

Electronic Supplementary Information

Hierarchical Pompon-like Cobalt Phosphide as Platinum-free Electrocatalyst for Dye-Sensitized Solar Cells

Chia-Lin Yeh^a, Yi-June Huang^a, Han-Ting Chen^a, Hsin-An Tsai^b,

Chun-Ting Li^{b,*}, Chuan-Pei Lee^c, and Kuo-Chuan Ho^{a,d,e,*}

^aDepartment of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan; ^bDepartment of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan; ^cDepartment of Applied Physics and Chemistry, University of Taipei, Taipei 10048, Taiwan; ^dInstitute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan; ^eAdvanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei 10617, Taiwan.

*Corresponding authors:

E-mail: kcho@ntu.edu.tw; Fax: + 886-2-2362-3040; Tel: + 886-2-2366-0739

E-mail: ctli@gapps.ntnu.edu.tw; Fax: + 886-2-2932-4249; Tel: + 886-2-7749-6146

Materials

Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), ethanol (EtOH, 99.5%), titanium (IV) tetraisopropoxide (TTIP, >98%), methanol, 2-methoxyethanol were purchased from Sigma Aldrich. Lithium iodide (LiI, synthetic grade), iodine (I_2 , synthetic grade), and poly(ethylene glycol) (PEG, MW~20,000) were received from Merck. Cis-diisothiocyanato bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium ruthenium (II) bis(tetrabutylammonium) (N719 dye), transparent TiO_2 paste (Ti-Nanoxide T/SP, average diameter of 20 nm), and Surlyn[®] (SX1170-60, 60 μm) were acquired from Solaronix (S.A., Aubonne, Switzerland). 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was purchased from Tokyo Chemical Industry Co. Ltd. Acetonitrile (ACN, 99.99%), Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and urea were purchased from J. T. Baker. Acetone (99%), 4-tert-butylpyridine (tBP, 96%) were purchased from Acros. 3-Methoxypropionitrile (MPN, 99%), hexamethylene tetramine, and sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) were purchased from Alfa Aesar. The flexible substrate, carbon cloth (W0S1002, thickness = 0.36 mm, basic weight = 120 g cm^{-2} , sheet resistance = 0.60 $\Omega \text{sq.}^{-1}$) was obtained from CeTech Co., Ltd., Taiwan.

Fabrication of the DSSCs

The TiO_2 photoanode was consisted of compact layer, transparent layer, and scattering layer. For fabrication of the compact layer, an uniform solution of tetraisopropoxide (TTIP, > 98%) and 2-methoxyethanol (weight ratio = 1:3) was deposited onto FTO glass by spin-coating method at 3000 rpm (~100 nm of thickness). For fabrication of the transparent layer, the commercial transparent TiO_2 paste (Ti-nanoxide HT/SP, average diameter of 20 nm) was coated on the compact layer (thickness of 10 μm) by the doctor-blade method. And then for fabrication of the scattering layer (a thickness of 5 μm), we employed the same doctor-blade method as in the transparent layer fabrication using a home-made TiO_2 slurry made by a four-step process. The four-step process was described as below: (1) 0.5 M TTIP was added into 0.1 M nitric acid aqueous solution with constant stirring; this solution

was heated to 88 °C and maintained at this temperature for 8 h. (2) The solution was cooled down to room temperature, transferred to an autoclave (PARR 4540, USA), gently heated to 240 °C, and kept at this temperature for 12 h; at this stage the TiO₂ nanoparticles attained an average diameter of 20 nm. (3) The autoclaved TiO₂ colloid was concentrated to contain 8 wt% of TiO₂ nanoparticles. (4) The TiO₂ slurry for scattering layer was obtained by the addition of 25 wt% PEG and 10 wt% of ST-41 (with respect to the weight of TiO₂) to the concentrated-TiO₂ colloid. To make the TiO₂ particles fully crystallized, each TiO₂ layer was sintered at 500 °C for 30 min in an air atmosphere. Finally, the as-prepared photoanode was immersed in a 5 x 10⁻⁴ M N719 dye solution with ACN and tBA as solvent (volume ratio = 1:1) for 24 h. The electrolyte used in this study for measurement of η contained the solution of 0.1 M LiI, 0.05 M I₂, 0.6 M DMPII, and 0.5 M tBP in the solvent of ACN and MPN (volume ratio = 8:2). The DSSCs were composed of dye-adsorbed TiO₂ photoanode, electrolyte, and a CE. The gap between the photoanode and CE was fixed by a 60 mm-thick Surlyn[®] ionomer and sealed by heating. Then the electrolyte was injected into the gap to complete the making of the DSSCs.

