

## Electronic Supplementary Information

# Generation of OH Radicals in Oxygen Reduction Reaction at Pt-Co Nanoparticles Supported on Graphene in Alkaline Solutions

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## Experimental section

**Chemicals** All chemicals used were at least analytical grade, and water was made by Milli-Q water purification system.  $K_2PtCl_4$  was purchased from Delan Fine Chemical Plant (Tianjin, China).  $CoCl_2 \cdot 6H_2O$ , sodium borohydride ( $NaBH_4$ ), formaldehyde, ascorbic acid and hydrazine were obtained from Jingchun Chemical Reagent Co. (Shanghai, China), terephthalic acid (TA) was purchased from Flukca Co.. Flake graphite (300 mesh) was obtained from Kanglong Co. (Qingdao, China).

**Preparation of Pt-Co/graphene** Graphene oxide (GO) was obtained by oxidizing graphite using modified Hummer's method.<sup>1</sup> Briefly, graphite powder was mixed with strong oxidizing reagents such as potassium permanganate, concentrated sulfuric acid, hydrogen peroxide and potassium persulfate. The mixture was sonicated and centrifuged, and then were washed by deionized water thoroughly. The dried powder was stored and dispersed in aqueous solution.

Weighted amounts of  $K_2PtCl_4$  and  $CoCl_2$  were added into GO solution (10 mL) to keep a fixed metal atomic ration as  $Pt_1Co_x$ , and the mixed solution of GO and metal ions was magnetically stirred and kept overnight. Finally, 10 mL 20 mM  $NaBH_4$  was added dropwise into the mixed solution. During the addition of  $NaBH_4$ , a gradual color change to darkish was observed. After continuously stirring for 1 h, the resulting solution was filtered and washed to remove halide ions. After drying at 80 °C, the graphene supported alloy catalysts with 20% (wt.) Pt-Co loading was obtained as  $Pt_1Co_x/graphene$  (atomic ratio,  $x = 0.25, 0.5, 0.75, 1, 2$ , respectively).

**Characterization of Pt-Co alloy nanoparticles** Pt<sub>1</sub>Co<sub>x</sub> alloy nanoparticles supported on graphene were prepared as above, the morphology and the size of which were characterized by transition electron microscopy (TEM) on a Hitachi-800 TEM. It was operated at an accelerating voltage of 150 kV coupled with a digital image system. Samples for TEM were prepared by placing a drop of the suspension on the carbon-coated copper grid. The composition of the alloy was confirmed by energy dispersive X-ray (EDX). X-ray photoelectron spectroscopy (XPS) analyses were performed to identify the state and the concentration of metals on the surface of catalysts. The measurements were performed using EscaLabMK2 (VG Scientific) spectrometer, with an Mg Ka X-ray source (1253.6eV).

**Electrochemical measurements** Typically, the ordinary glassy carbon electrode (GCE, 3 mm in diameter) and rotating ring disk electrode (RRDE) with a rotating Pt ring-GC disk (3.7 mm in diameter) were polished using 0.05 μm Al<sub>2</sub>O<sub>3</sub> slurry and washed ultrasonically with ethanol and water separate. An aliquot of 3.0 μL (1 mg mL<sup>-1</sup>) well-dispersed Pt<sub>1</sub>Co<sub>x</sub>/graphene catalyst suspension was pipetted onto the GC disk using a microsyringe. After drying, 0.5 μL 0.5 wt% Nafion (in ethanol) was placed immediately on the electrode surface to cover the graphene supported alloy catalyst. The electrochemical characterization of Pt<sub>1</sub>Co<sub>x</sub>/graphene was performed using a common three-electrode and RRDE systems (Jiangsu Jiangfen Electroanalytical Instrument Co. Ltd.). A Pt wire and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. The collection efficiency (*N*) of the ring electrode obtained by reducing potassium ferricyanide at the disk electrode is 0.55. The electrolyte solution was 0.1 mol L<sup>-1</sup> NaOH, and electrochemical measurements performed at room temperature (20 ± 2

°C) using a bi-potentiostat CHI 832 electrochemical workstation (Shanghai Chenhua Co., China).

The solution was degassed using N<sub>2</sub> (>99.99%), and the ORR measurements were carried out in the same solution, after saturating with air or O<sub>2</sub> (>99.99%).

**Detection of OH radicals** The prepared GCE was immersed in the mixing solution of 0.1 mM TA and 0.1 M NaOH. After scanned with potential ranging from 0 V to -1.0 V for 1500 cycles, the solution was transferred to an optical cell for fluorescence emission measurements. The fluorescence spectra of 2-hydroxyterephthalic acid (HTA), generated by the reaction of TA with the OH radical produced in ORR process were measured on a Perkin-Elmer LS-55 fluorescence spectrometer. The excitation and the emission wavelength were set at 315 nm and 425 nm, respectively.

