

## Supporting Information

### **Pt-Co Secondary Solid Solution Nanocrystals Supported on Carbon as Next-Generation Catalysts for Oxygen Reduction Reaction**

Yige Zhao, Jingjun Liu\*, Yanhui Zhao, Feng Wang\* and Ye Song

State Key Laboratory of Chemical Resource Engineering;

Beijing Key Laboratory of Electrochemical Process and Technology for Materials;

Beijing University of Chemical Technology, Beijing 100029, China.

#### **Corresponding Author**

\*E-mail: [liujingjun@mail.buct.edu.cn](mailto:liujingjun@mail.buct.edu.cn)(J. Liu),

[wangf@mail.buct.edu.cn](mailto:wangf@mail.buct.edu.cn)(F. Wang)

Tel: +86-10-64411301, +86-10-64451996;

Fax: +86-10-64411301, +86-10-64451996

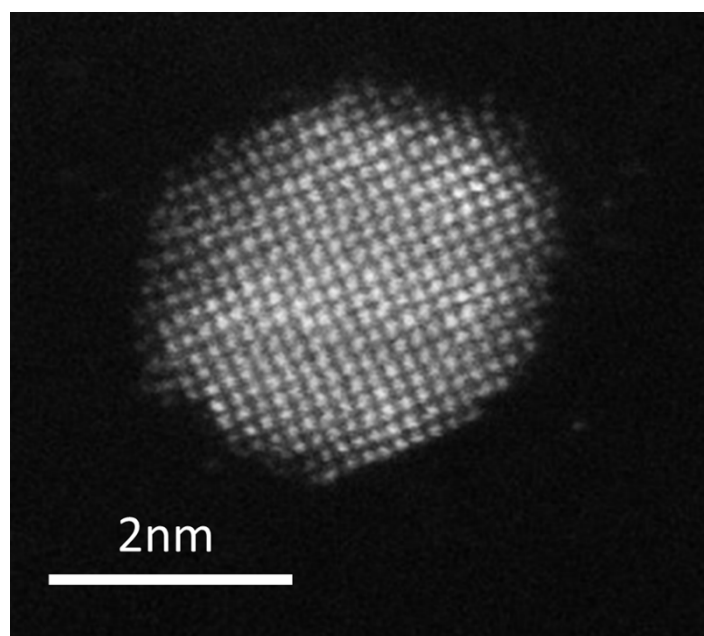
## Experimental details

**Preparation of Pt-Co/C secondary solid solution catalysts.** The synthesis of Pt-Co/C secondary solid solution alloys was done as follows: Initially, 100mg of carbon black (Vulcan XC-72) was added to 50ml of ethylene glycol (EG), followed by  $\text{H}_2\text{PtCl}_6$  (0.01M) and  $\text{CoCl}_2$  (0.1M) added to the carbon black suspension for a total metal loading of 20wt% and ultrasonication for 30min. Meanwhile, moderate NaOH solution was dropped to this mixture until its pH value reached 10. Then  $\text{NaBH}_4$  solution (1.89M) was added dropwise to the suspension solution. Subsequently, the resultant solution was constantly stirred at  $80^\circ\text{C}$  for 3h, after which the mixture was washed and dried to obtain catalyst powder. Finally, the powder was heat-treated in tube furnace under flowing Ar at  $900^\circ\text{C}$  for 30min and cooled to ambient temperature. The method was applied for a wide range of randomly mixed alloy samples with the composition of  $\text{Pt}_{75}\text{Co}_{25}$ ,  $\text{Pt}_{74}\text{Co}_{26}$ ,  $\text{Pt}_{72}\text{Co}_{28}$ ,  $\text{Pt}_{68}\text{Co}_{32}$  and  $\text{Pt}_{64}\text{Co}_{36}$ , whose compositions were obtained by inductively coupled plasma mass spectrometry (ICP-MS), finally forming the  $\text{CoPt}_3$ , Co-1%, Co-4%, Co-10% and Co-15% secondary solid solution alloys, respectively.

