Electronic Supplementary Information

Water-soluble Glucose-Functionalized Cobalt(III) Complex as Efficient Electrocatalyts for Hydrogen Evolution in Neutral Condition

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1. Experimental section

1.1 Materials All starting materials and solvents for the synthesis were purchased from commercial vendors and used without further purification unless otherwise specified. CH_2Cl_2 was redistilled from calcium hydride. 4-(azidomethyl) pyridine[1], and [Co^{III} $(dmgH)_2Cl_2$] (dmgH = dimethylglyoxime)[2] were prepared according to previous literature. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography.

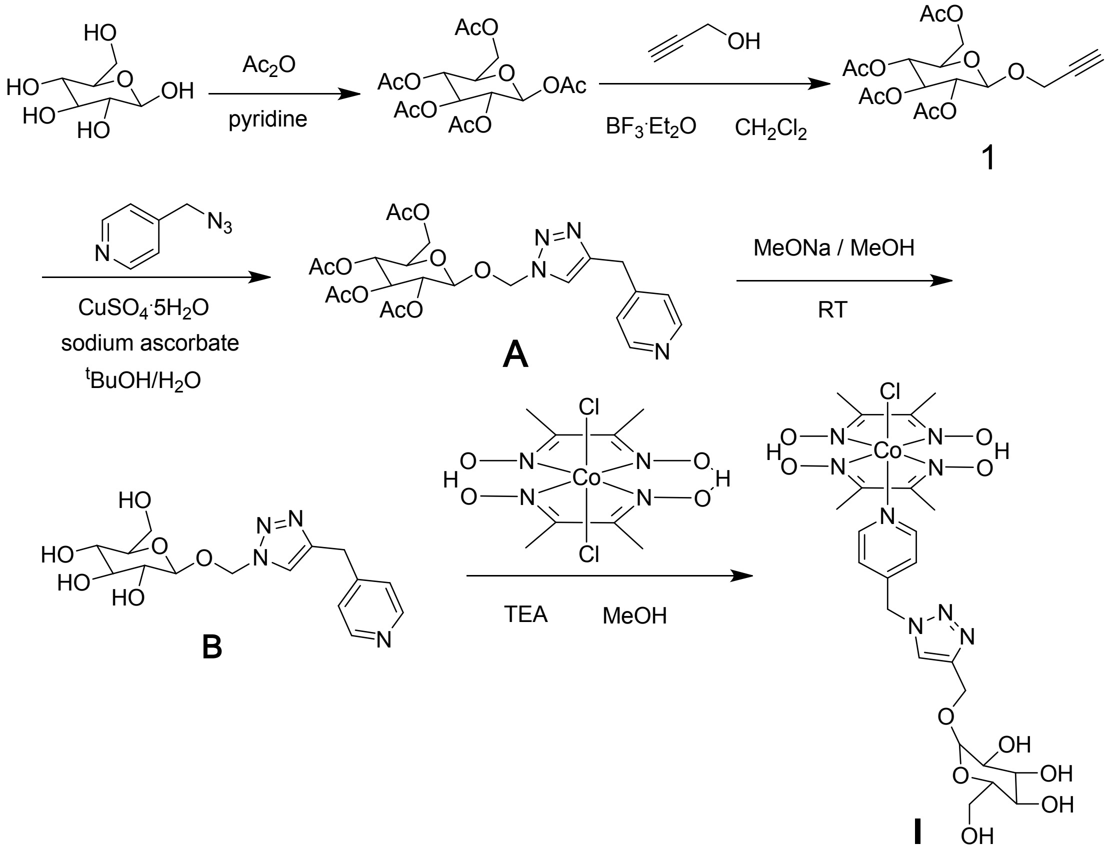
1.2 Measurements ^1H, ^{13}C NMR spectra were recorded at ambient temperature using a Varian Mercury Plus 400 instruments at 400 MHz (^1H NMR), 100 MHz (^{13}C NMR), and chemical shifts are given relative to tetramethylsilane. IR measurements were obtained on samples prepared as KBr slices using a Bio-Rad Excalibur FTS 3000 spectrometer. UV-vis spectra were measured on a Tu-1901 spectrophotometer. HRMS were recorded on a miorOTOF-QII mass spectrometer with APCI resource.