### Kinetic analysis for ORR by Wroblowa's method

The kinetic analysis of the ring-disk data was dealt with Wroblowa's method, from the general ORR scheme (**Scheme 1**) the rate of the disk to ring current is given as:

$$N \frac{I_D}{I_R} = 1 + \frac{2k_1}{k_2} + A + \frac{Ak_6}{Z\omega^{1/2}} \quad (\text{S1a})$$

Where  $N$  is the collection efficiency, and

$$Z = 0.62D^{2/3}\nu^{-1/6} \quad (\text{S1b})$$

$$A = \frac{k_1}{k_2k_5}(k_2 + k_3 + k_6) + \frac{2k_3 + k_4}{k_5} \quad (\text{S1c})$$

A representative plot of  $NI_D/I_R$  versus  $\omega^{-1/2}$  was shown in **Fig. S5**. The linear plots are potential dependent and the intercept increases with varying catalyst composition. In the Co content region

of 1:0.25 to 1:1, the intercepts decreased, whereas it increased for Pt<sub>1</sub>Co<sub>2</sub> and Pt as shown in **Fig.**

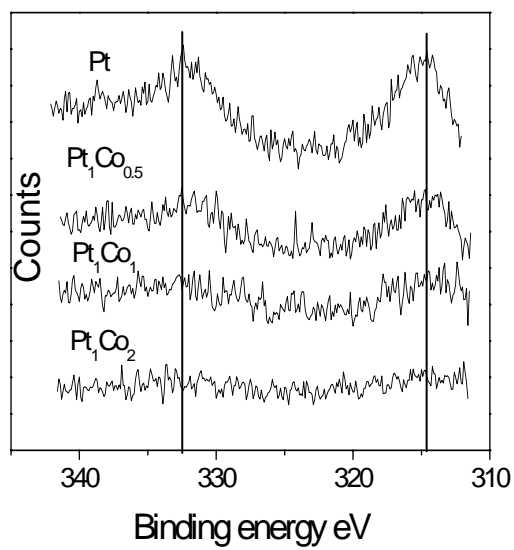
**S6.** According to Wroblowa's discussion, the intercept is

$$J = 1 + \frac{2k_1}{k_2} + \frac{SZ}{k_6} \quad (\text{S1d})$$

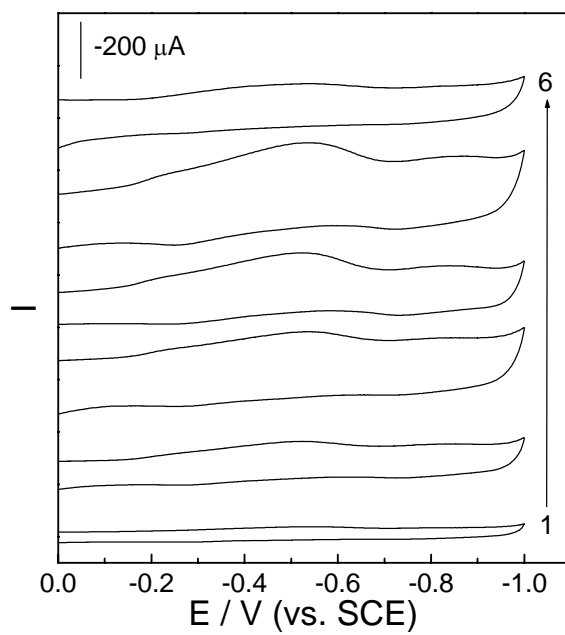
where  $S$  is the slope. We consider that  $k_1$  and  $k_2$  have the same potential dependence and the adsorption–desorption rate constants  $k_5$  and  $k_6$  depend little on potential, eq.S1d predicts a linear relationship between  $J$  and  $S$  with the intercept depending on the ratio of  $k_1$  and  $k_2$ .

