

Supporting Information

Bimetallic porous porphyrin polymer-derived non-precious metal electrocatalysts for oxygen reduction reactions

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1. Synthesis of (Metal-)Porphyrin Derivatives and CMPs

1.1 Synthesis of 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin

2.5 l propionic acid was heated to 130 °C. *p*-bromobenzaldehyd (202 g, 1.09 mol) freshly distilled pyrrole (75.5 ml, 1.09 mol) was added. The mixture was heated for 30 min to reflux and cooled down to room temperature with an ice bath. The violet precipitate was collected by filtration and washed with methanol and hot water. The product was dissolved in CHCl₃ and purified by precipitation in methanol. After filtration the product was dried in vacuo to yield 68 g (29%). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ = -2.86 (s, 2H), 7.91 (d, ³J=8.3 Hz, 8H), 8.08 (d, ³J=8.3 Hz, 8H), 8.84 (s, 8H) ppm. ¹³C-NMR (CDCl₃, 75 MHz, 298 K): δ = 119.0, 122.7, 130.0, 135.8, 140.8 ppm. MS (FD, 8 kV) m/z = 928.5 g/mol – calculated for C₄₄H₂₆Br₄N₄: 929.9 g/mol. Elemental analysis (%) calculated for C₄₄H₂₆Br₄N₄: C 56.81, H 2.82, N 6.02; found: C 56.66, H 2.78, N 5.82. UV-Vis (CHCl₃): λ_{max/nm}: 419.

1.2 Synthesis of iron (III) 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin

A mixture of 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin (10 g, 10.75 mmol) and FeCl₂•(H₂O)₄ (50 g, 251.5 mmol) were dried in vacuo for 2h. Degassed dimethylformamide (DMF) (1.4 l) was added and the mixture was stirred at 140 °C overnight. After cooling to room temperature aqueous HCl (3.0 M, 200 ml) was added dropwise into the mixture and stirred for 10 min. The resulting precipitate was filtered and washed with aqueous HCl (0.5 M, 250 ml) and H₂O until the pH value was neutral. The product was purified by recrystallization from methanol and chloroform three times. After subsequent drying 9 g (82%) of a purple powder was obtained. MS (FD, 8 kV) m/z = 1018.5 g/mol – calculated for C₄₄H₂₄Br₄N₄FeCl: 1018.8 g/mol. Elemental analysis (%) calculated for C₄₄H₂₄Br₄N₄FeCl: C 51.83, H 2.47, N 5.49; found: C 51.86, H 2.43, N 5.45. UV-Vis (CHCl₃): λ_{max/nm}: 417.

1.3 Synthesis of Cobalt (II) 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin

A mixture of 5,10,15,20-tetrakis(4'-bromophenyl)porphyrin (5 g, 5.37 mmol) and $\text{Co}(\text{OAc})_2 \cdot (\text{H}_2\text{O})_4$ (6.0 g, 24.1 mmol) were dried in vacuo for 2h. Degassed DMF (400 ml) was added and the mixture was stirred at 140 °C overnight. The resulted precipitate was filtered and washed with H_2O and methanol. The product was purified by recrystallization from methanol and chloroform (50/50). After subsequent drying 4.5 g (85%) of a purple powder was obtained. MS (FD, 8 kV) $m/z = 986.3$ g/mol – calculated for $\text{C}_{44}\text{H}_{24}\text{Br}_4\text{N}_4\text{Co}$: 986.8 g/mol. Elemental analysis (%) calculated for $\text{C}_{44}\text{H}_{24}\text{Br}_4\text{N}_4\text{Co}$: C 53.53, H 2.45, N 5.68; found: C 53.75, H 2.67, N 5.52. UV-Vis (CHCl_3): $\lambda_{\text{max/nm}}$: 412.