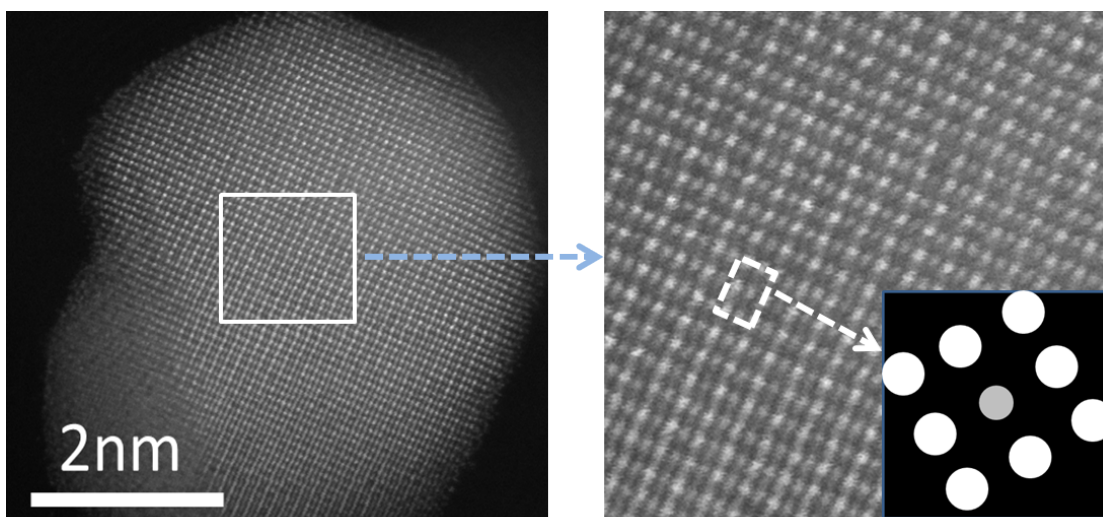
**Physical Characterizations:** The structure and phase analysis were performed using X-ray diffraction (XRD) with Cu  $\text{K}\alpha$  radiation at  $\lambda=1.5406 \text{ \AA}$  on a Philips Xpert X-ray diffractometer. The transmission electron microscopy (TEM) characterization was carried out with a JEOL TEM 2010 microscope and the atom arrangement were explored by an aberration-corrected scanning transmission electron microscope (STEM, JEOL ARM 200F) operated at 200 kV and by energy dispersive X-ray spectroscopic (EDX). X-ray photoelectron spectra (XPS, ESCALAB 250) were gained from a monochromator (Al KR source) calibrated with respect to the C (1s) peak at 284.6 eV.

**Electrochemical Measurements:** The catalysts were submitted to potentiodynamic polarization (Pine Instruments) in  $\text{O}_2$ -saturated NaOH (1M) and  $\text{O}_2$ -purged  $\text{HClO}_4$  (0.1M) solution to evaluate their activity and stability for the oxygen reduction reaction (ORR) in a conventional three-electrode system. Before recording the data, the current densities for catalysts were checked to make sure that they reached the diffusion limited and the mass-transport was not an issue in the measurements. Catalyst ink was fabricated by ultrasonically

