Supporting Information

Immobilization of molecular cobalt electrocatalyst by hydrophobic interaction with hematite photoanode for highly stable oxygen evolution

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Experimental

Materials. FTO (fluorine-doped tin-oxide; TEC 15, 2.2 mm-thick, Dyesol) coated glass slides (10 × 2.5 cm), cobalt nitrate ($Co(NO_3)_2.6H_2O$; 99.999%), hydrogenated and fluorinated Co-phthalocyanines (CoHPc, CoFPc), sodium hydroxide (NaOH), sodium phosphate dibasic (Na_2HPO_4; ACS reagent, anhydrous, ≥99.0%), and sodium phosphate monobasic (NaH_2PO_4; purum, anhydrous, ≥99.0%) were obtained from Sigma-Aldrich Co. and were used as received. The FTO/hematite samples were obtained from Everest Coatings (The Netherlands) and were prepared using atmospheric CVD with iron acetate as a precursor. Unless otherwise specified, the solutions were prepared in ultra-pure water (Millipore MilliQ® A10 gradient, 18.2 MΩ cm, 2–4 ppb total organic content). The electrochemical measurements were conducted in Ar-purged deoxygenated aqueous solutions at room temperature. The glassware and the electrochemical cell were cleaned as described previously.[S1] The FTO glass slides were cleaned using successive ultrasonication in water and isopropanol for 30 min. Next, the slides were dip-cleaned in acetone and dried in an oven. All of the solutions were prepared in ultra-pure water (Millipore MilliQ®), and all electrochemical measurements and photoelectrochemical experiments were performed in deoxygenated aqueous solutions at room temperature.

Functionalization of Co-phthalocyanines on the hematite/FTO substrates. The CoPc/hematite/FTO and CoPc/FTO were fabricated by drop casting from a stock solution (0.01 mM). With this procedure, a surface coverage of approximately 2-3 × 10^{-10} mol cm^{-2} was achieved by drop casting a 15-20 µmol catalyst stock solution.

Electrodeposition of Co-Pi (cobalt phosphate) catalyst film on hematite. For photoelectrochemical testing, the Co-Pi electrocatalyst film on the FTO/hematite was generated from a sodium phosphate buffer solution (pH 7) containing Co^{2+} (0.2–0.5 mM) during constant-potential experiment at ≥1.50 V vs. RHE in the low current density regime. The as-prepared catalytic film of Co-Pi on hematite was directly subjected to further experimentations.

We prepared hematite/Co-Pi system with different deposition times/amounts on top of hematite, and found that depositing more catalyst reduces the performance of the system attributed to the blockage of the incident light, and greater thickness of the Co-Pi system could resist the hole transfer through its bulk.

Instrumentation. The UV-Vis spectra were recorded using a Perkin Elmer Lambda 45 spectrophotometer and Teflon-stoppered quartz cells with a path length of 1 cm. FTO and hematite/FTO based samples were placed directly in the instrument with the holder clips. The scanning electron microscopy (SEM) images were taken using a FEI NanoSEM 200 microscope. The SEM images were taken using an acceleration voltage of 5–15 kV. The resolution at 15 kV is 1 nm, and the resolution at 1 kV is 1.8 nm. The hematite/FTO samples (cut in 0.5 × 0.5 cm dimensions) were placed on the aluminum holder and fixed with silver tape. Raman spectra were recorded on a Micro Lab Raman Aramis Spectrometer (Horiba Jobin Yvon) equipped with an Olympus BXFM-ILHS microscope with a 100´ long distance objective; 1800 l/mm gratings were used. A HeNe laser was used for excitation at 633 nm. Scans (#3) from 200 to 1800 cm^{-1} were recorded with a 5 sec acquisition time. Contact angles were measured using a contact angle goniometer (KRUSS EasyDrop Standard) at ambient pressure and temperature; static angle measurements were made form 1 μl drops of deionized water on the surface of FTO slides modified with Co-phthalocyanines 5×10^{-10} mol cm^{-2} by drop casting to obtain a surface evenly coated with a monolayer.