1.4 Synthesis of 5,10,15,20-tetrakis(4'-benzenediboronic acid bis(pinacol) ester) porphyrin

500 ml propionic acid was heated to 140 °C. Then 49.3 g (0.21 mol) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde and pyrrole were added and the mixture was heated under reflux for 1 h. The formed precipitate was filtered off after the mixture was cooled down to room temperature, rinsed twice with methanol and water before recrystallized from chloroform/methanol (1:1, 100 ml). After filtration the product was dried in vacuo to yield 13 g target molecule (22 %). ^1H NMR (C_2Cl_4 , 300 MHz, 298 K): $\delta = -2.69$ (s, 2H), 1.40 (m, 48H), 8.25 (d, $^3J = 7.9$ Hz, 8H), 8.31 (d, $^3J = 7.9$ Hz, 8H), 8.87 (s, 8H) ppm. ^{13}C -NMR (CDCl_3 , 75 MHz, 298 K): $\delta = 25.2, 84.6, 122.8, 128.1, 133.1, 134.6, 138.4, 142.2, 145.9$ ppm MS (MALDI-TOF) $m/z = 1116.9$ g/mol – calculated for $\text{C}_{68}\text{H}_{74}\text{B}_4\text{N}_4\text{O}_8$: 1118.6 g/mol. Elemental analysis (%) calculated for $\text{C}_{68}\text{H}_{74}\text{B}_4\text{N}_4\text{O}_8$: C 73.02, H 6.67, N 5.01; found: C 73.16, H 6.25, N 4.98. UV-Vis (CHCl_3): $\lambda_{\text{max/nm}}$: 421.

1.5 Synthesis of cobalt(II) 5,10,15,20-tetrakis(4'-benzenediboronic acid bis(pinacol) ester) porphine

A mixture of 5,10,15,20-tetrakis(4'-benzenediboronic acid bis(pinacol) ester) porphyrin (8 g, 7.15 mmol) and $\text{Co}(\text{OAc})_2$ (10.7 g, 40.2 mmol) were dried in vacuo for 2h. Degassed DMF (400 ml) was added and the mixture was stirred at 140 °C overnight. The mixture was cooled to 0 °C and the purple solid was filtered off, washed with methanol /chloroform (1:1) and dried in vacuo to yield 7.15 g target molecule (85%). MS (MALDI-TOF) $m/z = 1174.9$ g/mol – calculated for $\text{C}_{68}\text{H}_{72}\text{B}_4\text{N}_4\text{O}_8\text{Co}$: 1174.5 g/mol. Elemental analysis (%) calculated for $\text{C}_{68}\text{H}_{72}\text{B}_4\text{N}_4\text{O}_8\text{Co}$: C 69.48, H 6.17, N 4.77; found: C 68.76, H 7.03, N 5.35. UV-Vis (CHCl_3): $\lambda_{\text{max/nm}}$: 426.

Synthesis of CMPs

Monometallic CMPs were synthesized by following procedure: 100 mg porphyrin was mixed in a Schlenk flask with 1,4-benzenediboronic acid bis(pinacol) ester (2 equivalents), dioxane (20 ml) and aqueous potassium carbonate (3.6 ml, 0.4 M). The mixture was degased by three freeze pump thaw cycles before heating to 80 °C. After 30 min tetrakis(triphenylphosphine)palladium (0) (0.16 equivalents) was added and the mixture was heated to reflux (110 °C) for 16 h. The mixture was allowed to cool down to room temperature and poured into water. The precipitate was collected by filtration and washed rigorously with water, methanol and tetrahydrofuran (THF) and acetone, transferred into a Soxhlet extractor and washed 24 h with methanol, THF and acetone, respectively, and dried in vacuo to give a red purple solid.

The metal-free and the bimetallic CMPs were synthesized by the same procedure substituting 2 equivalents 1,4-benzenediboronic acid bis(pinacol) ester by 1 equivalent of 5,10,15,20-tetrakis(4'-benzenediboronic acid bis(pinacol) ester) and cobalt(II) 5,10,15,20-tetrakis(4'-benzenediboronic acid bis(pinacol) ester) porphine, respectively.