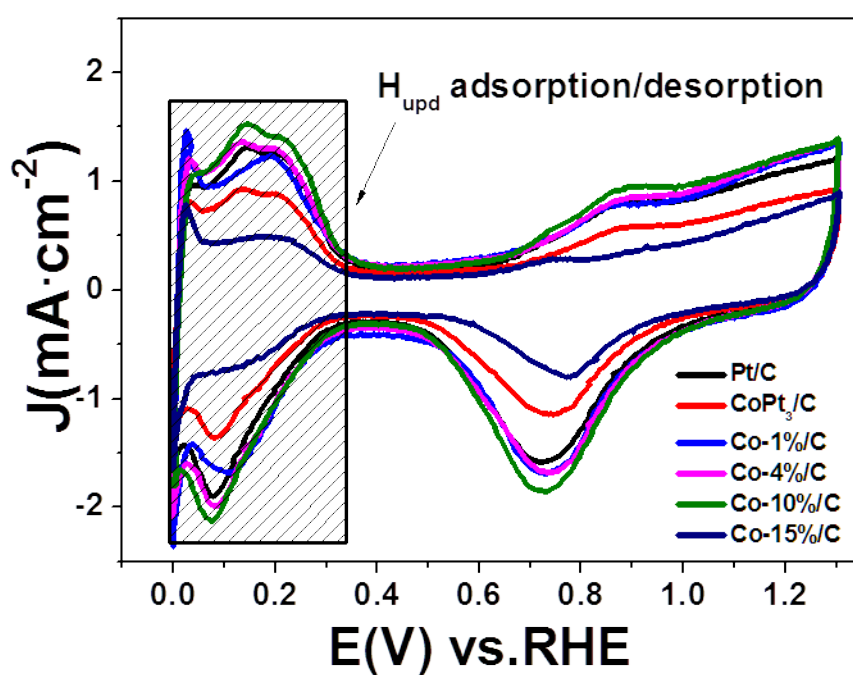
blending 10mg of the catalysts with 2mL of alcohol and 100  $\mu$  L of the Nafion solution (5wt.%), which was applied to form a capping layer in order not to influence mass transport at the electrocatalyst layer. Then, 20  $\mu$  L of the prepared catalyst ink was pipetted onto rotating disk electrode (RDE,  $S=0.247\text{cm}^2$ ) to form a working electrode. A Pt foil and saturated calomel electrode (SCE) with a salt bridge were served as the counter electrode and reference electrode, respectively. According to the calibration formula  $E_{\text{vs RHE}} = E_{\text{vs SCE}} + 0.241 \text{ V} + 0.059 \times \text{pH}$ ,<sup>1</sup> all potentials are calibrated to RHE. For the synthesized Pt-Co/C catalysts with different Co solid solubility (0%, 1%, 4%, 10%, 15%), the amount of each catalyst used on the electrode is 58.1, 57.8, 57.3, 56.0, 54.7  $\mu\text{g}/\text{cm}^2$  of Pt, respectively. For comparison, the amount of Pt (the commercial Pt/C) used on the electrode is 64.0  $\mu\text{g}/\text{cm}^2$  of Pt. The cyclic voltammetry (CV) were conducted in  $\text{N}_2$ -purged  $\text{HClO}_4$  (0.1M) solution in a conventional three-electrode system. All electrochemical measurements were performed at room temperature and at ambient pressure. The kinetic current densities ( $J_k$ ) at 0.09V (vs. RHE) were calculated on basis of polarization curves applying the Koutecky-Levich equation<sup>2</sup> expressed as the formula:  $1/J=1/J_k+1/J_d$ , Where  $J$  is the measured current density at 0.09V (vs. RHE),  $J_k$  is the kinetic current density,  $J_d$  is the diffusion limited current density.