## Notes and references

- 1 W. S. Hummers and J. R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

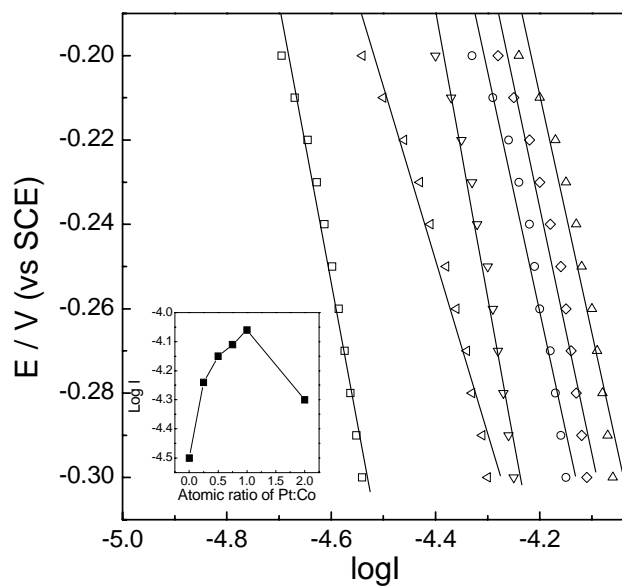


**Fig. S1** Pt 4d XPS of prepared Pt-Co alloy catalysts with different metal atomic ratios

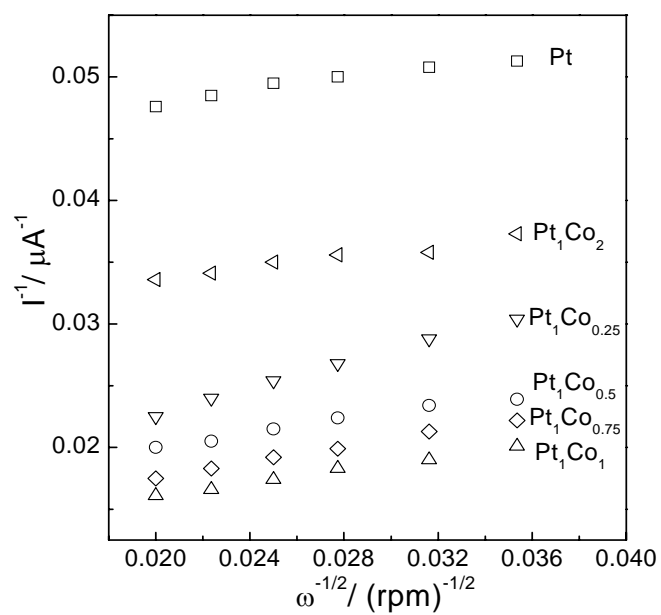


**Fig. S2** Cyclic voltammetry of oxygen reduction at Pt<sub>1</sub>-Co<sub>x</sub>/graphene/GC with different metal atomic ratios in 0.1 M air-saturated NaOH solution. Scanning rate: 50 mV s<sup>-1</sup>. From 1 to 6: bare graphene/GC, Pt<sub>1</sub>Co<sub>0.25</sub>, Pt<sub>1</sub>Co<sub>0.5</sub>, Pt<sub>1</sub>Co<sub>0.75</sub>, Pt<sub>1</sub>Co<sub>1</sub>, and Pt<sub>1</sub>Co<sub>2</sub>/graphene/GC, respectively.

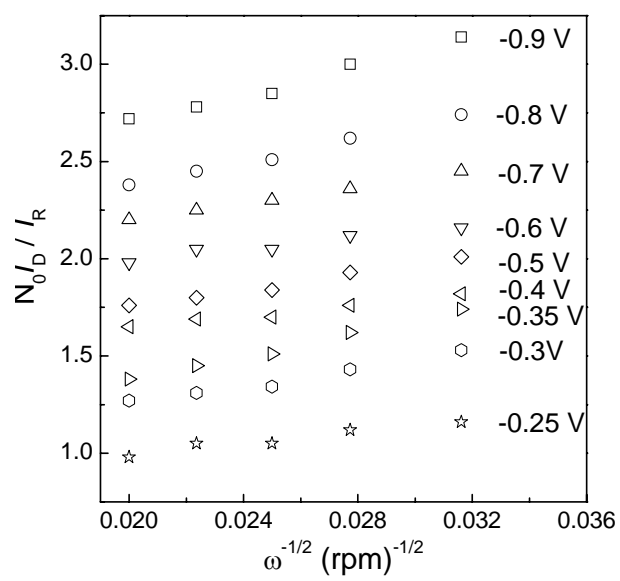




**Fig. S3** Tafel plots for the reduction of oxygen in 0.1 mol L<sup>-1</sup> air-saturated NaOH solution at GCE disk modified Pt-Co/graphene with different metal atomic ratios. Rotating rate was fixed at 2500 rpm and scan rate was 10 mV s<sup>-1</sup>. Inset: plot of current at -0.3 V to atomic ratio of Pt to Co.