2. Characterization of CMPs and metal nitrogen doped carbons

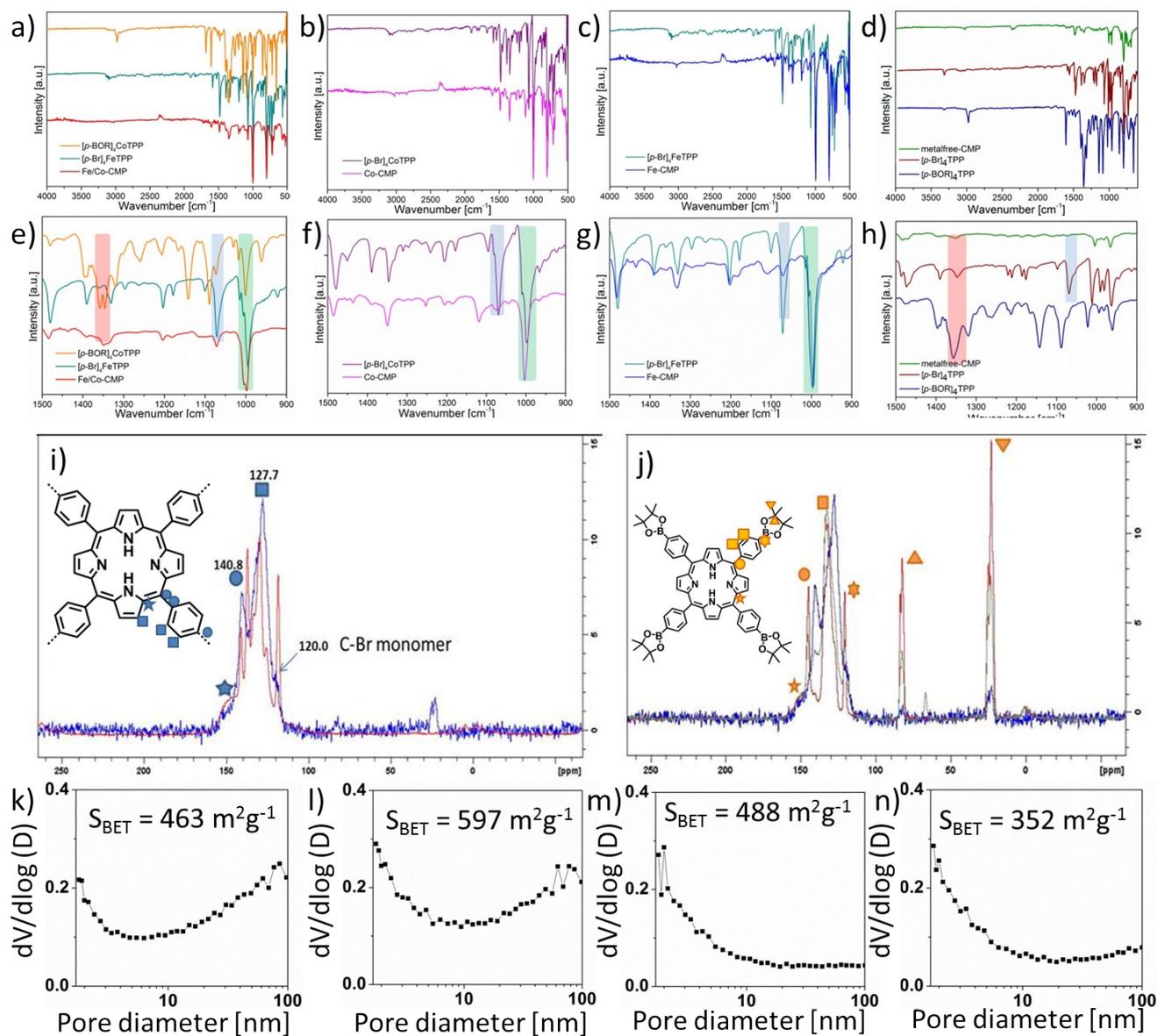


Figure S1. a-h) Survey (a-d) and detail (e-h) of IR-spectra of a) [p-Br]₄FeTPP, [p-BOR]₄CoTPP and Fe/Co-CMP, b) [p-Br]₄CoTPP and Co-CMP, c) [p-Br]₄FeTPP and Fe-CMP, d) [p-Br]₄TPP, [p-BOR]₄TPP and metal-free CMP; showing intensity of B-O stretching band (1357 cm⁻¹) and C-Br band (1068 cm⁻¹) decreasing intensively and the retention of the M-N₄ peak (ca. 1000 cm⁻¹). i) MAS ¹³C-NMR of [p-Br]₄TPP monomer (red) and the Suzuki condensation polymer (blue). j) MAS ¹³C-NMR [p-BOR]₄TPP monomer (red) and the Suzuki condensation product after 2 h (green) and 24 h (blue). k-n) Pore size distribution and BET surface area of k) Fe/Co-CMP, l) Co-CMP, m) Fe-CMP, and n) metal-free CMP.