Electrochemical testing and photoelectrochemical measurements. A three-electrode configuration Pyrex glass cell was used for the electrochemical studies, including cyclic voltammetry (CV) and constant-potential electrolysis (CPE). The working electrode (WE) in the CVs and the catalytic water electrolysis experiments consisted of FTO-coated glass substrates. The catalytic water electrolysis and the oxygen evolution measurement investigations were performed using a three-electrode, double-junction, H-type glass cell, where the reference electrode chamber was separated by a glass frit with a very fine porosity. Platinum wire (thickness: 1 mm) was shaped into a spiral and was used as a counter electrode (CE). A silver-silver chloride reference electrode (Ag/AgCl in saturated KCl aq.) was used to investigate the aqueous solutions with neutral and higher pH values. All potentials are referred to reversible hydrogen electrodes (RHE). Electrochemical experiments were performed using a BioLogic Science Instrument potentiostat electrochemical workstation (VMP-300). Photoelectrochemical studies were conducted in a photochemical glass cell with an optical window under simulated AM1.5 solar illumination (100 mW cm^{-2}) using a SAN-EI ELECTRIC Class AAA solar simulator (model XES-40S2-CE). Photoelectrochemical measurements under full light were conducted at a scan rate of 10 mV s^{-1}

during chopped light linear sweep voltammetry, and a five second interval was applied between turning the light on and off.

Online oxygen evolution measurements. Oxygen generation was monitored with online gas chromatographic (GC) measurements using micro-GC, T-3000 SRI instruments. The gas mixture from the cell was delivered at a constant flow rate of He carrier gas (99.9999%, typically at 10 ml min^{-1} using a mass flow controller) directly to the sampling injection port of a gas chromatograph. Sampling was conducted every 10 min, and the gaseous products were analyzed using a packed MolSieve 5A coupled with a thermal conductivity detector (TCD).

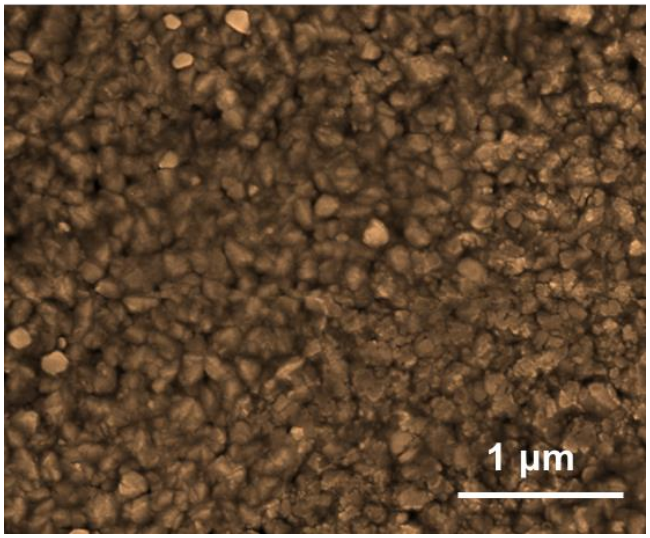

Figure S1. Scanning electron microscope (SEM) images of the nanoparticulate hematite/FTO.