1.3 Electrochemical Methods Electrochemical measurements were performed with a model CHI660D electrochemical workstation (CH instruments) and a three-electrode system consisting of a glassy carbon (GC) working electrode (0.07 cm^2) or carbon paper (4.0 cm^2), platinum wire counter electrode, and a saturated calomel reference electrode. All potentials are referenced to the normal hydrogen electrode (by adding 0.241 V). Cyclic voltammetry experiments were conducted in a one compartment cell with TEOA (triethanolamine) and Na_2SO_4 (0.1 M each) in 15 mL water as electrolyte solution. All measurements were performed at 25℃ under air.

Controlled-potential electrolysis experiment (CPE) was carried out with [Co$^{\text{III}}$(dmgH)$_2$(py-glucose)Cl] (0.5 mM) in an aqueous solution of TEOA/Na_2SO_4(0.1 M each) with neutral pH at -0.90 V versus NHE for the duration of 8 h. A N_2 (containing 2% CH_4 as internal standard for GC measurements) atmosphere was used and the electrolyte solution had been vigorously purged with Ar for 15 minutes prior to beginning the CPE experiment. H_2 was detected by gas chromatographic (Aglient 7890A) and using the methane (2%) as internal standard gas.

1.4 The synthesis and characterization of [Co^{III}(dmgH)$_2$(py-glucose)Cl]

The synthetic rout for [Co^{III}(dmgH)$_2$(py-glucose)Cl] complex is shown as follows: (Scheme S1) and the preparation of **1** is according to the literature report.[3,4]



Scheme S1 The synthetic rout for [Co^{III}(dmgH)$_2$(py-glucose)Cl] complex.

Synthesis of A. A mixture of **1** (1.9 g, 5.0 mmol), 4-(azidomethyl)pyridine (1.0 g, 7.5 mmol), $CuSO_4 \cdot 5H_2O$ (125 mg, 0.5 mmol), and sodium ascorbate (198 mg, 1 mmol) were added to a solution of ^{t}BuOH/H_2O (20 ml V:V 7:3) under argon, after stirring for 12 h at room temperature the solvents were removed in vacuo, and the crude product was extracted three times with CH_2Cl_2 (3×100 ml), combined the organic phase, dried over anhydrous magnesium sulfate and contracted in vacuum. The resulting residue was further purified by column chromatography on silica gel with petroleum / ethyl acetate as eluent to afforded 2.3 g of **A** as a white solid (88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.5 Hz, 2H), 7.54 (s, 1H), 7.12 (d, *J* = 5.5 Hz, 2H), 5.56 (s, 2H), 5.20 (dd, *J* = 12.3, 6.6 Hz, 1H), 5.13 – 5.05 (m, 1H), 5.03 – 4.91 (m, 2H), 4.84 (d, *J* = 12.7 Hz, 1H), 4.68 (d, *J* = 7.9 Hz, 1H), 4.25 (dd, *J* = 12.3, 4.6 Hz, 1H), 4.15 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.77 – 3.69 (m, 1H), 2.07 (s, 3H), 2.03 (d, *J* = 5.6 Hz, 3H), 1.99 (d, *J* = 6.4 Hz, 3H), 1.93 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) [ppm] δ 170.6, 170.1, 169.4, 169.3, 150.6, 145.2, 143.4, 123.1, 122.1, 100.2, 72.7, 71.9, 71.2, 68.3, 63.1, 61.8, 52.7; **IR** (KBr) ν (cm^{-1}): 3117.69, 3077.44, 2939.84, 2894.72, 1739.53, 1602.90, 1563.83, 1422.62, 1378.60, 1226.77, 1041.81, 910.19, 859.80, 789.66, 605.03; **HRMS** (ESI) found: m/z 543.1696 $[M+Na]^+$; calcd. for $C_{15}H_6F_4N_4$+Na.543.1699.