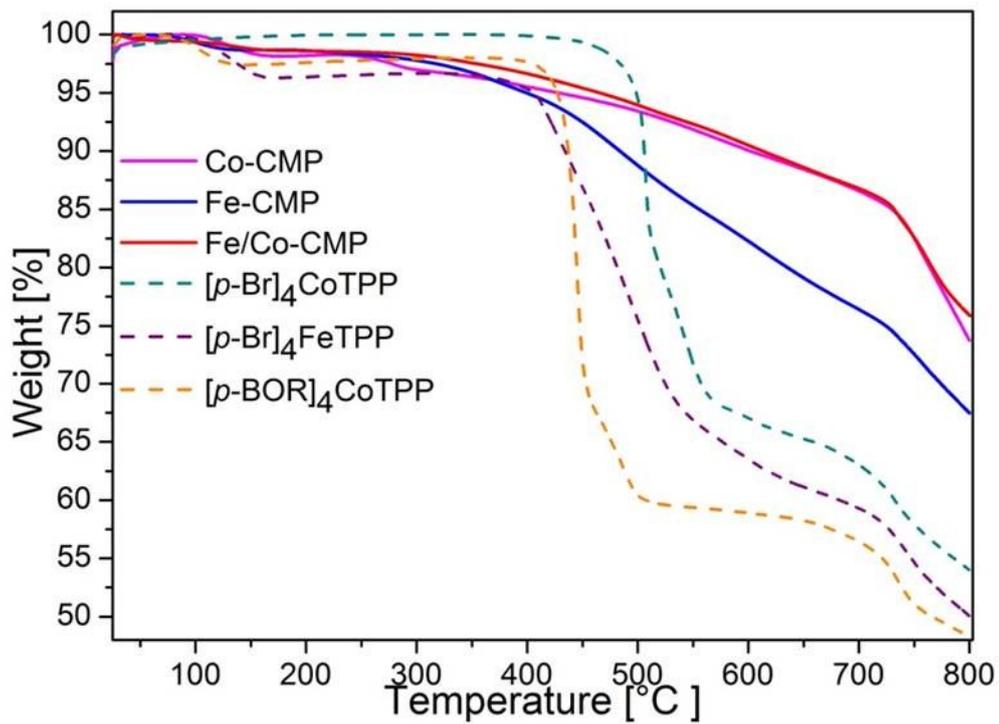


Figure S2. Thermogravimetric analysis (TGA) of M-CMPs and their monomers.

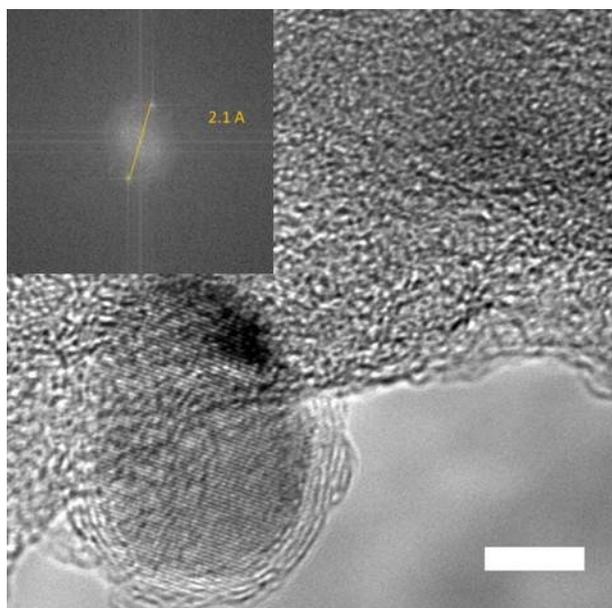


Figure S3. HRTEM image (scale bar 5 nm) of Fe-CMP-800* showing iron carbide nanoparticle encapsulated in a carbon shell and its diffractogram (inset).

