Supporting information

Efficient oxygen reduction catalysts formed of cobalt phosphide nanoparticles decorated heteroatoms-doped mesoporous carbon nanotubes

Materials**:**Hexachlorocyclotriphosphazene was synthesized as described in the literature[1] and recrystallized from dry hexane followed by twice sublimation before use. Cobalt(Ⅱ) acetate tetrahydrate (AR), 4,4'-sulfonyldiphenol, potassium hydroxide (KOH), triethylamine, tetrahydrofuran , acetonitrile and ethyl alcohol were purchased from Shanghai Chemical Reagents Corp. (Shanghai, China) and used without further purification.

Synthesis of **Co_xP*-CNTs-Ts*:** PNTs were prepared by referring to our previous preparation method.[2] 0.2 g PNTs was dispersed in 20 ml anhydrous ethanol (EtOH), followed the addition of0.1 ml of 0.6 M $Co(Ac)_2$ aqueous solution. After magnetic stirring for 3 hours, 0.1 ml of NH_4OH (30% solution) was added to the solution. The mediate product was obtained by centrifugation, washing and freeze-dry. The carbonization process was conducted in a tube type resistance furnace. In a typical procedure, 0.20 g of the mediate product in a ceramic boat was heated to 500 °C with a rate of 5 °C/min under a flow of pure N_2. Following an isaothermal process at 500°C for 5 hour, the temperature was ramped to the desired value at a heating rate of 5 °C/min, and kept at that value for 2 hours.

Electrochemical measurements**:** The electrochemical measurements were conducted using a conventional three-electrode cell filled with 0.1 M KOH solution. Ag/AgCl and platinum wire electrodes were used as the reference and counter electrodes, respectively. CVs and RDE experiments were performed with a scanning rate of 10 mV s^{-1}.

Characterization: Transmission electron microscopy (TEM) was performed with a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 Kv. Field-emission scanning electron microscopy (SEM) measurements were conducted by a NOVA NANOSEM 450 field emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Kratos Axis Ultra DLD spectrometerwith Al Kα X-ray radiation (hv = 1486.6 eV), as the X-ray source for excitation. X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advance instrument with Cu Ka radiation operated at 40 kV and 40 mA. The scan range was 6°/min from 10° to 70° (2θ). Nitrogen adsorption and desorption isotherms were measured at 77 K with an ASAP 2010 M+C Surface Analyzer (Micromeritics Inc., USA). Raman spectra were recorded using a Nicolet Almega XR dispersive Raman spectrometer with 532-nm excitation wavelength.

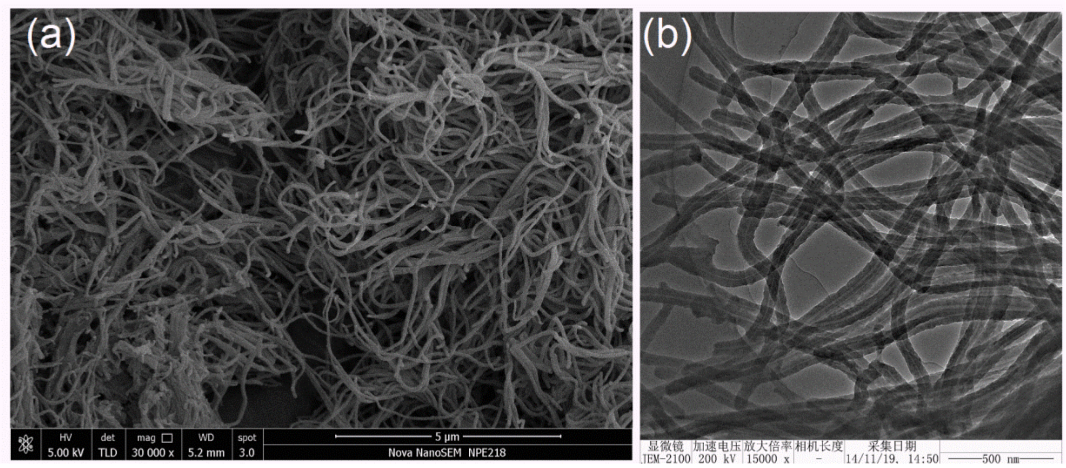

Fig. S1. SEM (a) and TEM (b) images of PNTs.