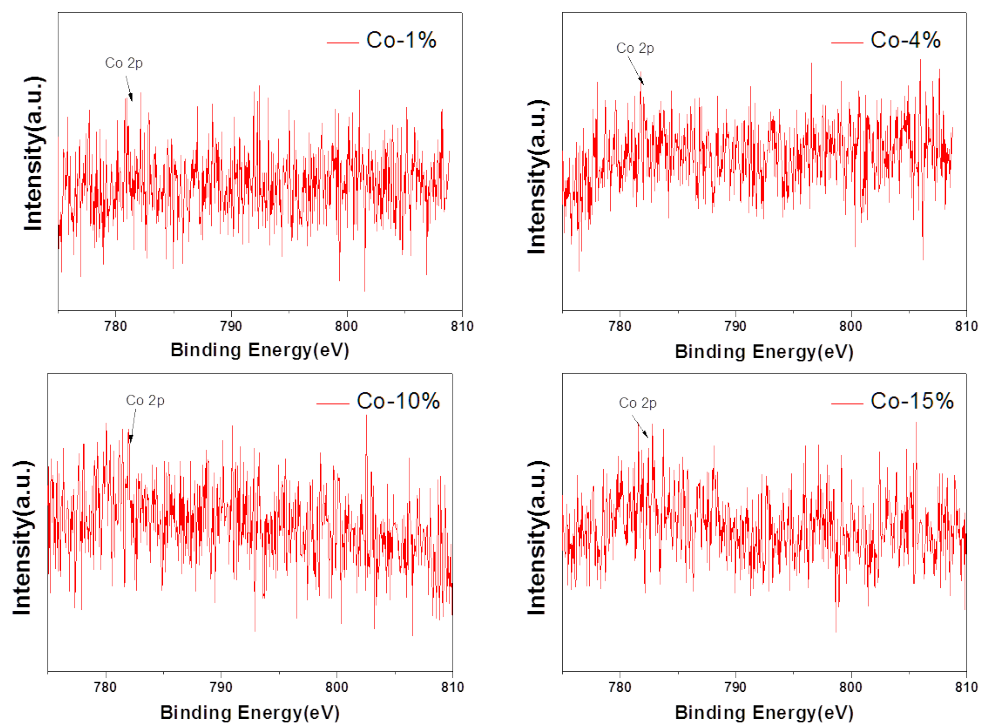
**Figure S1:** HAADF-STEM image of  $\text{Pt}_{75}\text{Co}_{25}/\text{C}$  primary solid solution alloy catalyst



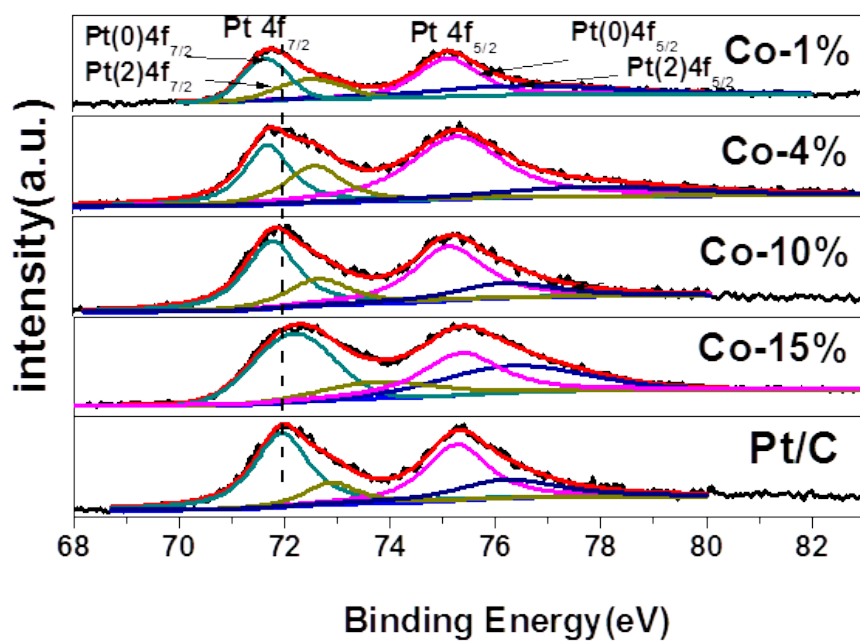
**Figure S2:** HAADF-STEM image of Co-10% secondary solid solution alloy catalyst