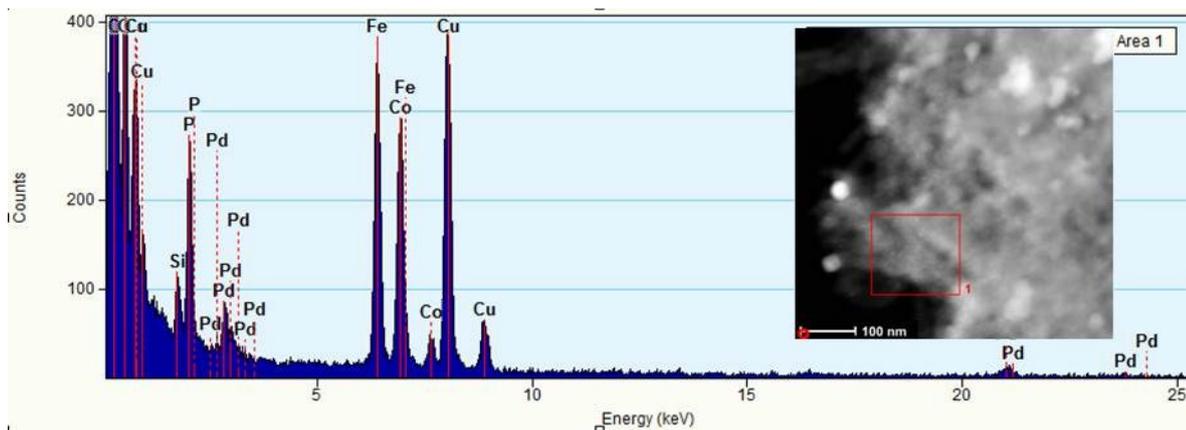


Figure S4. Dark field TEM image and EDX-spectra of Fe/Co-CMP-800*.