Characterizations and measurements

X-Ray diffraction (XRD) patterns were recorded by Multipurpose X-ray diffraction system (Ultima IV, Rigaku, USA). X-Ray photoelectron (XPS) spectra were obtained by Theta Probe Angle-Resolved X-ray Photoelectron Spectrometer (ARXPS) System (Thermo Scientific[™], England). Surface morphology of various CEs were observed by a field-emission scanning electron microscope (FE-SEM, Nova NanoSEM 230, FEI, Oregon, USA). The Brunauer-Emmett-Teller (BET) surface area was measured by a nitrogen sorption isotherm apparatus (Micromeritics, ASAP2010). Photovoltaic parameters of the DSSCs with various CE were measured by a potentiostat/galvanostat (PGSTAT 30, Autolab Eco-Chemie, Utrecht, the Netherlands). The power conversion efficiency of DSSCs was obtained under light illumination of 100 mW cm⁻², using a class A quality solar simulator (XES-301S, AM1.5G, San-Ei Electric Co. Ltd., Osaka, Japan). The incident light intensity was calibrated with a standard Si cell (PECSI01, Peccell Technologies, Inc., Kanagawa, Japan). The

incident light intensity was calibrated with a standard Si cell (PECSI01, Peccell Technologies, Inc., Kanagawa, Japan). The IPCE curves of the DSSCs were obtained in the wavelength region of 380 to 800 nm by another class A quality solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc., Kanagawa, Japan), equipped with a monochromator (model 74100, Oriel Instrument, California, USA). The incident radiation flux (ϕ) was measured via an optical detector (model 818-SL, Newport, California, USA) and a power meter (model 1916-R, Newport, California, USA). The ambient light measurements were performed under the T5 fluorescent lamp (TOA lighting, FH14D-EX, 14W, 6500K) and a height-tunable platform. The light lux and power density were measured by a sun spectroradiometer (S-2440 model II, Soma Optics Ltd., Tokyo, Japan).

Electrocatalytic properties and electrochemical active surface area (ECSA) of different CEs were quantified by cyclic voltammetry (CV). The CV analysis was measured in an electrolyte containing 10 mM LiI, 1.0 mM I₂, and 0.1 M LiClO₄ in ACN by using the above-mentioned potentiostat/galvanostat. The synthesized electrodes with Pt, CoP-N, CoP-S, and CoP-P were used as the working electrode; a Pt foil and an Ag/Ag⁺ electrode were used as the counter and reference electrodes, respectively. The scan rate was 100 mV s⁻¹. Impedance properties of the CEs were also quantified by Tafel polarization curves and electrochemical impedance spectroscopy (EIS). Symmetric cells consist of the same film on both anode and cathode, where the films were Pt, CoP-N, CoP-S, and CoP-P, separately. The data were recorded by the above-mentioned potentiostat/galvanostat equipped with a FRA2 module. The electrolyte consisted of 0.1 M LiI, 0.6 M DMPII, 0.05 M I₂, and 0.5 M tBP in the solvent of ACN and MPN (volume ratio = 8:2). A scan rate of 50 mV s⁻¹ was used for Tafel analysis. Under the open-circuit condition, the EIS analysis was performed between 10 MHz to 65 kHz with an AC amplitude of ± 10 mV.

