 (m, 6H), 7.20-7.70 (m, 10H), 6.35 (s, 1H), 6.19, 5.99 (s, 2H), 2.95-3.05 (m, 4H), 2.71 (s, 2H).
**Nash’s reagent method for the products in the aqueous phase:**

Nash reagent was prepared by adding 25.0 g of ammonium acetate, 2.1 mL of acetic acid and 0.2 mL of acetylacetone into water and making the total volume of the solution 100 mL. Then 2.0 mL of liquid sample was mixed with 2.0 mL of fresh Nash reagent and shaken for 1 h at 60 °C. The final solution was analyzed by UV-Vis spectroscopy and the absorbance at 413 nm was used for quantification of formaldehyde.

For quantification of formic acid, 0.5 mL of liquid sample was added into magnesium powder (50 mg) following by drop-wise addition of 0.5 mL 37% hydrochloric acid (10 M) at 0 °C and then 3 mL 1 M sodium hydroxide. The resultant suspension was centrifuged at 10 000 rpm for 5 min and 2 mL of supernatant was mixed with 2 mL of fresh Nash reagent and stirred for 1 h at 60 °C for UV-Vis analysis to determine the total amount of formaldehyde. Formic acid can be determined after subtracting the amount of formaldehyde in the total formaldehyde.
Fig. S1 The XRD spectra of TiO$_2$/Cu$_2$O in various ratio
Fig. S2 The UV-visible spectrum (a) and band gap information of TiO$_2$/Cu$_2$O
Fig. S3 The CuLMM Auger spectra of the Ru-BNAH/TiO$_2$/Cu$_2$O photocathode.
Fig. S4 a) c) Chronoamperometric i-t curves in N$_2$ or CO$_2$ saturated 0.1 molL$^{-1}$ KCl solution at an applied potential of -0.8 V (vs. SCE) with periodical irradiation (interval of 200 s) of TiO$_2$/Cu$_2$O and Ru-BNAH/TiO$_2$/Cu$_2$O photocathode. b) Chronoamperometric i-t curves in CO$_2$ saturated 0.1 molL$^{-1}$ KCl solution at an applied potential of -0.8 V (vs. SCE) with periodical irradiation (interval of 200 s) of Ru-BNAH/TiO$_2$/Cu$_2$O, Ru-PLA/TiO$_2$/Cu$_2$O (with the presence of BNAH) and Ru-PLA/TiO$_2$/Cu$_2$O(without the presence of BNAH) photocathode.
Fig. S5 The detection of CO (a), methane and ethylene (b) by GC spectrum for gas phase under 8 hours PEC CO$_2$ reduction with different ratio of Cu$_2$O
Fig. S6 The product generation and TON of formic acid with different ratios of TiO$_2$ and Cu$_2$O photocathode under -0.9 V (vs. NHE)
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