Synthesis of B. To a solution of **A** (2.1g, 4.0 mmol) in 15 ml methanol was added 2N NaOMe (0.8 ml). The reaction mixture was stirred at room temperature for 5 h. Upon completion monitoring by TLC, the solvent was removed and the crude product was purified by flash column chromatography to give B as a white solid (1.2 g, 90%). **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.56 (s, 2H), 8.24 (s, 1H), 7.21 (s, 2H), 5.68 (s, 2H), 4.86 (d, *J* = 11.8 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.27 (d, *J* = 6.5 Hz, 2H), 3.48 (s, 3H), 3.11 (dd, *J* = 31.3, 8.0 Hz, 3H), 2.98 (s, 1H), 1.66 (s, 2H); **^{13}C-NMR** (100 MHz, DMSO-D6) [ppm] δ 150.5, 145.4, 144.9, 125.4, 122.8, 102.7, 77.5, 77.1, 73.9, 70.6, 62.0, 61.6, 52.0; **IR** (KBr) ν (cm^{-1}): 3419.54, 1664.29, 1572.74, 1406.99, 1227.29, 1026.62, 824.52, 763.50, 626.65; **HRMS** (ESI) found: m/z 375.1287 $[M+Na]^+$; calcd. for $C_{15}H_6F_4N_4$+Na.375.1281.

Synthesis of $[Co^{III}(dmgH)_2(py\text{-}glucose)Cl]$. To a solution of $[Co^{III}(dmgH)_2Cl_2]$ (1.08 g, 3.0 mmol) in 20 ml methanol was added TEA (303 mg, 417 ml). The mixture was stirred at room temperature until the solid was completely dissolved, then solid **B** (1.06 g, 3.0 mmol) was added to the solution. The reaction was stirred further at room temperature for 24 h. Upon completion, the solvent was removed in vacuum and the compound was obtained as a deep brown solid (1.6 g, 80% yield). **^{13}C CP/NMR** spectra [ppm] δ 181.1, 177.8, 162.0, 153.5, 131.6, 125.1, 123.6, 76.5, 73.8, 65.2, 59.6, 56.6, 48.1, 31.3, 23.9, 13.5, 10.4. **IR** (KBr) ν (cm^{-1}): 3401.37, 2932.81, 1719.30, 1568.37, 1409.31, 1238.53, 1065.43, 796.79, 742.22, 652.01, 620.67, 512.47; **ESI-MS** found**:** m/z 678.2028 $[M+2H]^{2+}$; calcd. for $C_{36}H_{34}ClCoN_8O_{10}$+2H. 678.1575; and m/z 642.5759 $[M\text{-}Cl+H]^+$; calcd. for $C_{23}H_{34}CoN_8O_{10}$–Cl+H. 642.5048.

References.

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2 M. Razavet, V. Artero, M. Fontecave, *Inorg. Chem.,* 2005, **44**, 4786-4795.

3 P. M. Williams, G. N. Sheldrake, S. J. F. Mcdonald, C. J. Hamilton, *Carbohyd. Res*., 2011, **346**, 1257-1261.

4 S. K. Mamidyala, M. G. Finn, *J. Org. Chem.,* 2009, **74**, 8417-8420.

2. Catalyst Characterisation

2.1 UV/Vis spectra of [Co^{III}(dmgH)$_2$(py-glucose)Cl] and [Co^{III}(dmgH)$_2$Cl$_2$]

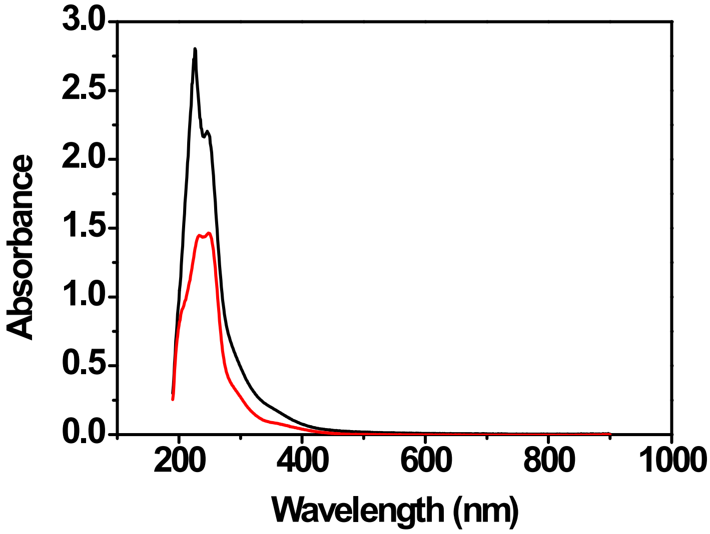

Figure S1. UV/Vis spectra of [Co^{III}(dmgH)$_2$(py-glucose)Cl] (red line) and [Co^{III}(dmgH)$_2$Cl$_2$] (black line) in water.