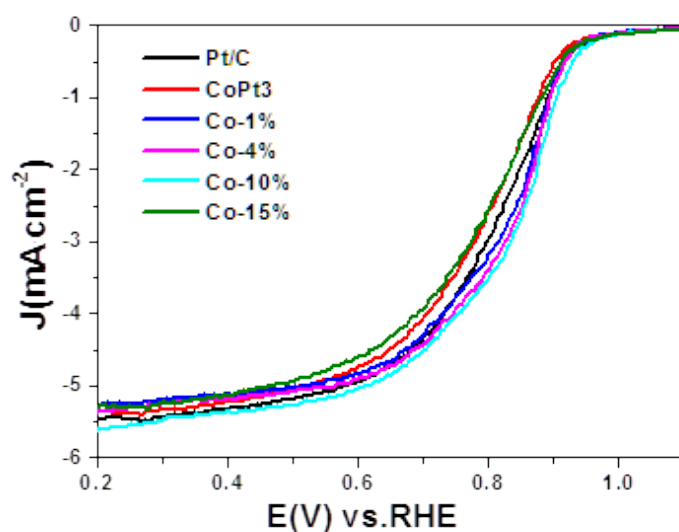
**Figure S3:** cyclic voltammetry (CV) conducted in  $\text{N}_2$ -purged  $\text{HClO}_4$  (0.1M) solutions at a sweep rate of 50mV/s.



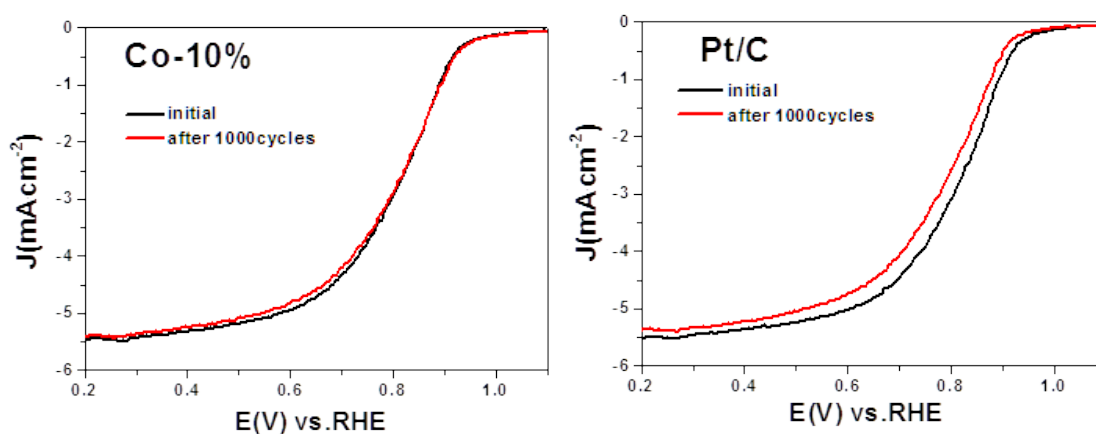
**Figure S4:** High resolution XPS spectra showing Co 2p peaks



**Figure S5:** High resolution XPS spectra showing Pt 4f peaks of all the secondary solid solution catalysts



**Figure S6:** The ORR polarization curves measured at 1600rpm in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution with a sweep rate of 5mV/s in the negative direction



**Figure S7:** Characterization of stability for ORR: Polarization curves of Co-10% and Pt/C catalysts before and after ADT. The ADT was conducted by potential cycling between 0~1.3V vs. RHE in the O<sub>2</sub>-purged 0.1 M HClO<sub>4</sub> solution at a scan rate of 100mV/s for 1000 cycles.

1. X. Ge, A. Sumboja, D. Wu, T. An, B. Li, F. T. Goh, T. A. Hor, Y. Zong and Z. Liu, *ACS. Catal.*, 2015, **5**, 4643-4667.
2. B. Lim, M. Jiang, P. H. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu and Y. Xia, *Science*, 2009, **324**, 1302-1305.