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High-Performance Electrocatalyst for Oxygen Evolution Reaction Based on Electrochemical Post-Treatment of Ultrathin Carbon Layer Coated Cobalt Nanoparticles

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1. Experimental details

1.1 Materials synthesis

Firstly, $Co(NO_3)_2 \cdot 6H_2O$ and urea were dissolved in deionized water with a molar ratio of 1 : 100 and ultrasonicated for 0.5 h at room temperature to generate a pink solution. Then, the solution was stirred and evaporated at 80 ^oC to achieve powder. Subsequently, the powder was annealed at 900 ^oC at an atmosphere of argon for 1 h. It was reported that the pyrolysis of urea may produce some reductive gas,[1] which can reduce cobalt compound to metallic cobalt. The resulting material is donated as Co@C. The Co@C sample was further electrochemical oxidized at an applied constant potential of 0.8 V vs. Ag/AgCl for 1200 s to obtain ECPT-Co@C. We also calcined urea and $Co(NO_3)_2 \cdot 6H_2O$ respectively as the above conditions for control experiments. Of note, the urea was decomposed with little product left in porcelain boat. The product of calcining $Co(NO_3)_2 \cdot 6H_2O$ donated Co-C-0. Besides, we also mixed cobalt powder and graphite mechanically at the same proportion as Co@C and derived ECPT-Co/Gr by ECPT.

1.2 Electrochemical measurements

Electrochemical tests were performed at room temperature in a standard three electrode system controlled by a CHI 760D electrochemistry workstation. Rotating disk electrode (PINE, 5.61mm diameter, 0.2475 cm^2), Pt wire and Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. The glass carbon electrode was polished and cleaned before use. 1.0 mg of catalyst was dispersed in a mixture of 985 μl alcohol and 15 μl Nafion solutions and sonicated to form a homogeneous ink. Then, 10 μl of the dispersion was drop-dried onto a glass carbon disk, leading to the catalyst loading ~0.04 mg cm^{-2}. Linear sweep voltammetry (LSV) was obtained by sweeping the potential from 0.3 to 1.2 V *vs.* Ag/AgCl at room temperature with a sweep rate of 1 mV s^{-1}. The measured potentials *vs.* Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale. Experiments involving RDE were carried out with the working electrode continuously rotating at 2000 rpm to get rid of the oxygen bubbles. The catalyst was applied for a number of potential sweeps until the data was stable before measuring polarization curves, which were all corrected with 95% iR-compensation.

1.3 Gas Chromatography measurement

To determine whether the graphite in ECPT-Co@C catalyst was oxidized to CO_2 / CO during the OER operation, we have used gas chromatography (GC) to confirm the gas product and determine the side reaction. OER catalysis was performed in a gas-tight home-made electrochemical cell with 1 M KOH electrolyte and Ag/AgCl as reference electrode. The working electrode was prepared by drop-drying 1.0 mg

Co@C catalyst onto ITO, leading to the catalyst loading ~1.0 mg cm^{-2}. After ECPT, we collected the gas product per 30 minutes and analyzed it by GC. During 30000 s electrolysis with ECPT-Co@C electrode at an applied potential of 1.62 V, we found that oxygen was the only product, as seen Fig. S7. Also, we complemented LSV test with pure graphite electrode as control experiment. As shown in Fig. S7, compared with ECPT-Co@C electrode, pure graphite electrode exhibited negligible current. Therefore, it suggests that the high anodic current density of ECPT-Co@C catalyst should be dominantly contributed from OER. This result is in agreement with that previously reported by H.A. Gasteiger et.al.,[2] where the graphitized carbon showed higher resistance to electrochemical oxidation. In addition, the Faradic Efficiency for OER at the ECPT-Co@C electrode was calculated to be ca. 95%, not 100%. This should be due to either the occurrence of side reaction or the gas tightness of the reactor. Faradaic efficiency for water oxidation was determined by comparing the total charge passed with the corresponding amount of evolved oxygen measured with a fluorescence based-oxygen sensor.

