

Supporting Information

## Microporous Cobaloxime–Graphene Composite: Reloadable Non-Noble Metal Catalyst Platform for Proton Reduction Reaction

Ahmed B. Soliman,<sup>a,b</sup> Rana R. Haikal,<sup>a</sup> Arwa A. Abugable,<sup>a</sup> and Mohamed H. Alkordi<sup>a\*</sup>

### Experimental

All reagents were used as received without further purification. Solvents, catalysts, and common chemicals were purchased from Sigma-Aldrich or Fisher Scientific-UK. Brominated aromatics were purchased from Combi-Blocks. Triethynylbenzene was synthesized as described below. Nitrogen gas for sorption were purchased from Airliquide (N<sub>2</sub> AlphaGaz2 (99.999%), Graphene (Alfa Aesar, catalogue 47312), copper(I) iodide (CuI, 98%, Acros Organics); triethylamine (Chromanorm®, HPLC grade, VWR); Acetonitrile (fischer, analytical reagent grade 99.99%).

Gas sorption analysis was performed on Micromeritics **ASAP2020**. The apparent surface areas were determined from the nitrogen adsorption isotherms collected at 77 K by applying the Brunauer-Emmett-Teller (BET) and Langmuir models. Pore size analyses were performed using a slit NLDFT pore model system by assuming a carbon finite pores surface. CHN elemental analyses were conducted on ThermoScientific **Flash 2000**. Infra-red absorption spectra were recorded on ThermoScientific **Nicolet is-10**. Thermogravimetric analyses were conducted on Thermal Analysis-**Q50** under nitrogen atmosphere. SEM images were acquired on a NOVA NANOSEM 450, equipped with EDAX EDX detector and operated at 30 KV.

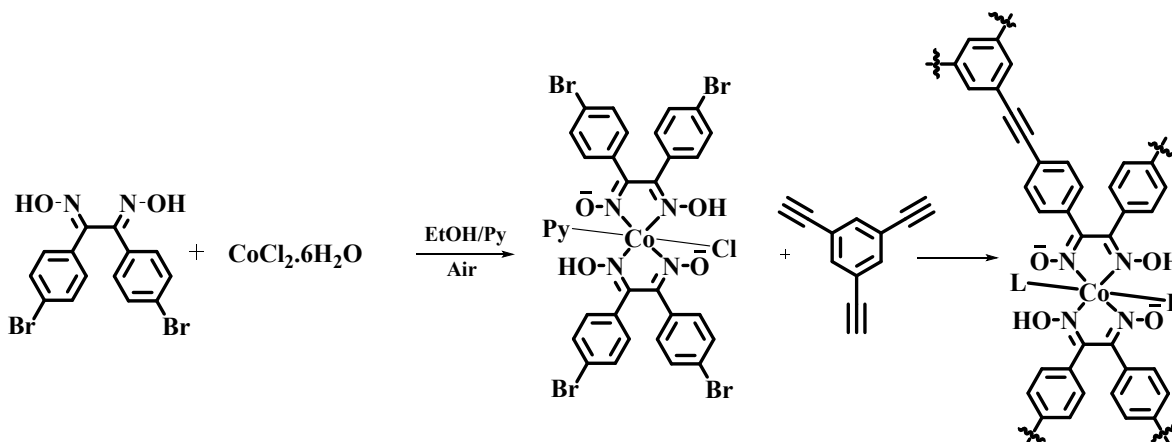
### Electrochemical measurements:

In a typical run, 5 mg of the studied solid (PCoP@G or G) was mixed with 15 mg of carbon paste and grinded in agate mortar to ensure homogenous distribution inside the carbon paste. This prepared material was then packed inside a carbon paste electrode (CPE) of 3 mm cross section. The electrochemical measurements were conducted on a biologic SP-50 potentiostat/galvanostat in a three electrodes configuration. The working electrode was a CPE packed with the prepared slurry, Pt wire as a counter electrode and Ag|AgCl as a reference electrode. The electrolyte was aqueous NaCl (0.1 M) degassed through bubbling of N<sub>2</sub> for 30 minutes (99.9999%, alphagaz2, AirLiquide). For the soluble oxime and cobaloxime, the solution was prepared in degassed DMF (0.8 mM) with a supporting electrolyte of (NH<sub>4</sub>)<sub>2</sub>(PF<sub>6</sub>) (0.1 M) and the working electrode was glassy carbon electrode.