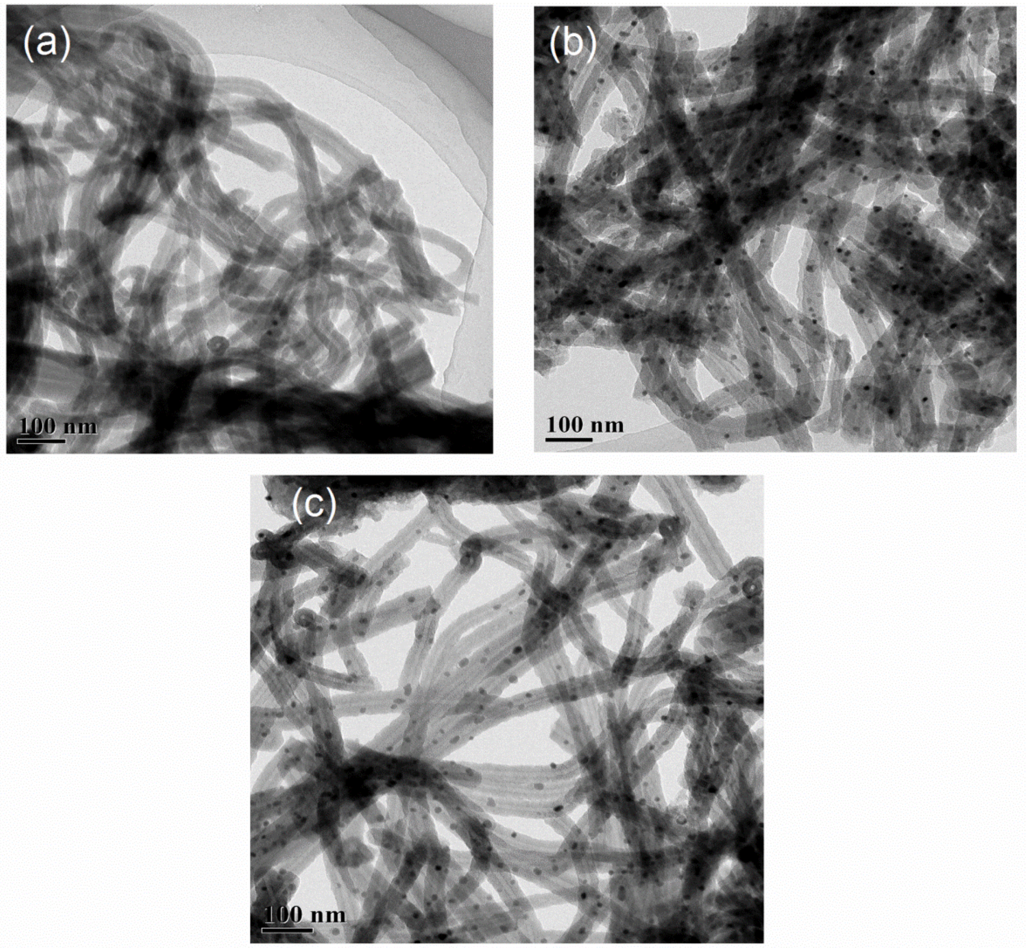

Fig. S2. TEM of Co_xP-CNTs-700 (a), Co_xP-CNTs-800 (b), Co_xP-CNTs-900 (c).