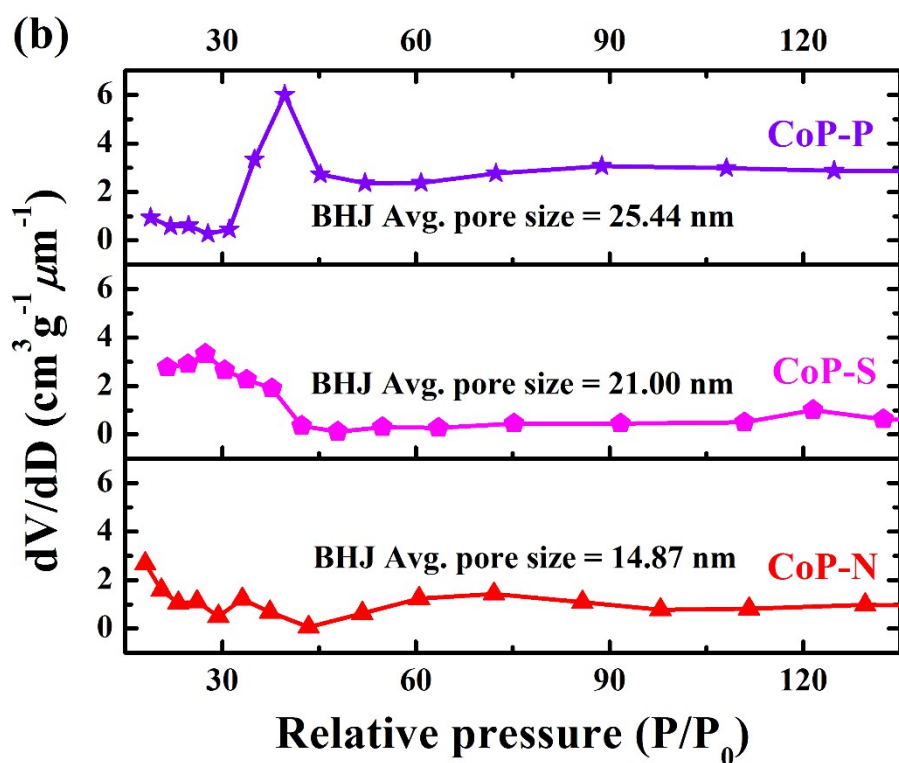
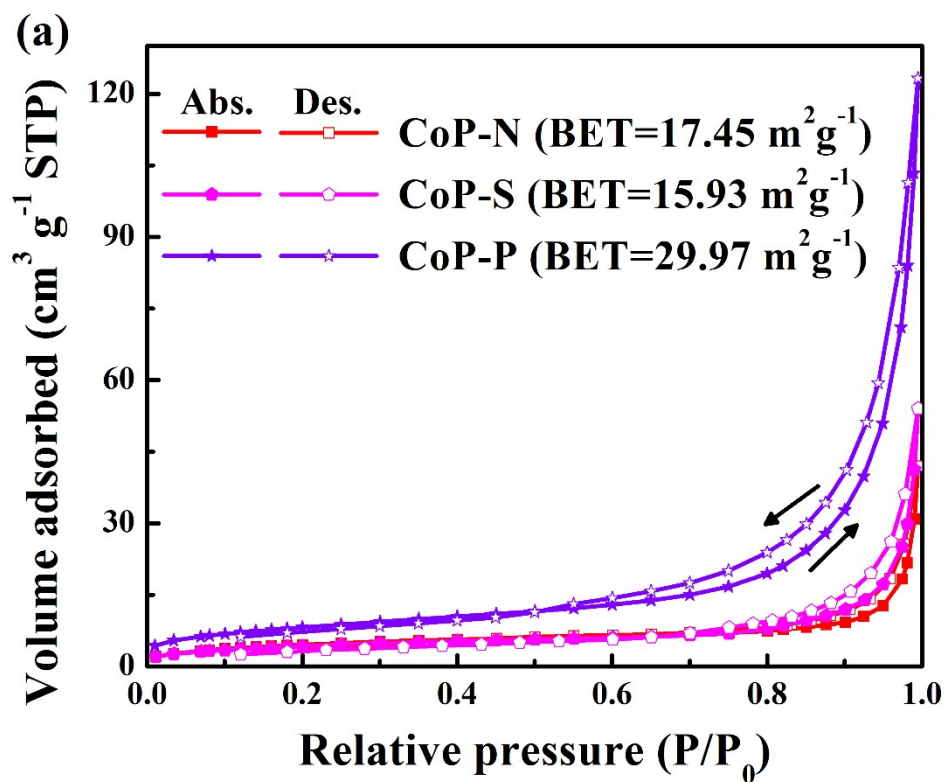


Fig. S1 (a) Plots of nitrogen absorption-desorption isotherms and (b) plots of Barrett-Joyner-Halenda (BJH) pore size distribution for CoP-N, CoP-S, and CoP-P particles.