1.4 Characterization

The morphology was characterized by scanning electron microscope (SEM, QUANTA FEG 250) and transmission electron microscope (TEM, FEI Tecnai G2 T30). The obtained products were characterized by X-ray diffraction (XRD, Rigaku Ultima IV, Cu Kα radiation, 40 KV, 40 mA). X-ray photoelectron spectroscopy (XPS) was carried out on Physical Electronics 5400 ESCA. Inductively Coupled Plasma-

Atomic Emission Spectrometry (ICP-AES) was carried on Profile Spec to determine the content of cobalt element.

2. Turnover frequency (TOF) calculation of the catalysts

The TOF value is calculated using the following equation:

$$TOF = \frac{J \times A}{4 \times F \times \mathrm{m}}$$

J is the current density in A cm^{-2}. A is the area of glass carbon disk (0.2475 cm^2). F is the faraday constant (a value of 96485 C mol^{-1}). m is the number of moles the cobalt that are deposited onto the working electrode.

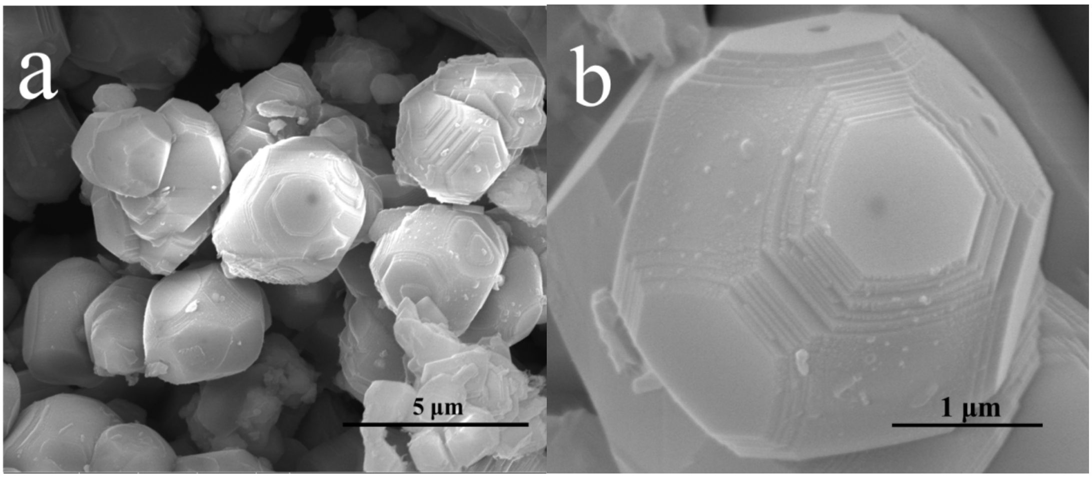

Fig. S1 SEM images of the morphology of Co-C-0 in low (a) and high magnitude (b).