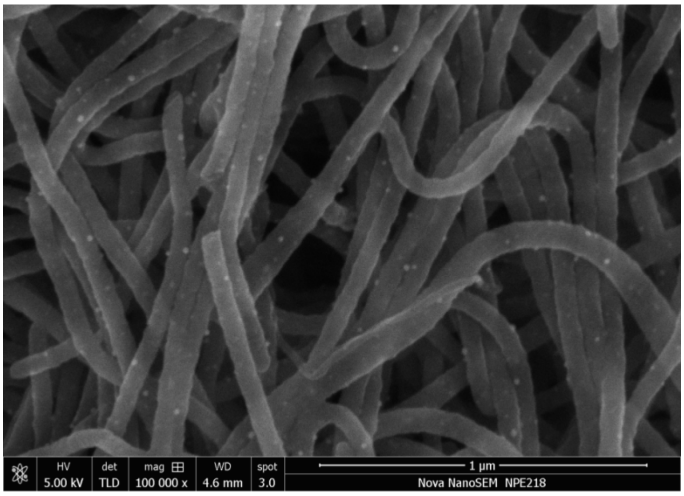

Fig. S3. SEM image of Co_xP-CNTs-1000.

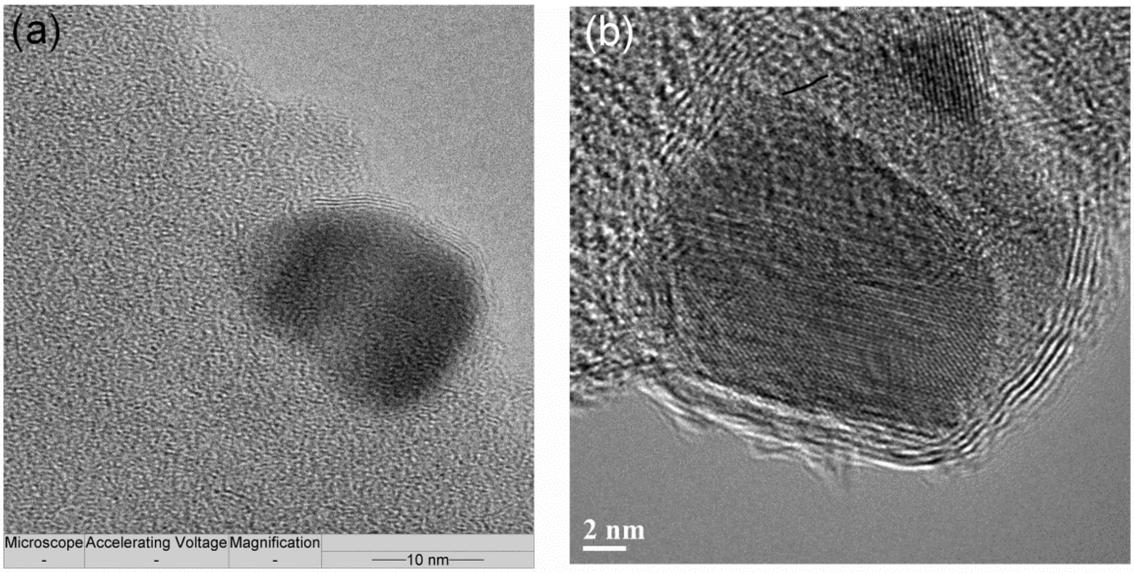

Fig. S4. TEM images of cobalt phosphide nanoparticles on Co_xP-CNTs-800 and Co_xP-CNTs-900, respectively.

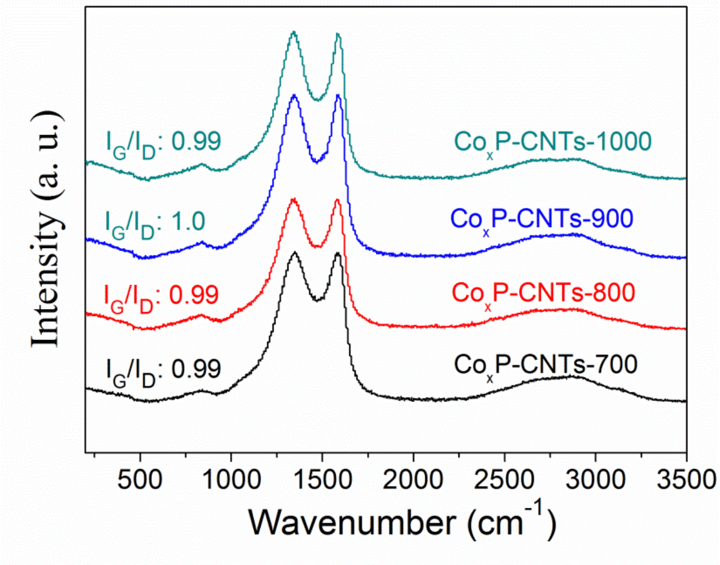

Fig. S5. Raman spectra of the samples carbonized at different temperatures.