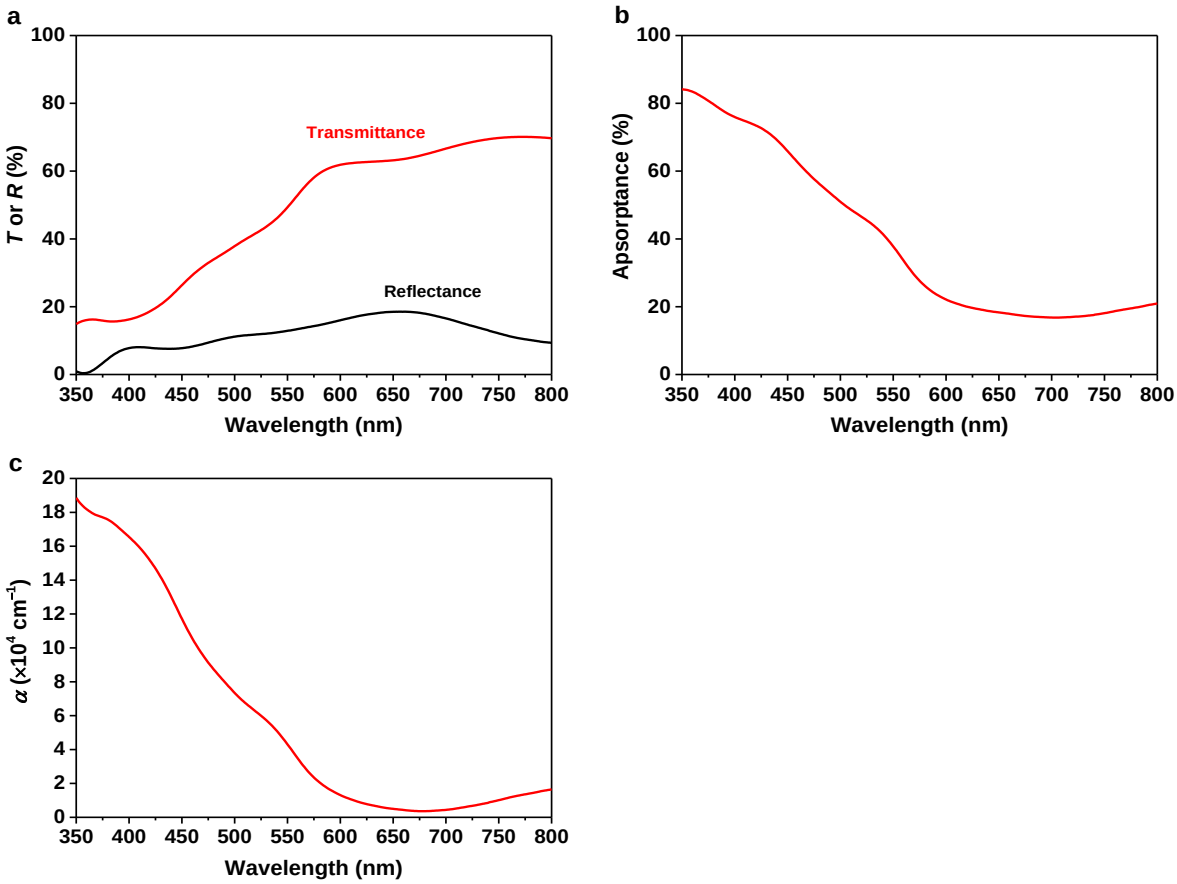

Figure S2. (a) Transmittance and reflectance spectra for hematite/FTO, (b) absorptance obtained from (a) for hematite/FTO, and (c) absorption coefficient ($\alpha = -\frac{1}{d}\ln\frac{T}{(1-R)^2}$) for hematite/FTO calculated based on the assumption that hematite has 100 nm thickness.[S2]