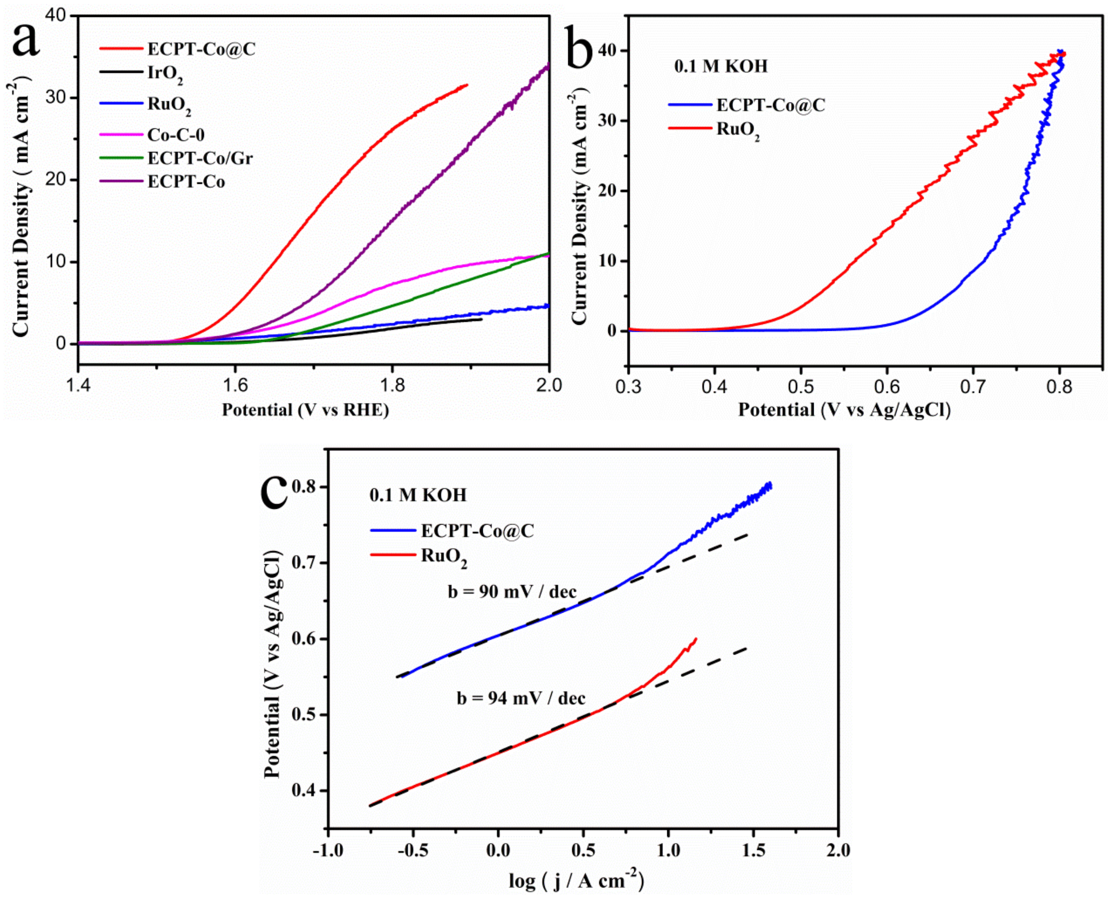

Fig. S2 (a) OER Polarization curves for ECPT-Co@C, IrO$_2$, RuO$_2$, Co-C-0, ECPT-Co/Gr and ECPT-Co, respectively. The corresponding specific surface areas of the samples were 13.745, 145.964, 35.614, 0.488, 2.121, and 1.421m^2 g^{-1}, respectively. (b) OER Polarization curves for ECPT-Co@C and RuO$_2$ in 0.1 M KOH solution. (c) Tafel plots (overpotential *vs.* log current) of ECPT-Co@C and RuO$_2$ derived from (b).

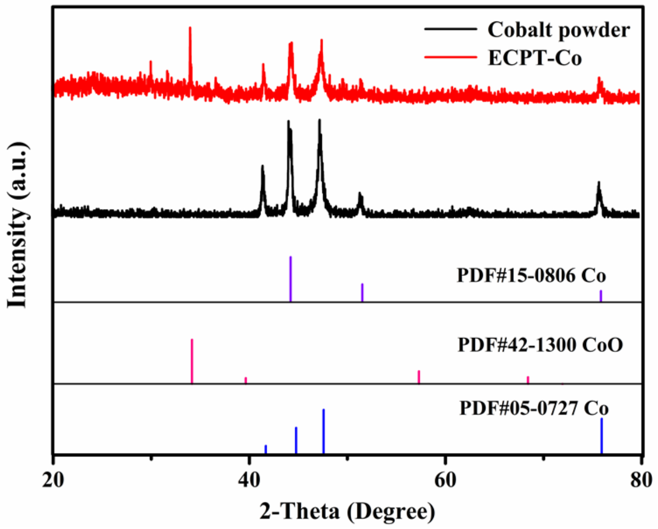

Fig. S3 XRD spectra of cobalt powder before and after ECPT. The bottom lines correspond to standard XRD patterns of metallic cobalt and CoO.