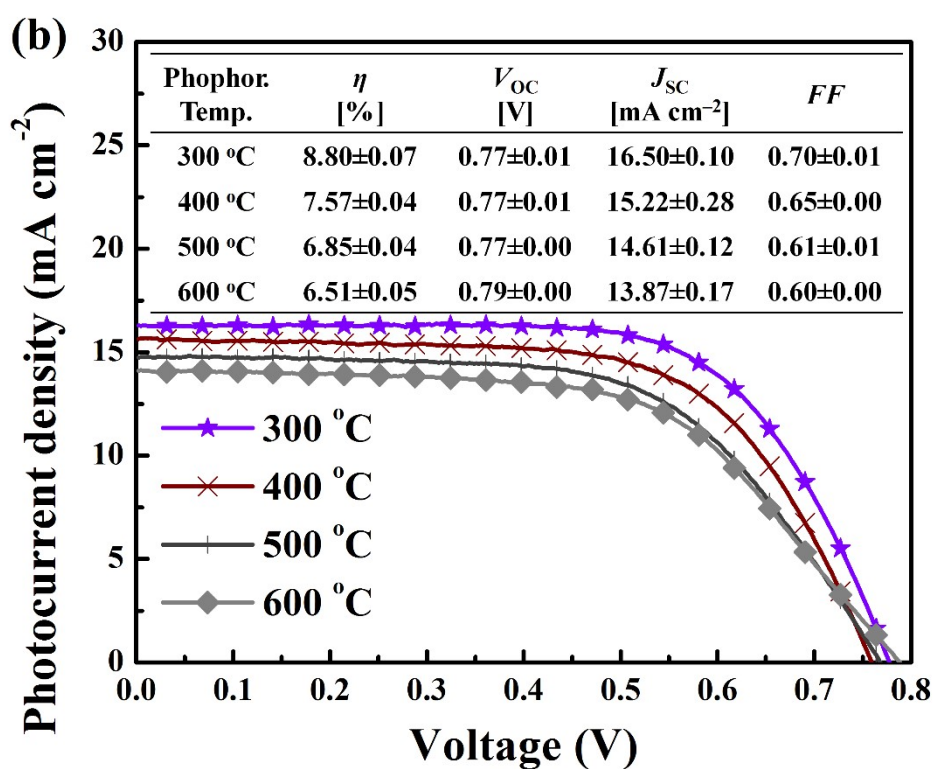
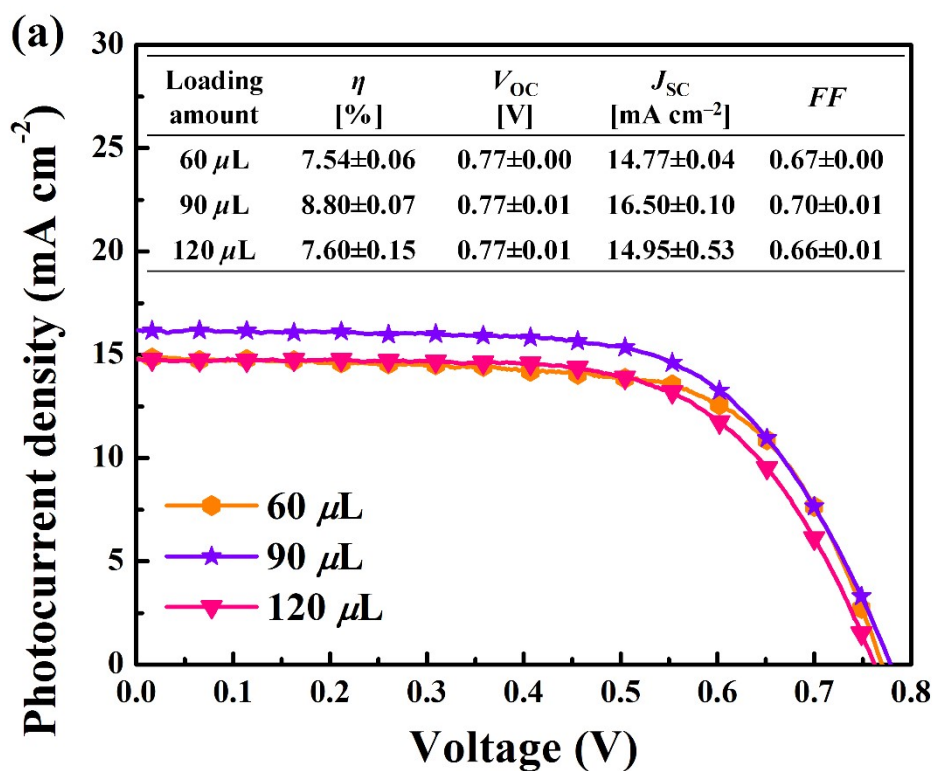


