Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enhancement of the Oxygen Reduction Reaction Electrocatalytic Activity of Metallo-Corroles Using Contracted Cobalt(III) CF3-Corrole Incorporated in High Surface Area Carbon Support

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Experimental

Synthesis

Cobalt(III)-5,10,15-tris(trifluoromethyl)-corrole (CF_3-corrole) and Cobalt(III)-5,10,15-tris(pentafluoro phenyl)-corrole (tpf-corrole) were synthesized according to previously published methods.[2] [3]

Catalyst slurry preparation

10 mg of BP2000 carbon and 0.8 mg of corrole were mixed in 1 mL of isopropanol and stirred overnight to allow the corrole to adsorb inside the carbon, according to a procedure described elsewhere.[4] The samples were then centrifuged, and the carbon was separated from the excess corrole and solvent. According to calibration curve using UV-vis, 0.48mg/10mg CF_3-corrole/BP2000 and 0.56mg/10mg tpf-corrole/BP2000 were the amount of corrole adsorbed on the carbon. Then, 1 mL of solution containing 2:1 (volumetric ratio) of isopropanol/deionized water and 0.2 wt% Nafion was added the carbon-corrole composite. [4]

Electrochemistry

Rotating ring-disk electrode (RRDE) (glassy carbon electrode disc with surface of 0.2475 cm^2, and a platinum ring, collection efficiency of 0.37 from Pine instrument) measurements were conducted using a Biologic VSP potentiostat coupled with a Pine Instruments rotator. 10 µL of the catalyst slurry were deposited using spin-coater in order to maintain uniform coating on the surface of a glassy carbon disk of a rotating ring-disk electrode and were left to dry at room temperature while spinning. A glassy carbon rod and a reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. All measurements were conducted in 0.1 M aqueous solution of KOH (Acros, 98%).[5] Background currents were measured after purging Ar (99.99%) into the cell and were subtracted from the results. When testing the catalytic performance of the system toward ORR, O_2 (99.99%) was purged into the cell for 20 min prior to the measurement and during the measurement to assure the saturation of the solution with dissolved oxygen. All the measurements were repeated to ensure reproducibility of the results are displayed. The collection efficiency of the modified electrode was measured by RRDE in 1mM $K_4Fe(CN)_6$ and 1M KNO_3 solution (Fig. S1).

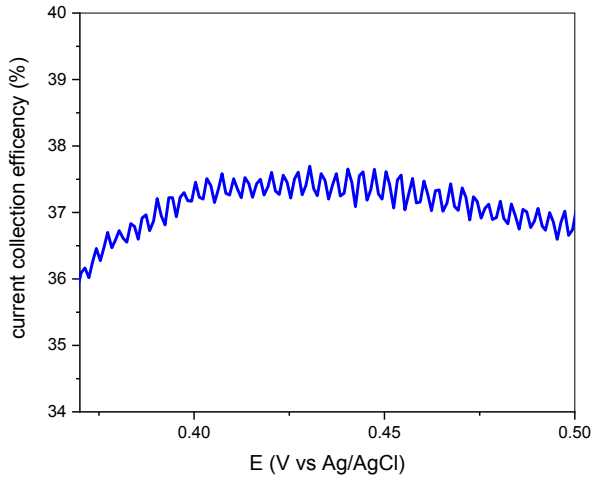


Figure S1. Current collection efficiency of the modified electrodes. Scan rate 20mV/s and 900rpm in 1mM $K_4Fe(CN)_6$ and 1M KNO_3 solution.