## Synthetic Procedures

### Synthesis of 1,3,5-triethynylbenzene.

In a 100 mL pressure vessel, a mixture of THF (15 mL) and Et<sub>3</sub>N (3 mL) was added, cooled in liquid nitrogen bath, degassed through three freeze-pump-thaw cycles and maintained under nitrogen atmosphere. To this prepared solution was added 1,3,5-tribromobenzene (3 mmol), ethynyltrimethylsilane (12 mmol, 1.22 g), CuI (10 mg, 0.05 mmol), PPh<sub>3</sub> (26 mg, 0.1 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (70 mg, 0.1 mmol). The reaction mixture was then placed in an oil bath maintained at 80°C for 24 hrs. The solution was then filtered through fritted funnel and the volatiles removed under reduced pressure. The crude product was then purified through flash chromatography on silica gel using hexane (1%EtOAc) to isolate white crystalline solid (777 mg, 70% yield). The trimethylsilyl group was removed by dissolving the above product in THF (10 mL) and MeOH (10 mL) followed by addition of K<sub>2</sub>(CO<sub>3</sub>) (1.8 g, 13 mmol) and stirring at room temperature overnight. The reaction was quenched by addition of HCl (1M) and the product extracted in DCM, then dried over Mg(SO<sub>4</sub>), filtered and the volatiles were removed under reduced pressure to yield the 1,3,5-triethynylbenzene in 222mg, 1.48 mmol, 70% yield. <sup>1</sup>H NMR (CHLOROFORM-d ,300MHz): d = 7.59 (s, 3 H), 3.13 ppm (s, 3 H)



### Synthesis of the cobaloxime

A solution of the oxime (126 mg, 0.137 mmol) in 20 mL of absolute ethanol was prepared, to which was added CoCl<sub>2</sub>·6H<sub>2</sub>O (34.1 mg, 0.144 mmol) and pyridine (0.1 mL) was added and the reaction mixture heated to almost reflux, the color changed from blue to greenish blue. After 10 minutes of heating, 1mL of water was added where the color changed to blue-green then yellow-green. The reaction mixture was filtered through a cotton plug, the solvents were removed under reduced pressure and the residue dissolved in 30 mL DMF for subsequent use in constructing the polymer.

### Synthesis of the PCoP

To synthesize the PCoP, 20 mL of the above prepared cobaloxime solution (~ 0.08 mmol) was transferred into a 100 mL sealable pressure vessel charged with a magnetic stirrer, to which was added triethylamine (5mL) and the solution degassed through three freeze-pump-thaw cycles, and kept under nitrogen. To this mixture and under nitrogen flow was then added **1,3,5-triethynylbenzene** (33 mg, 0.22 mmol), **Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>** (0.005 g, 0.007 mmol), **triphenylphosphine** (0.005 g, 0.018 mmol), and **CuI** (0.005 g, 0.026 mmol) were added. The vessel was then sealed under nitrogen and the reaction mixture was stirred at 90°C for 40 h. The reaction mixture was then cooled down to room temperature, filtered through frit funnel and washed with ACN, MeOH, then ACN (Note: Don't let the solid to dry), then kept to exchange in acetonitrile in sealed vial at 80°C for 24 hr for guest exchange before filtering and drying (yield 60 mg) for subsequent characterization.

### Synthesis of the PCoP@G

An identical procedure as reported above was used except for addition of the graphene.