2.2 Infrared spectroscopy of [Co^{III}(dmgH)$_2$(py-glucose)Cl] and [Co^{III}(dmgH)$_2$Cl$_2$]

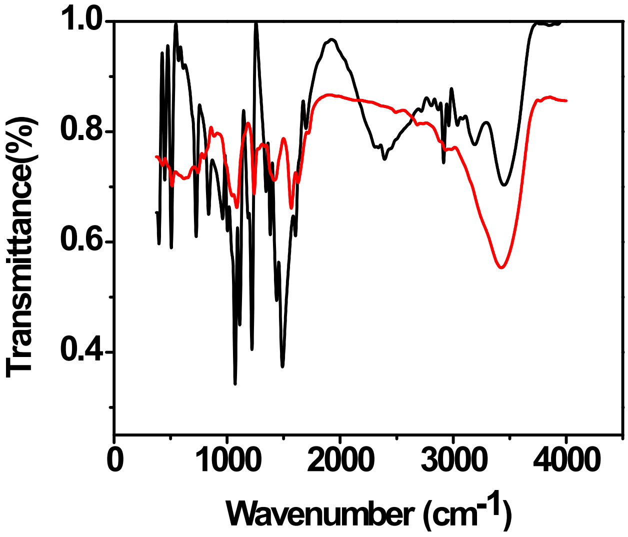

Figure S2. Infrared spectroscopy of [Co^{III}(dmgH)$_2$Cl$_2$] (black line) and [Co^{III}(dmgH)$_2$(py-glucose)Cl] (red line).

2.3 CVs of [Co^{III}(dmgH)$_2$(py-glucose)Cl] in DMF

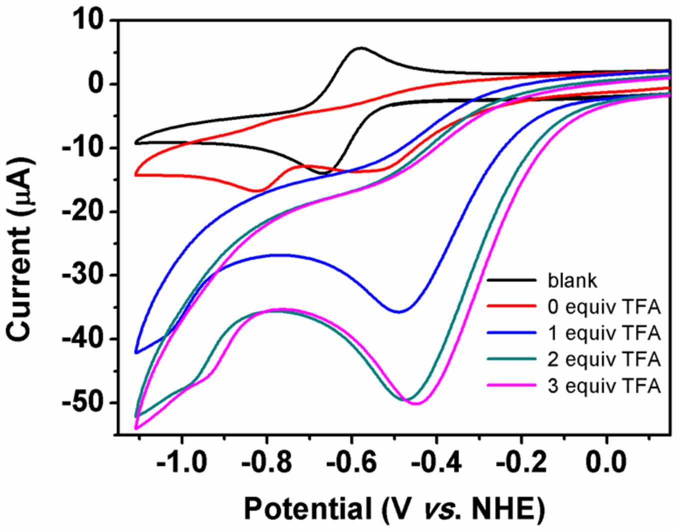

Figure S3. Cyclic voltammograms was conducted with 1.0 mM of catalyst **I,** 0.1 M (Bu$_4$N)PF$_6$ in 15 mL DMF on a glassy carbon electrode (0.07 cm^2) at a scan rate of 50 mV/s^{-1}, in the presence of different equiv trifluoroacetic acid (TFA).