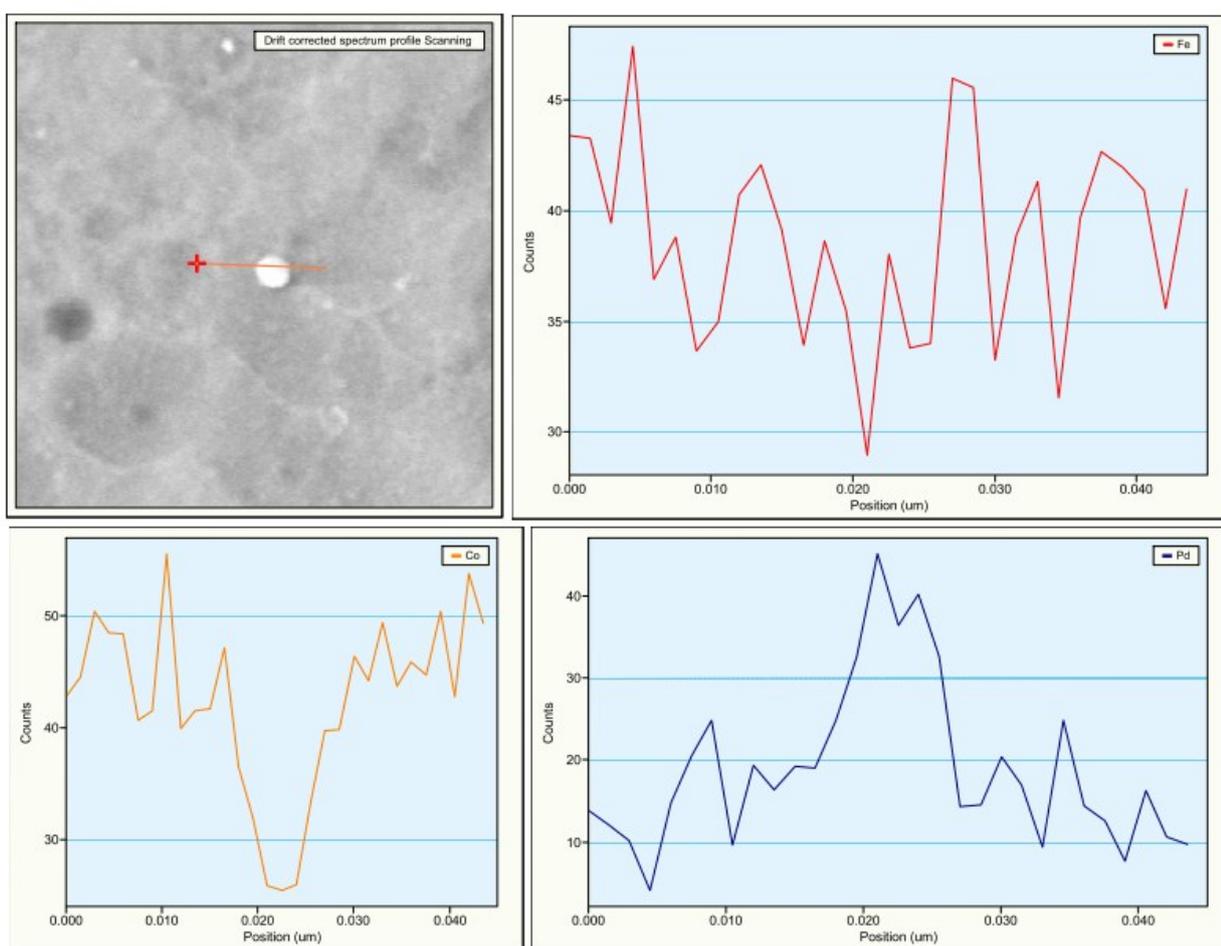


Figure S5. Dark field TEM image of Fe/Co-CMP-800 and EDX profile of selected range showing Pd nanoparticle on a Fe/Co/N-doped carbon matrix.

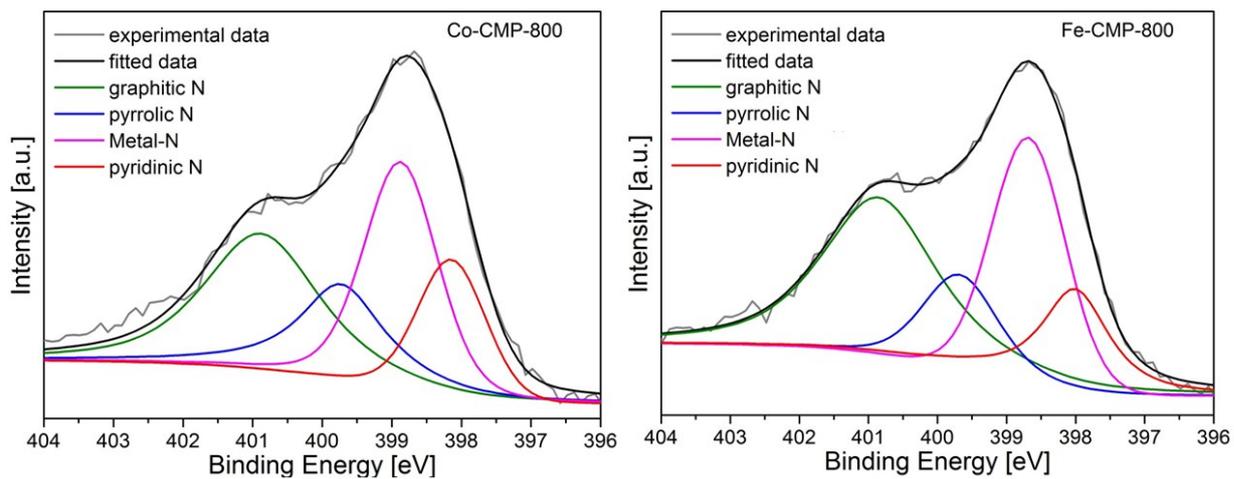


Figure S6. High resolution N1s XPS spectra of Co-CMP-800 and Fe-CMP-800.

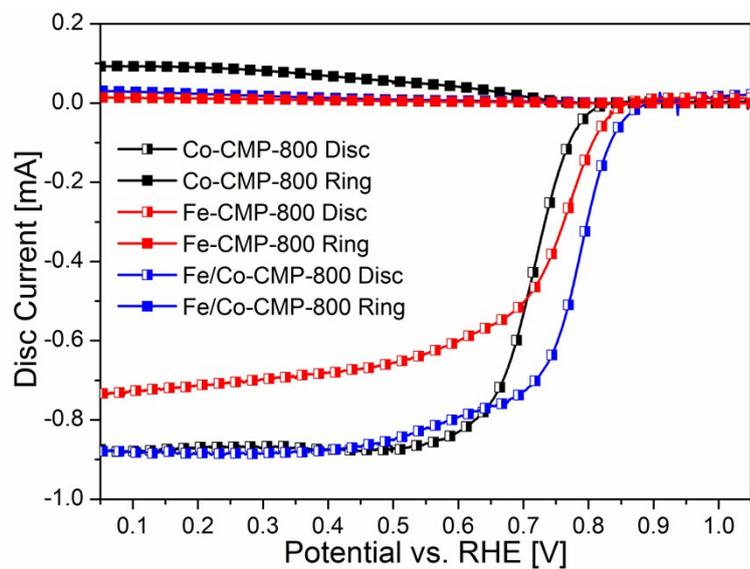


Figure S7. RRDE polarization curves of M-CMP-800 (M = Co, Fe, Co/Fe) with a catalyst loading of 0.6 mg/cm².