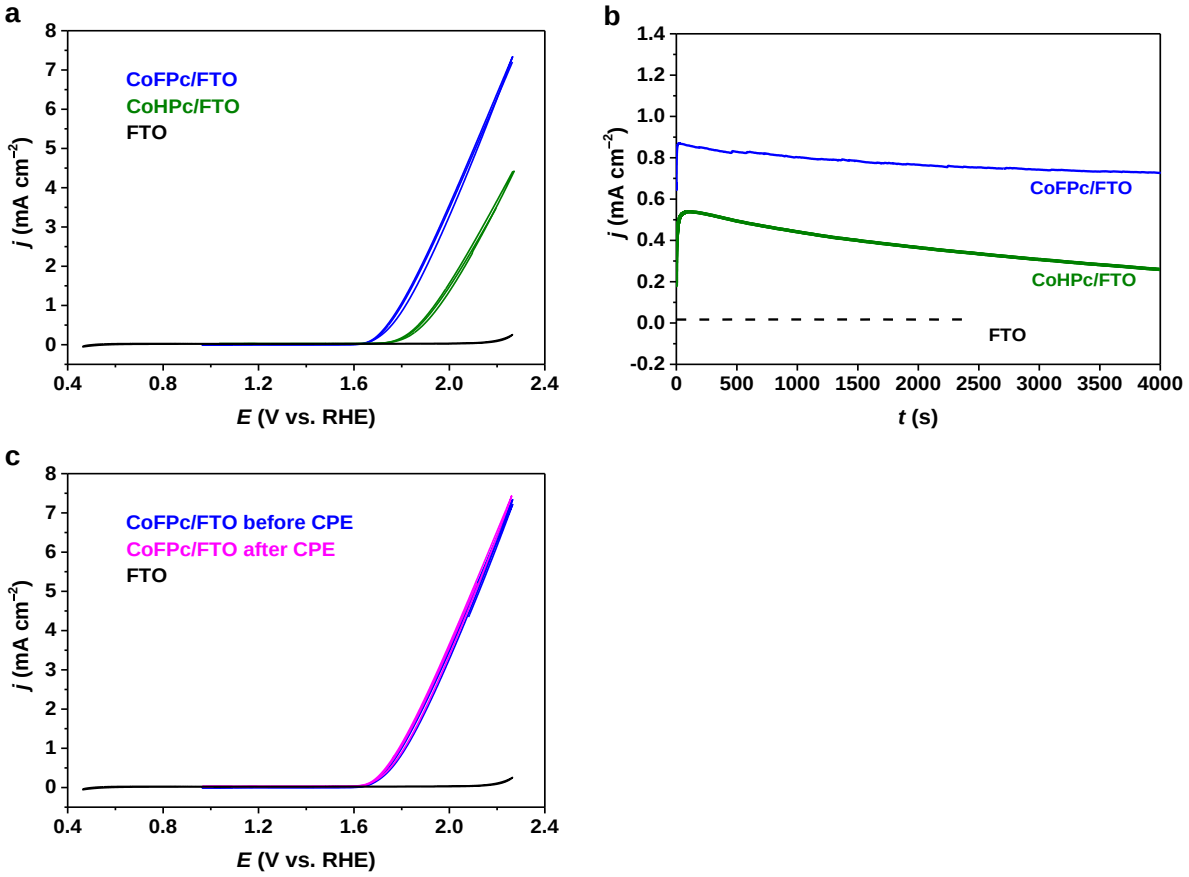

Figure S3. (a) Cyclic voltammograms for CoFPc/FTO, CoHPc/FTO and bare FTO, (b) controlled potential electrolysis (CPE) at 1.85 V vs. RHE for CoFPc/FTO (blue) and CoHPc/FTO (green), and (c) cyclic voltammograms for CoFPc/FTO before (blue line) and after (green line) the CPE test shown in (b) (scan rate 20 mV sec^{-1}, 0.1 M NaOH solutions, pH=13, Ar-purged, CoPc surface densities ~ 2.5×10^{-10} mol cm^{-2}).