Fig. S2 The J - V curves of DSSCs with the counter electrode of CoP-P/CC, fabricated by (a) loading different amounts of the $\text{Co}(\text{OH})_x\text{-P}$ suspension, and then phosphorized under 300 °C; (b) loading 90 μL of the $\text{Co}(\text{OH})_x\text{-P}$ suspension, and then phosphorized under different temperatures.

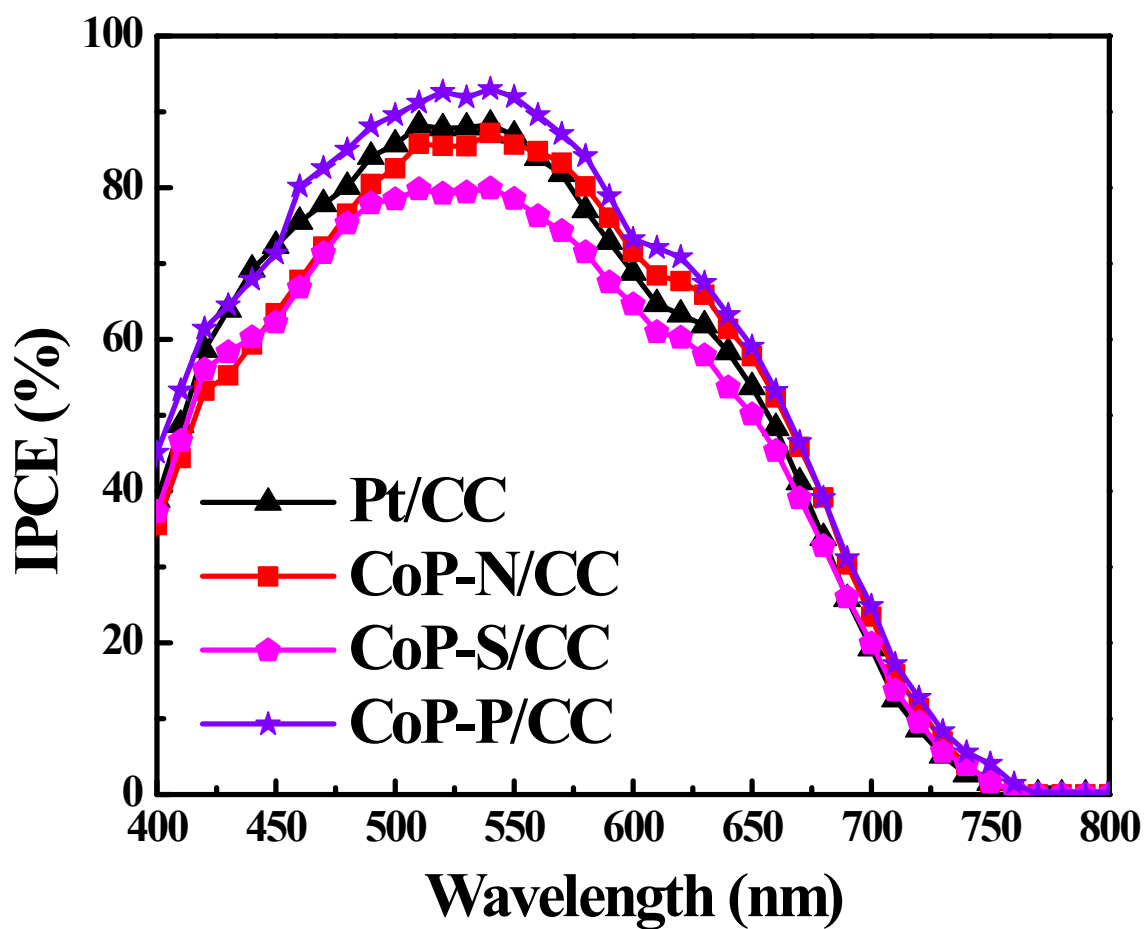


Fig. S3 Incident photon-to-current conversion efficiency (IPCE) spectra of the DSSCs with various counter electrodes of Pt/CC, CoP-N/CC, CoP-S/CC, and CoP-P/CC.