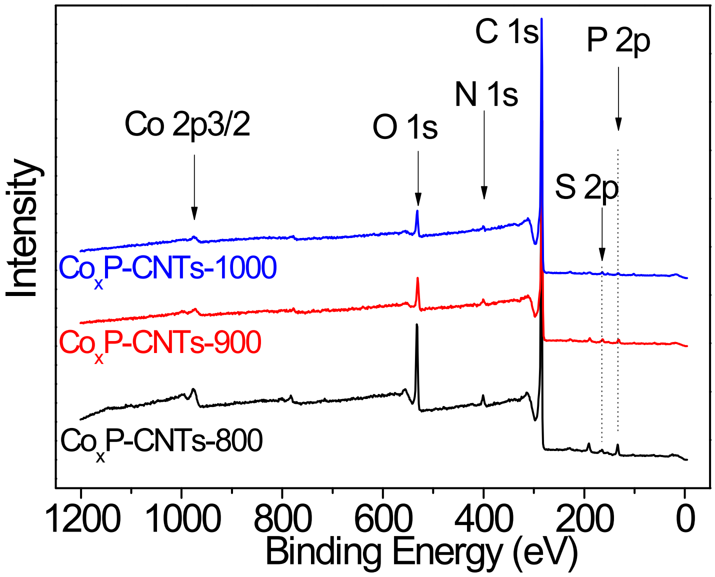

Fig. S6. Wide survey XPS spectra of the samples.

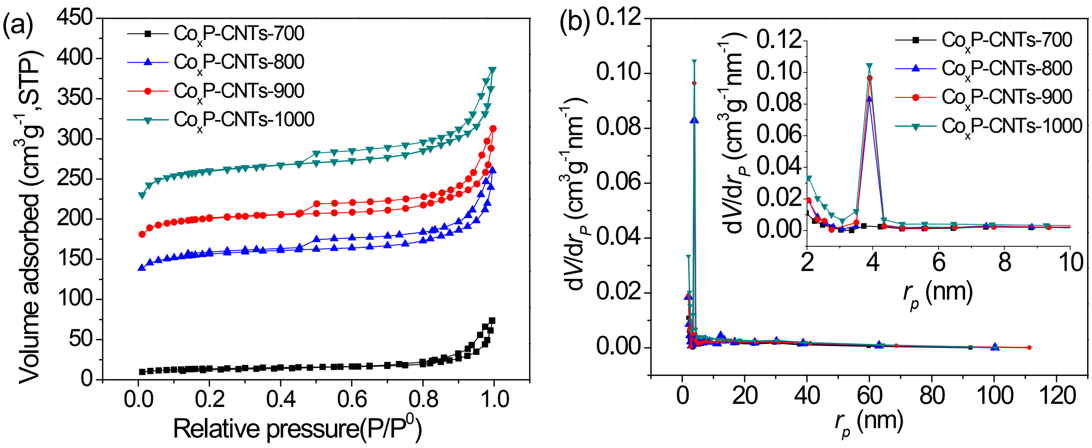

Fig. S7. Nitrogen adsorption–desorption isotherms (c) and pore size distribution curves (d) of the samples carbonized at different temperatures.

Table S1. Quantitative XPS analysis, textural properties and electrochemical capacitance performance of the samples.

Sample	C (at.%)	N (at.%)	O (at.%)	P (at.%)	S (at.%)	Co (at.%)	S$_{BET}$[a] m^2/g	V$_{pore}$[b] cm^3/g
Co$_x$P/CNTs-800	82.30	2.38	10.43	3.43	1.00	0.46	502.1	0.403
Co$_x$P/CNTs-900	88.24	1.85	6.37	2.10	1.02	0.42	641.3	0.484
Co$_x$P/CNTs-1000	93.17	1.21	3.73	0.91	0.62	0.36	833.3	0.598

[a] specific surface area calculated by BET method. [b] pore volume of the samples.