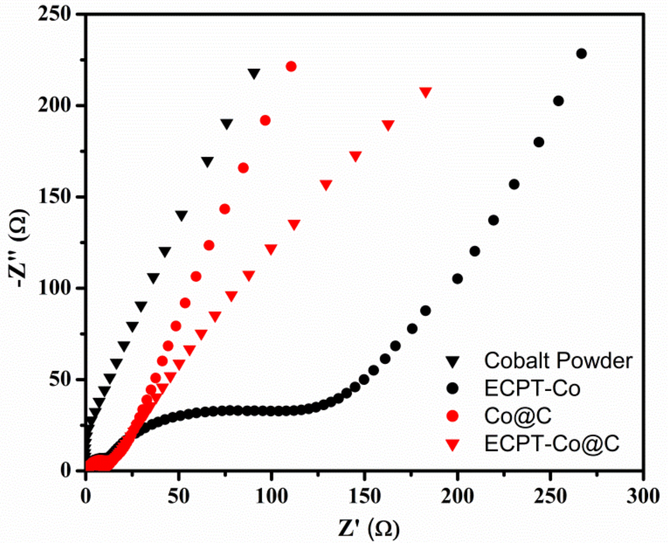

Fig. S4 Electrochemical impedance spectra of Co@C (red) and cobalt powder (black) before and after ECPT.

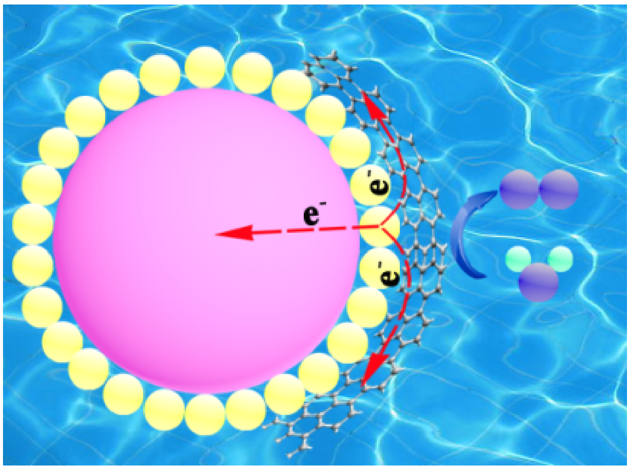

Fig. S5 A schematic depiction of the OER process on ECPT-Co@C catalyst. Pink and yellow balls correspond to metallic cobalt and CoO_x, respectively.

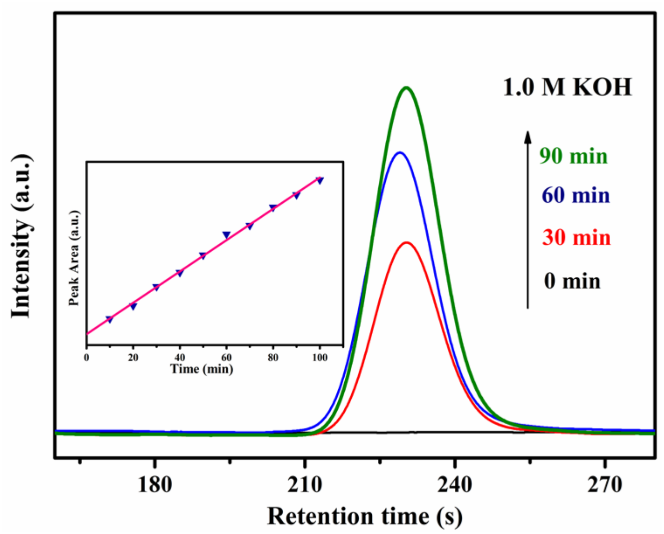

Fig. S6 Gas chromatography curves of O_2 from the OER catalyzed by ECPT-Co@C loaded on ITO at an applied potential of 1.62 V. The inset shows the plot of integral areas of peaks as a function of time.