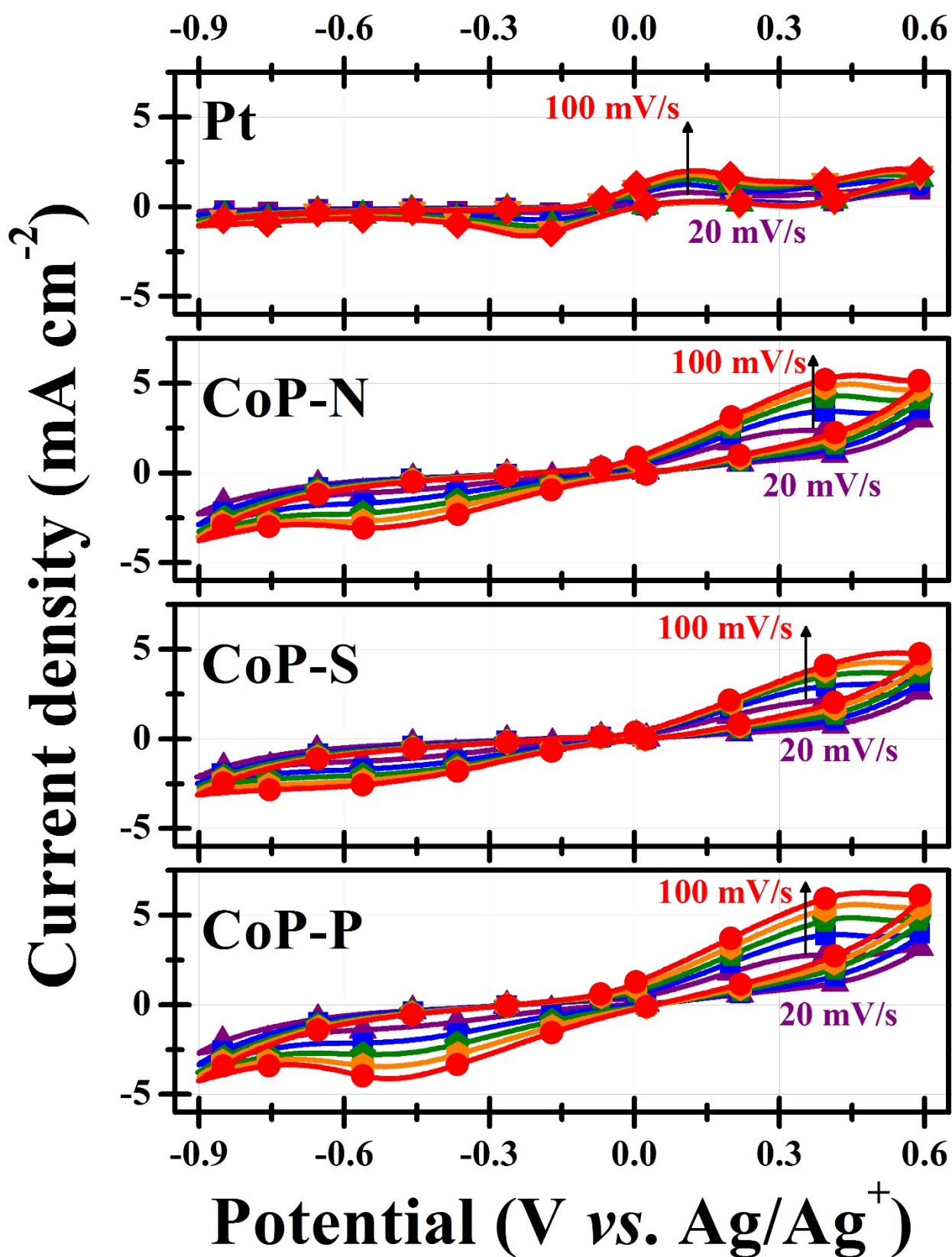


Fig. S4 Cyclic voltammograms of the Pt/CC, CoP-N/CC, CoP-S/CC, and CoP-P/CC electrodes, measured at different scan rates of 100, 80, 60, 40, and 20 mV s^{-1} .