All the samples are identified to compose C, N, O, P, S and Co elements. The contents of N, O, P and S, which are mainly derived from the PNTs, are decreased with the increase of the carbonization temperature. The level of Co is decreased with the increase of carbonization temperature, which may be caused by the coverage of relatively thicker carbon layers on the Co$_x$P nanoparticles.

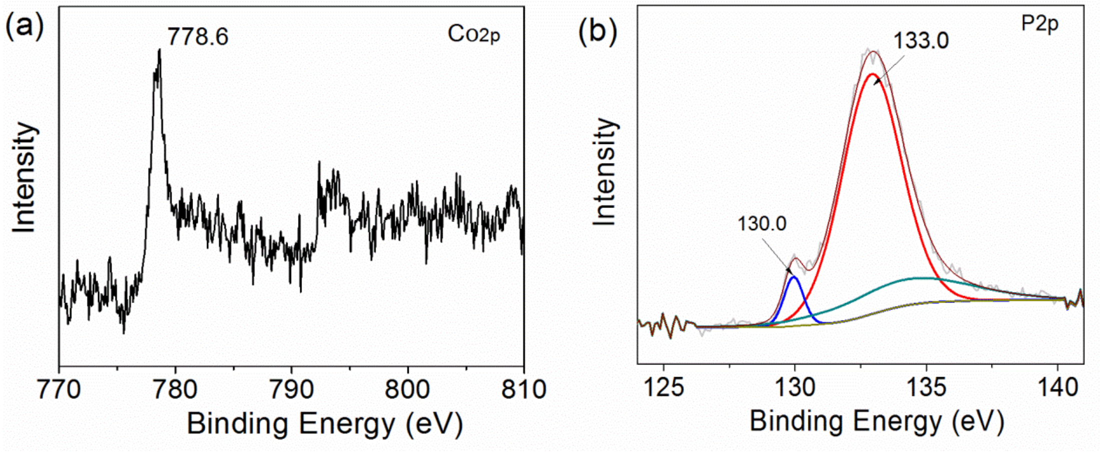

Fig. S8. High-resolution XPS spectra of Co$_x$P-CNTs-900 in the Co (2p3/2) (a) and P 2p (b) regions.