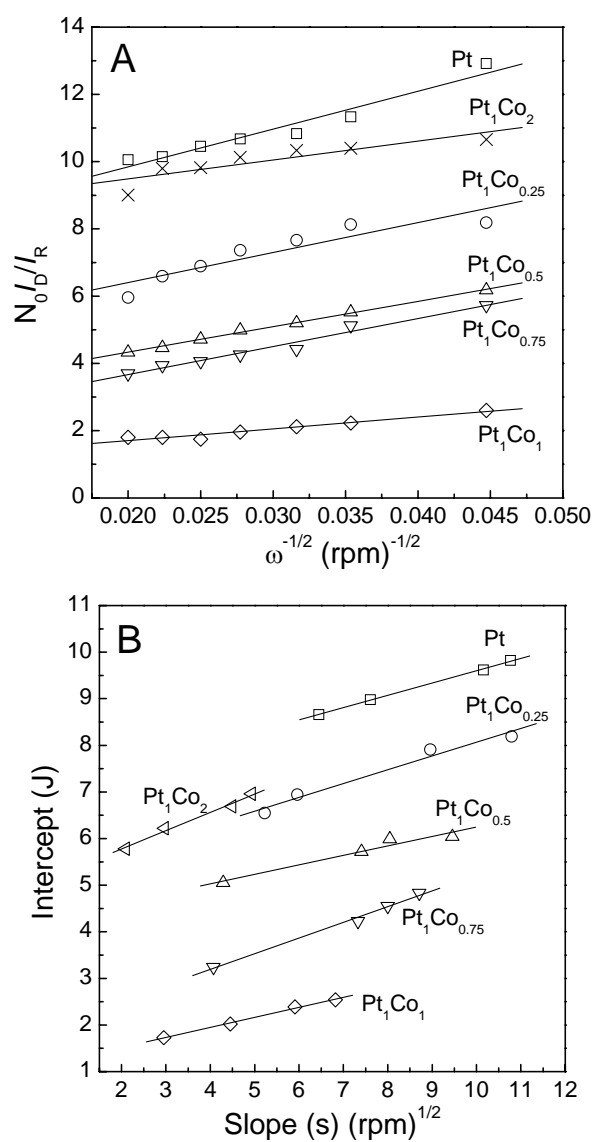


**Fig. S4** Comparison of Koutecky-Levich plots for the reduction of oxygen in  $0.1 \text{ mol L}^{-1}$  air-saturated NaOH solution at GCE modified  $\text{Pt}_1\text{Co}_x/\text{graphene}$  with different metal atomic ratios. The potential was fixed at  $-0.3\text{V}$ . The number of electron transfer and kinetic rate constant of ORR listed in Table 1.



**Fig. S5**  $N \frac{I_D}{I_R}$  vs.  $\omega^{-1/2}$  plots for the ORR at bare ring-Pt<sub>1</sub>Co<sub>1</sub>/graphene/GC in air-saturated

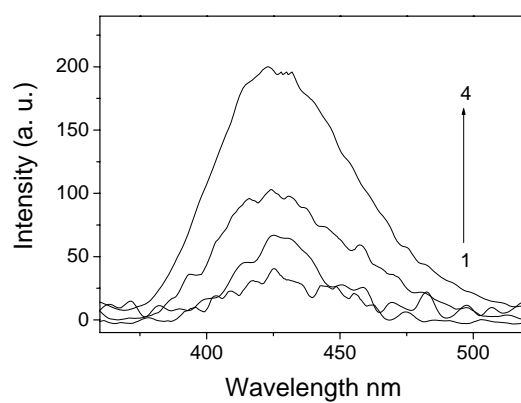
NaOH solution.



**Fig. S6**  $N \frac{I_D}{I_R}$  vs.  $\omega^{-1/2}$  plots (A) and  $J$  vs.  $S$  plots (potentials selected: -0.2, -0.3, -0.4, -0.5 V,

respectively) (B) for ORR at bare ring-Pt-Co/graphene/GC with different atomic ratios for Pt and

Co in air-saturated NaOH solution.



**Fig. S7** Fluorescence spectra of (1) 0.1 mM TA plus 10 mM H<sub>2</sub>O<sub>2</sub>; (2) 0.1 mM TA plus 10 mM H<sub>2</sub>O<sub>2</sub> in the suspension of Pt<sub>1</sub>Co<sub>1</sub>/graphene; (3) 0.1 mM TA plus 20 mM H<sub>2</sub>O<sub>2</sub> in the suspension of Pt<sub>1</sub>Co<sub>1</sub>/graphene; (4) 0.1 mM TA plus 30 mM H<sub>2</sub>O<sub>2</sub> in the suspension of Pt<sub>1</sub>Co<sub>1</sub>/graphene.