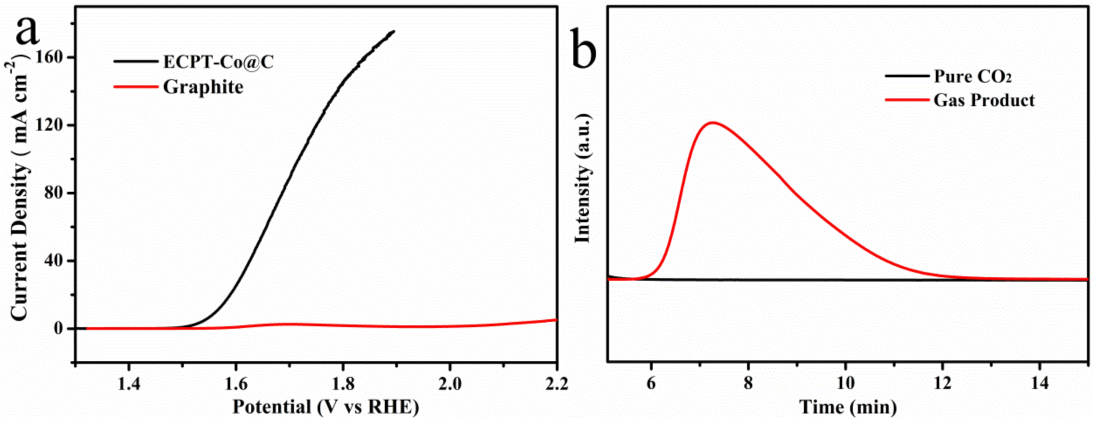

Fig. S7 (a) OER Polarization curves for ECPT-Co@C and graphite in 1.0 M KOH solution. (b) Gas chromatography curves of gas product catalyzed by ECPT-Co@C and pure CO_2.

Table S1. OER performance of different electrocatalysts in alkaline or neutral solutions.

Materials	Electrolyte	Over-potential (mV)	TOF (s^{-1})/ J (mA cm^{-2})	Tafel slope (mV dec^{-1})	catalyst loading(mg cm^{-2})	Reference
ECPT-Co@C	0.1M KOH	450	0.05 s^{-1} 7.58 mA cm^{-2}	90	0.04	This work

	1.0M KOH	450	0.412 s^{-1} 75.55 mA cm^{-2}	58	0.04	This work
RuO_2	0.1M KOH	450	0.22 s^{-1} 25.75 mA cm^{-2}	94	0.04	This work
	1.0M KOH	450	0.287 s^{-1} 31.37 mA cm^{-2}	85	0.04	This work
Co_3O_4/N-rmGO	1.0M KOH	340	0.006 s^{-1} 20 mA cm^{-2}	67	1.0	Ref.15
Co_3O_4 (~0.4ML)/Au substrate	0.1M KOH	351	1.8 s^{-1}	--	--	Ref.23
$Mn_3O_4/CoSe_2$	0.1M KOH	450	10 mA cm^{-2}	49	0.2	Ref.24
Co_3O_4/CNT	PBS (PH=7.0)	511	0.12 s^{-1}	104	0.05	Ref.25

1. Z. Lin, G. Waller, Y. Liu, M. Liu, C.-P. Wong, Adv. *Energy Mater.,* 2012, 2, 884-888.
2. P.T. Yu, W. Gu, R. Makharia, F.T. Wagner, H.A. Gasteiger, *ECS Trans.,* 2006, 3, 797-809.