To synthesize the PCoP@G, 10 mL of the above prepared cobaloxime solution (~ 0.04 mmol) was transferred into a 100 mL sealable pressure vessel charged with a magnetic stirrer, to which was added DMF (10 mL) and triethylamine (5mL) and the solution degassed through three freeze-pump-thaw cycles, and kept under nitrogen. To this mixture and under nitrogen flow was then added **graphene** (24 mg), **1,3,5-triethynylbenzene** (16.5 mg, 0.11 mmol), **Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>** (0.005 g, 0.007 mmol), **triphenylphosphine** (0.005 g, 0.018 mmol), and **CuI** (0.005 g, 0.026 mmol) were added. The vessel was then sealed under nitrogen and the reaction mixture was stirred at 90°C for 40 h. The reaction mixture was then cooled down to room temperature, filtered through frit funnel and washed with ACN, MeOH, then ACN (Note: Don't let the solid to dry), then kept to exchange in acetonitrile in sealed vial at 80°C for 24 hr for guest exchange before filtering and drying (yield 62 mg) for subsequent characterization.

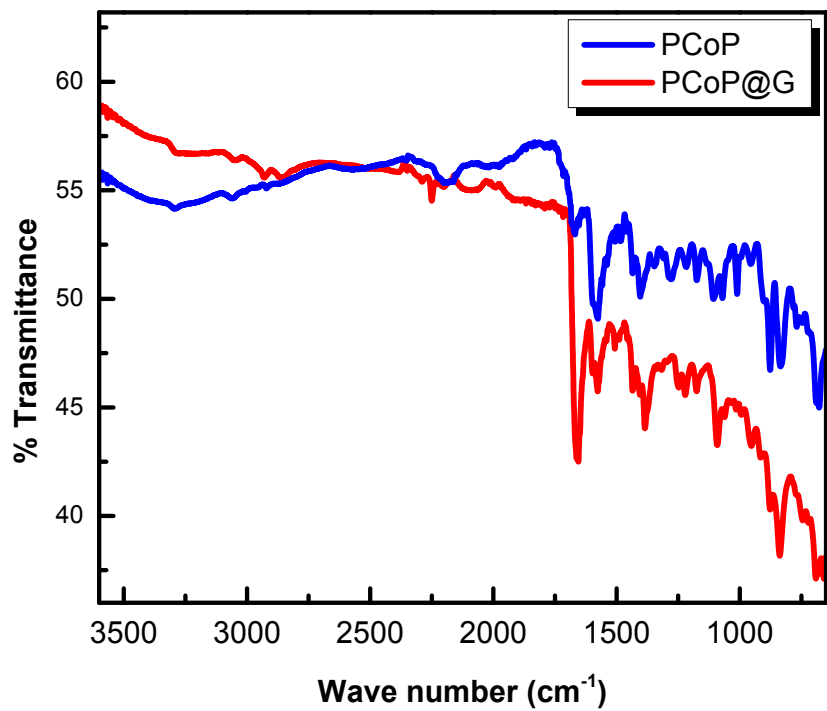


Figure S1. FTIR spectra for the PCoP and PCoP@G

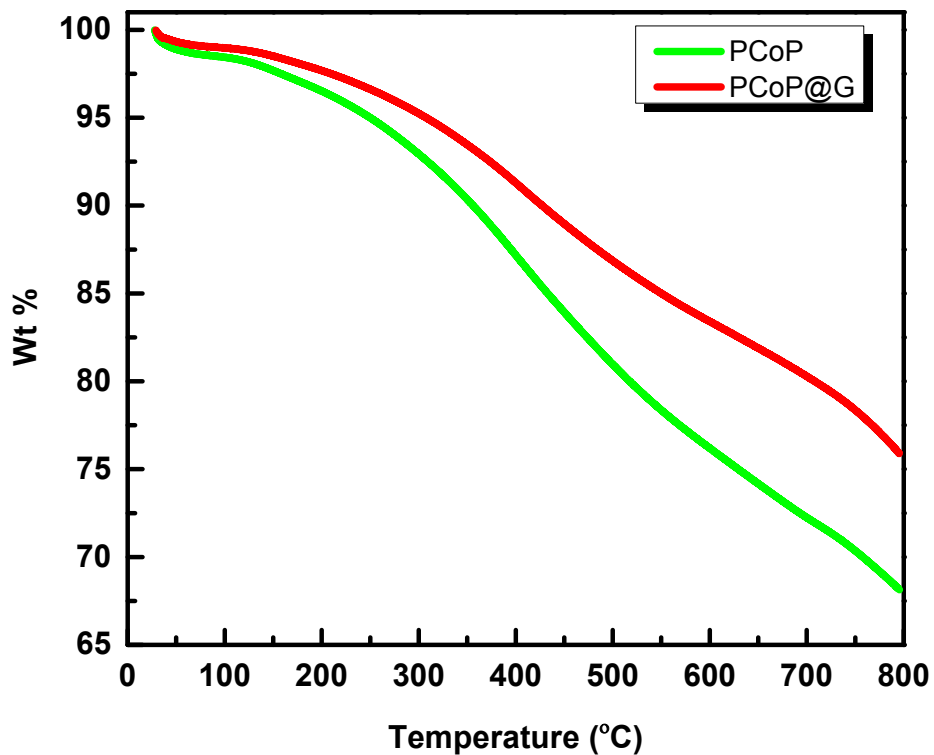


Figure S2. TGA analysis traces for the PCoP and PCoP@G

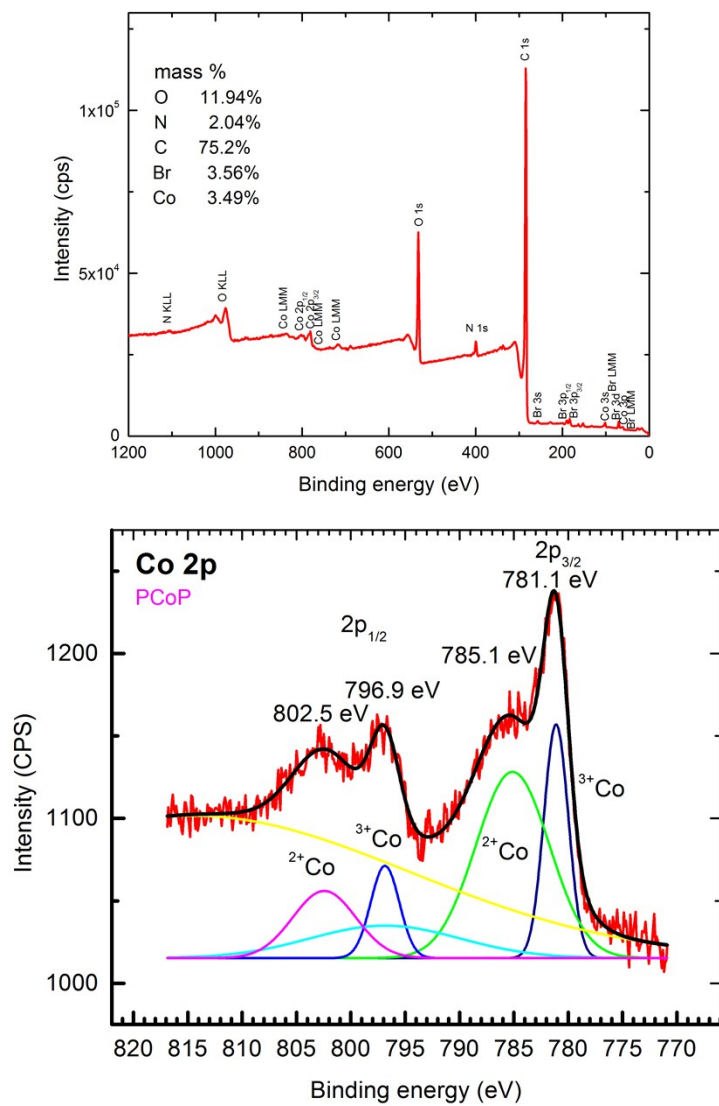


Figure S3. XPS survey spectrum for the PCoP and the detailed scan for the Co 2p peaks.