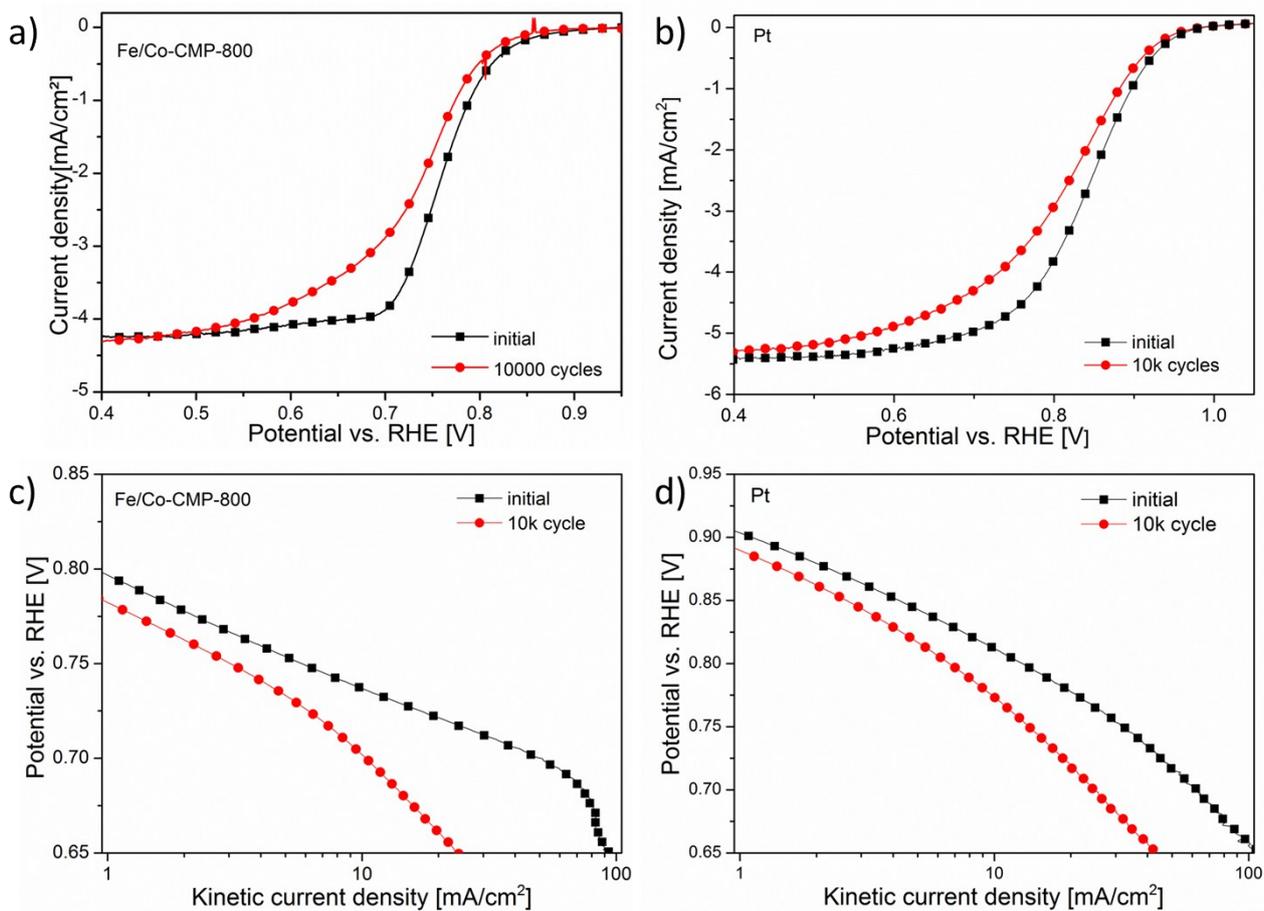


Figure S8. ORR polarization curves (a, b) and corresponding Tafel slopes (c, d) before and after 10,000 CV cycles in oxygen saturated 0.5 M H₂SO₄ of Fe/Co-CMP-800 (a, c) and Pt/C (b, d).