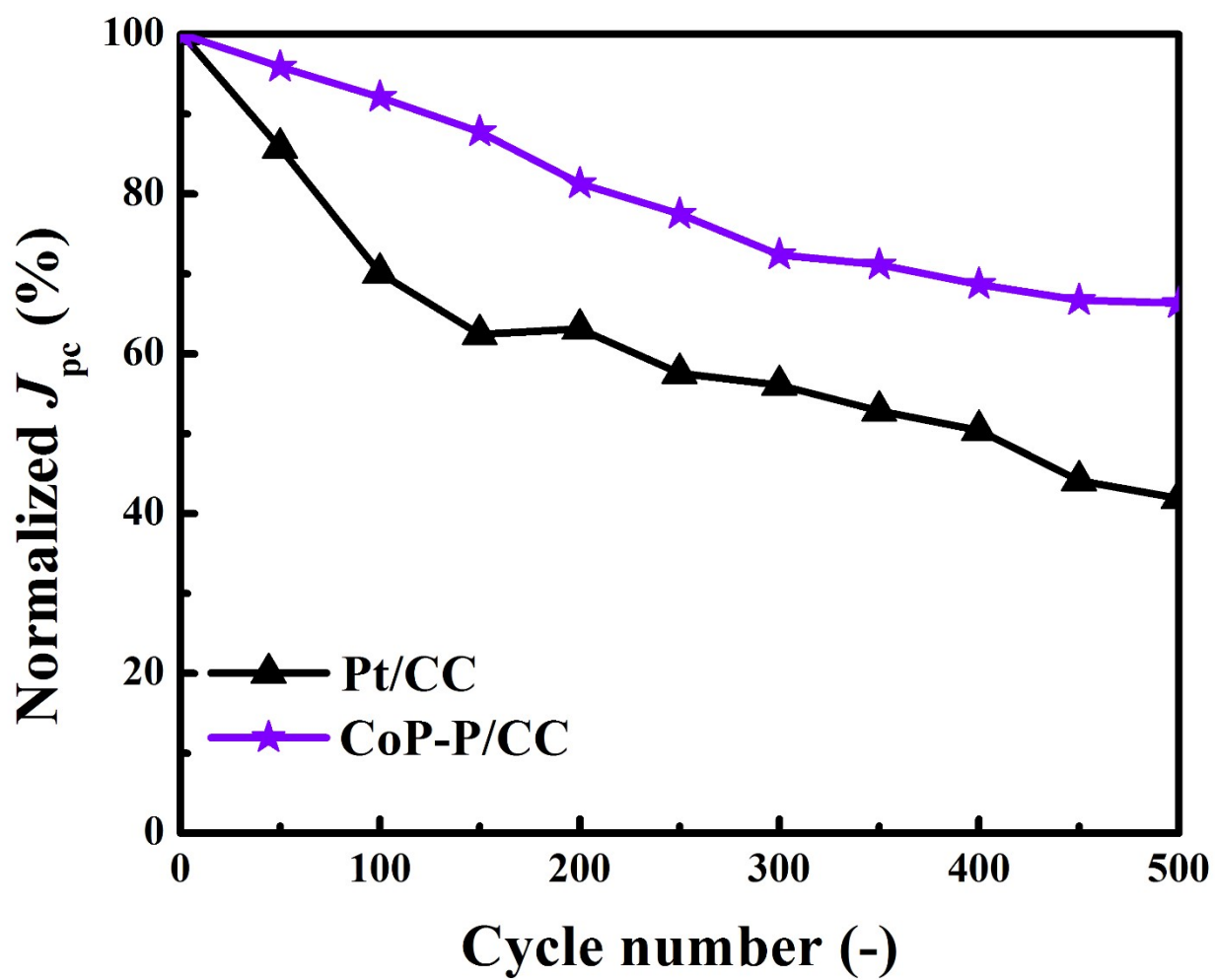


Fig. S5 Long-term cyclic voltammograms of the Pt/CC and CoP-P/CC electrodes, measured at a continuous scanning with a scan rates of 100 mV s^{-1} .