2.4 CVs of [Co^{III}(dmgH)$_2$(py-glucose)Cl] in different buffers

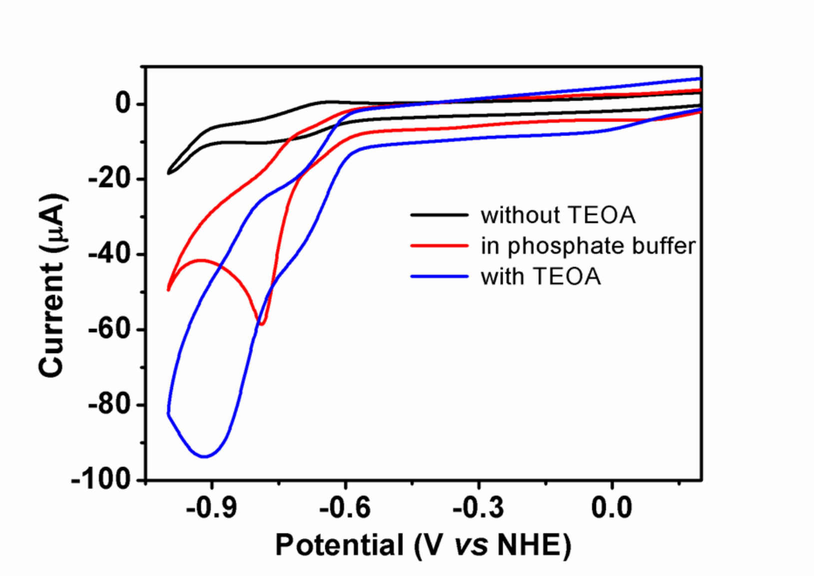

Figure S4. The cyclic voltammogram experiments were measured with 1 mM catalyst I in different solutions. The black line was obtained in an aqueous solution of Na_2SO_4 (0.1 M) without TEOA; the red line was obtained in phosphate buffer (0.1 M); the blue line was measured in an aqueous solution of TEOA/Na_2SO_4 (0.1 M each). All experiments were conducted at pH 7 and room temperature.

2.5 CVs of [Co^{III}(dmgH)$_2$(py-glucose)Cl] at various scan rates

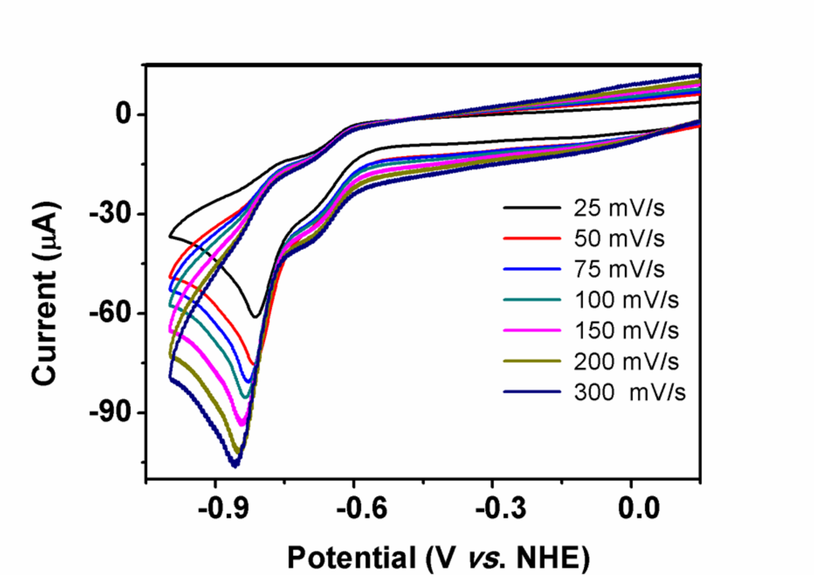

Figure S5. Cyclic voltammograms of catalyst **I** (1.0 mM) at various scan rates was conducted in an aqueous solution of TEOA/Na_2SO_4 (0.1 M each) at room temperature.