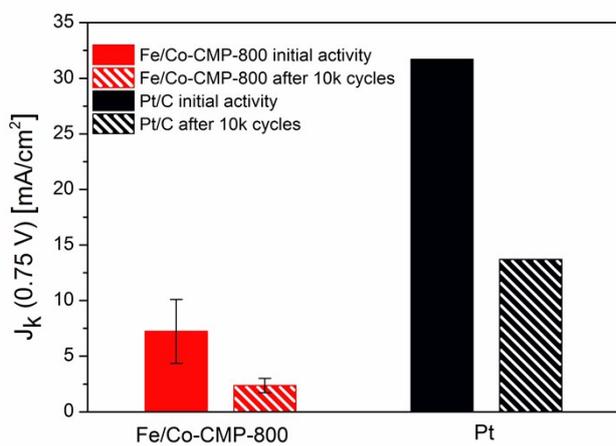


Figure S9. Kinetic current density at 0.75 V at beginning and after 10,000 CV cycles.

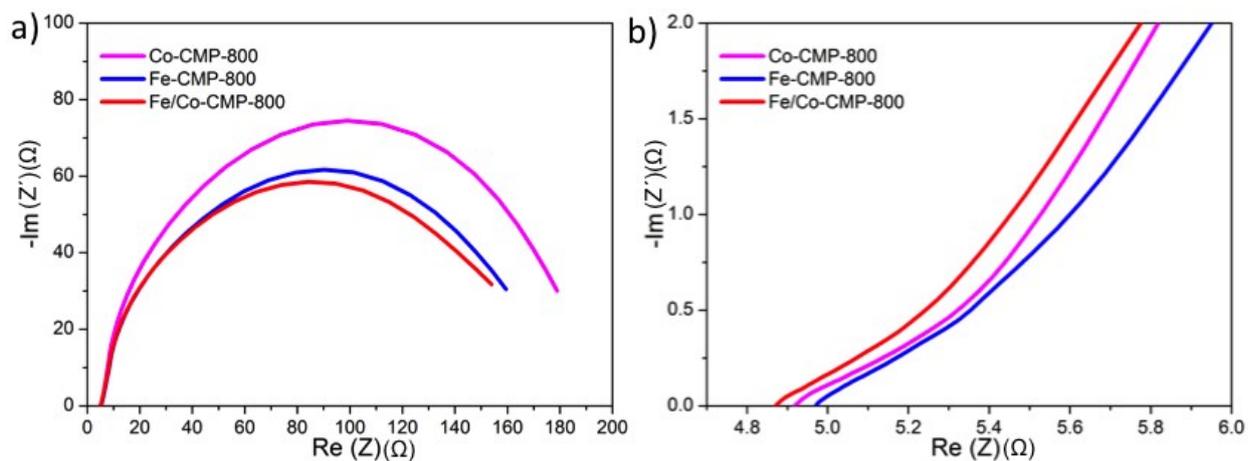


Figure S10. Electrochemical impedance spectroscopy (EIS) analyses of the catalysts (a). High-frequency region of the impedance spectra of the catalysts (b). EIS were recorded in O_2 -saturated 0.5 M H_2SO_4 at 0.78 V vs RHE with 5 mV ac potential from 10 kHz to 0.01 Hz. The loading was 0.6 mg/cm^2 for all materials. Electrode rotation speed, 1600 rpm.

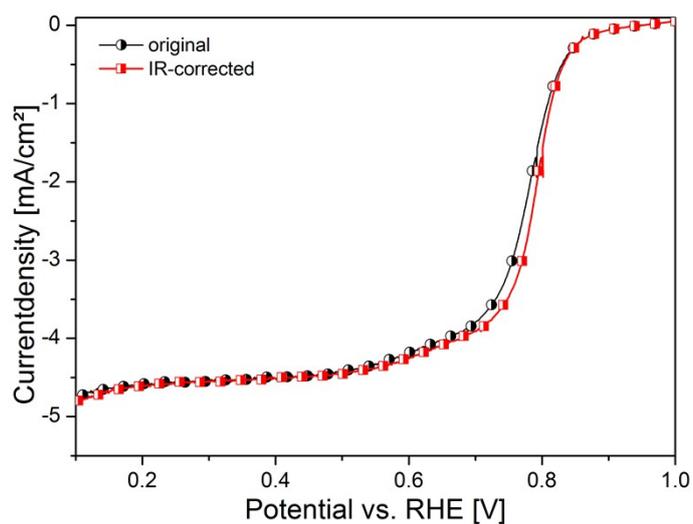


Figure S11. RDE polarization curve of Fe/Co-CMP-800, before and after IR-compensation