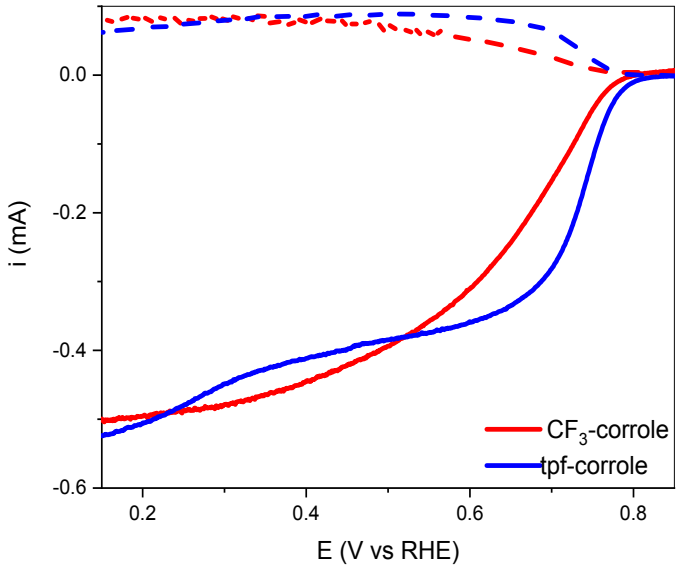
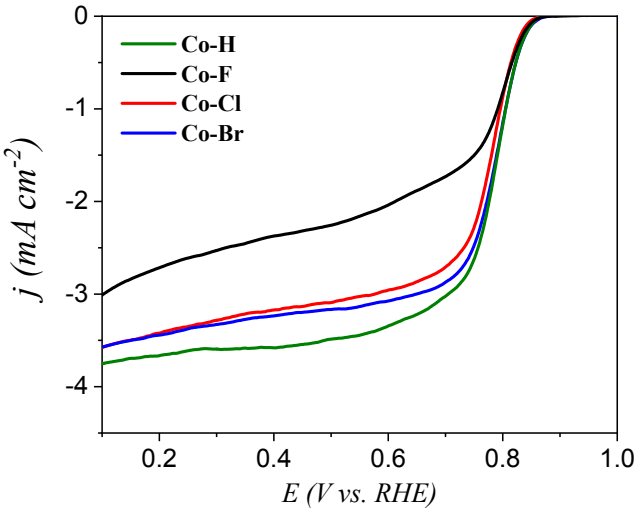


Figure S2. Corroles adsorbed on BP2000 in 0.5M H2SO4 @ 900 RPM (dashed-ring currents, solid- disk currents)



XPS

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Nexsa spectrometer (England) equipped with a mono-chromated, micro-focused, lower Al Ka X-ray (photon energy 1486.6 eV).

Figure S3. Corroles adsorbed on BP2000 in 0.1M KOH @ 900 RPM[1]

Survey and high-resolution spectra were acquired at pass energy of 200 eV and 50 eV, respectively. Source power was normally 72 W. The binding energies of all the elements were recalibrated by setting the CC/CH component of the adventitious carbon 1s peak at 285 eV. Despite the disadvantages of the calibration method, it is still the most common technique and there is consensus of using it. [6] The measurements had been carried out under UHV conditions, at base pressure of $5x10^{-10}$ torr (and no higher than $3x10^{-9}$ torr). Data analysis was performed using AVANTAGE software. A linear background subtraction was used for all spectra.

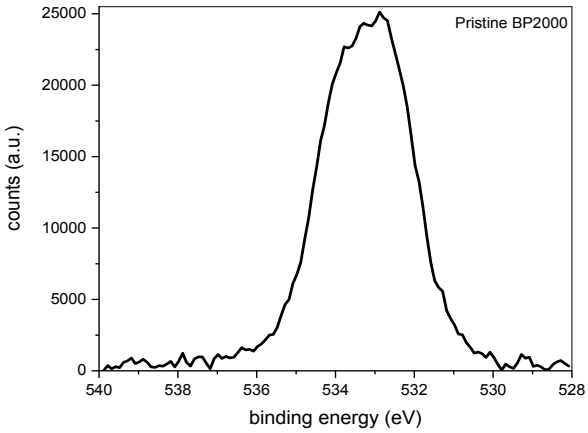


Figure S4. O1s spectrum of pristine BP2000

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3. Q.-C. Chen, M. Soll, A. Mizrahi, I. Saltsman, N. Fridman, M. Saphier and Z. Gross, *Angewandte Chemie International Edition*, 2018, **57**, 1006-1010.
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