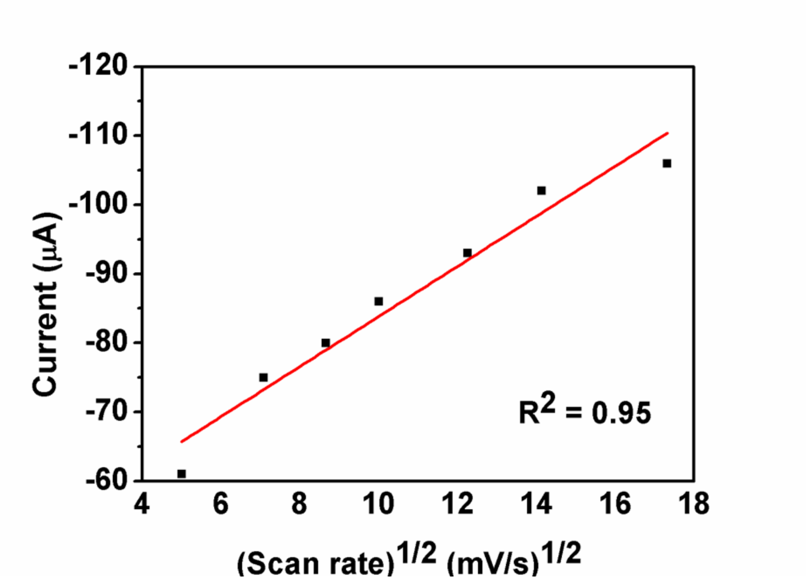

Figure S6. Plot of the peak current of the cathodic scans versus the square root of the scan rate for an aqueous solution of 1.0 mM catalyst **I** with TEOA/Na_2SO_4 (0.1 M each). Scan rates: 25-300 mV s^{-1}.

2.6 The contrast experiment of [$Co^{III}(dmgH)_2$(py-glucose)Cl] before and after CPE

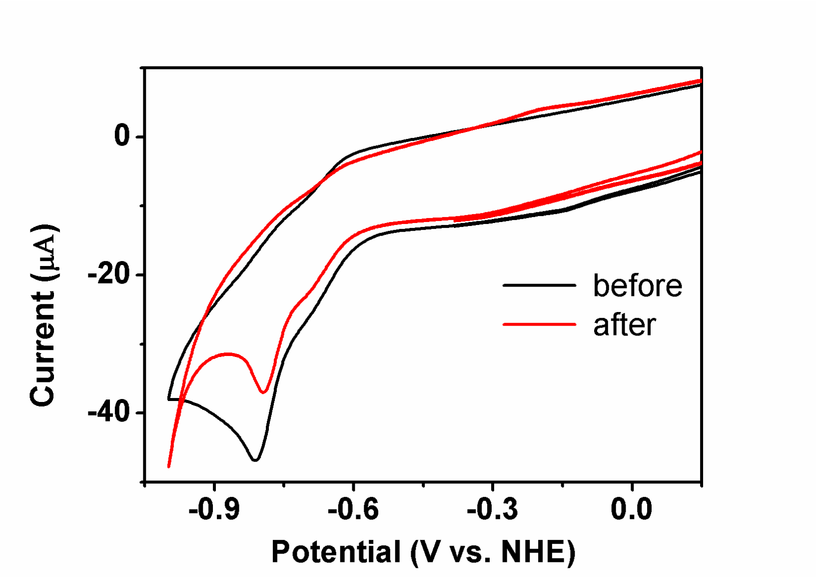

Figure S7. Cyclic voltammograms recorded the catalyst **I** before (black line) and after (red line) 8 h CPE experiment at -0.90 V versus NHE in a TEOA/Na_2SO_4 (0.1 M) aqueous solution. Scan rate: 50 mV/s^{-1}.

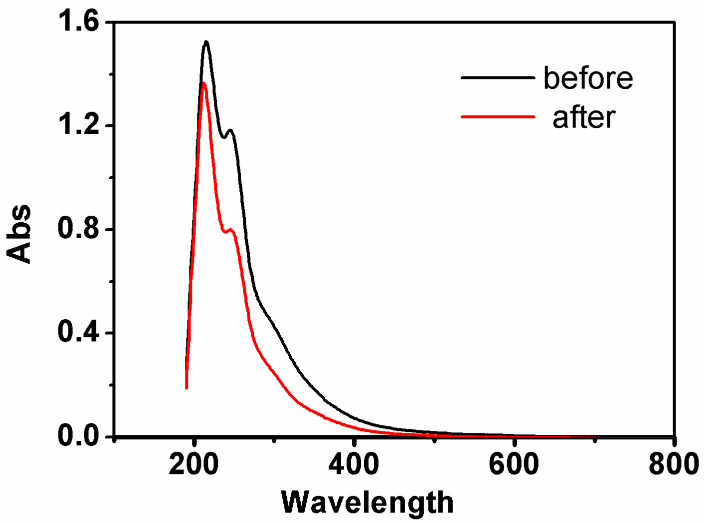

Figure S8. UV/Vis spectra of catalyst **I** before (black line) and after (red line) 8 h controlled-potential electrolysis (CPE) experiment at -0.90 V vs. NHE.