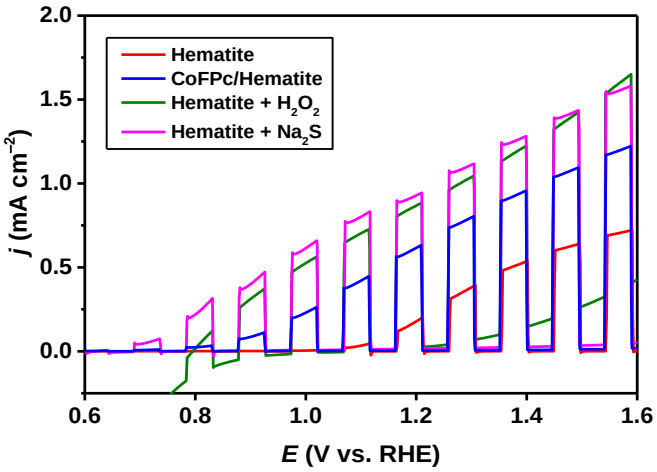

Figure S4. Linear sweep voltammograms for the fresh CoFPc/hematite/FTO sample under chopped light (corresponding to the data shown in Figure 3c) and for the CoFPc/hematite/FTO sample in the presence of different sacrificial reagents (scan rate 20 mV s^{-1}, pH=13, 0.1 M NaOH, 0.5 M H_2O_2 or 0.5 M Na_2S when present, Ar-purged, CoPc surface densities ~ 2.70×10^{-10} mol cm^{-2}).

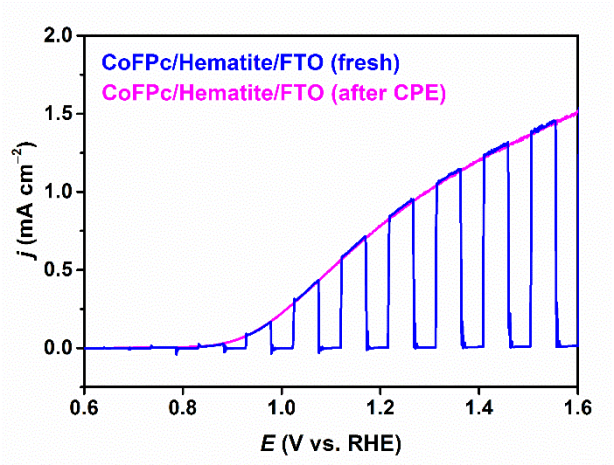

Figure S5. Linear sweep voltammograms for the fresh CoFPc/hematite/FTO sample under chopped light (corresponding to the data shown in Figure 3c) and for the CoFPc/hematite/FTO sample after the CPE experiment, as shown in Figure 3d, under full light illumination (scan rate 20 mV s^{-1}, pH=13, 0.1 M NaOH, Ar-purged, CoPc surface densities ~ 2.70×10^{-10} mol cm^{-2}).

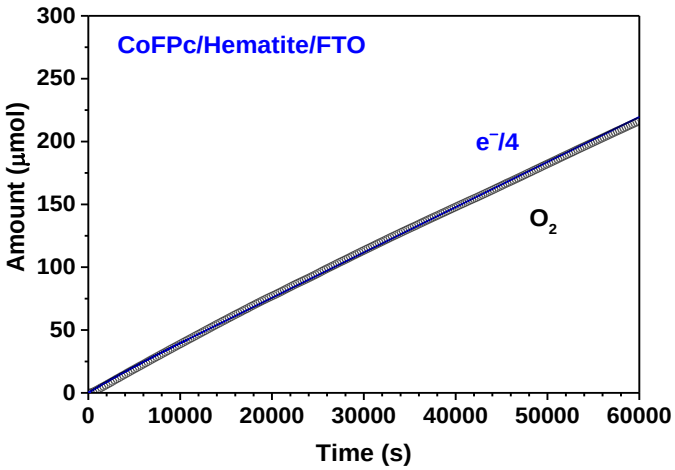

Figure S6. Long-term controlled potential electrolysis at 1.7 V vs. RHE in 0.1 M NaOH on CoFPc/hematite (pH 13, 0.1 M NaOH, CoFPc catalyst densities ~ 2.70×10^{-10} mol cm^{-2}).

Reference

S1. K. S. Joya, N. K. Subbaiyan, F. D'Souza and H. J. M. de Groot, *Angew. Chem. Int. Ed.* 2012, **51**, 9601–9605.

S2. K. Takanabe, *Top. Curr. Chem.* in press, DOI: 10.1007/128_2015_646.