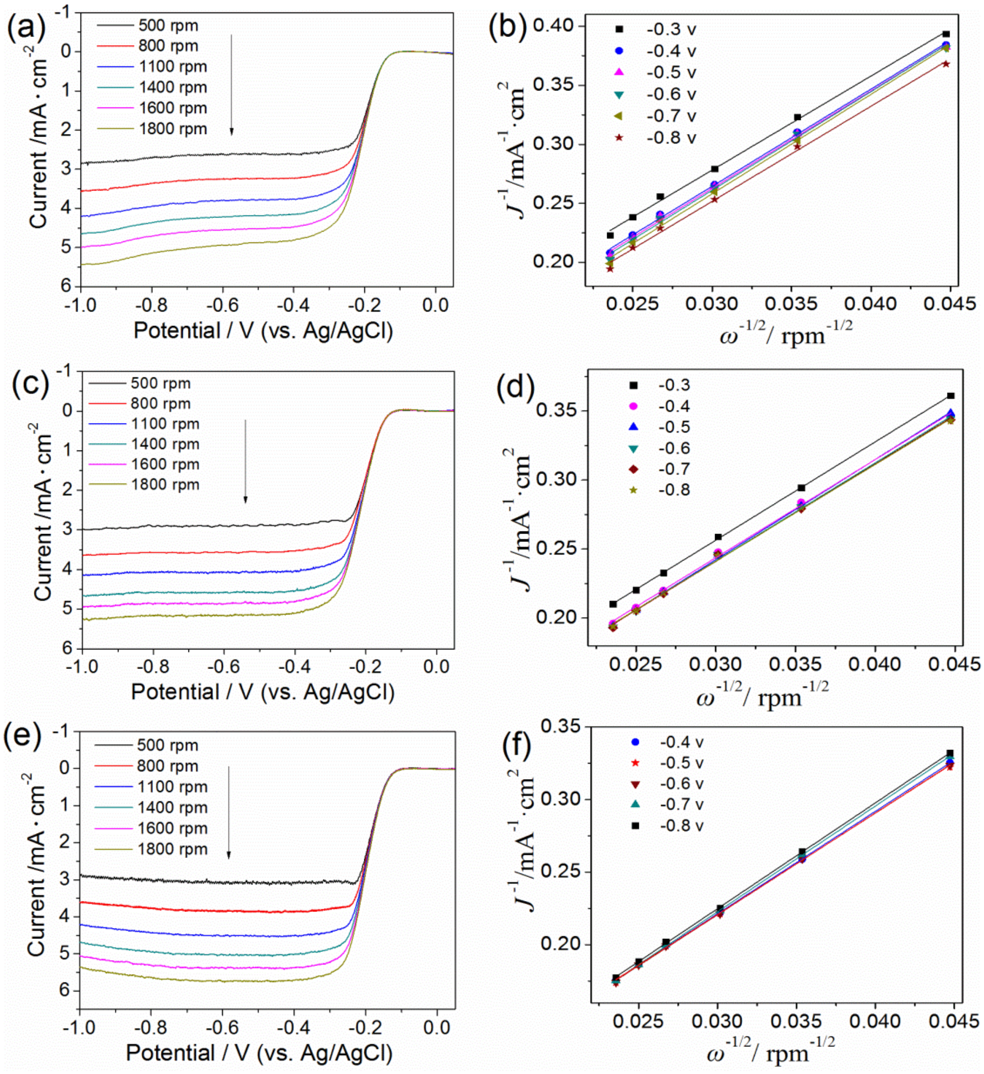

Fig. S9. Linear sweep voltammograms (LSVs) curves of Co$_x$P-CNTs-800 (a), Co$_x$P-CNTs-900 (c) and Co_xP-CNTs-1000 at various rotating rates in O_2 saturated 0.1 M KOH and the corresponding Kouteckye Levich plots recorded at selected potentials (b, d,f).

Koutechy_Levich equation:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{B\omega^{0.5}} \qquad \text{(i)}$$

J_k represents the kinetic current and ω is the electrode rotating rate (rpm).

$$B = 0.2nF(D_{O_2})^{3/2}\upsilon^{-1/6}C_{O_2} \qquad \text{(ii)}$$

B could be determined from the slope of K-L plots by equation (i), F is the Faraday constant (F = 96485 C/mol), D_{O2} represents the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2/s), υ is the kinetic viscosity (0.01 cm^2/s), and C_{O2} represents the bulk concentration of O_2 (1.2×10^{-6} mol/cm^3). n is the transferred electron transfer number per oxygen molecule, and could be calculated via equation (i) and (ii).

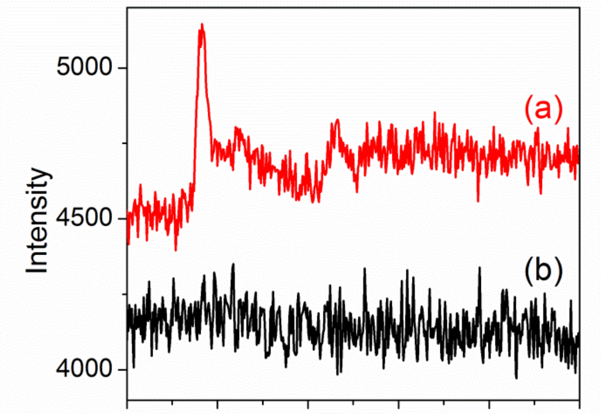

Fig. S10. High-resolution XPS spectra of Co_xP-CNTs-1000 (a) and Co_xP-CNTs-1000E (b) in the Co (2p3/2) regions, respectively.

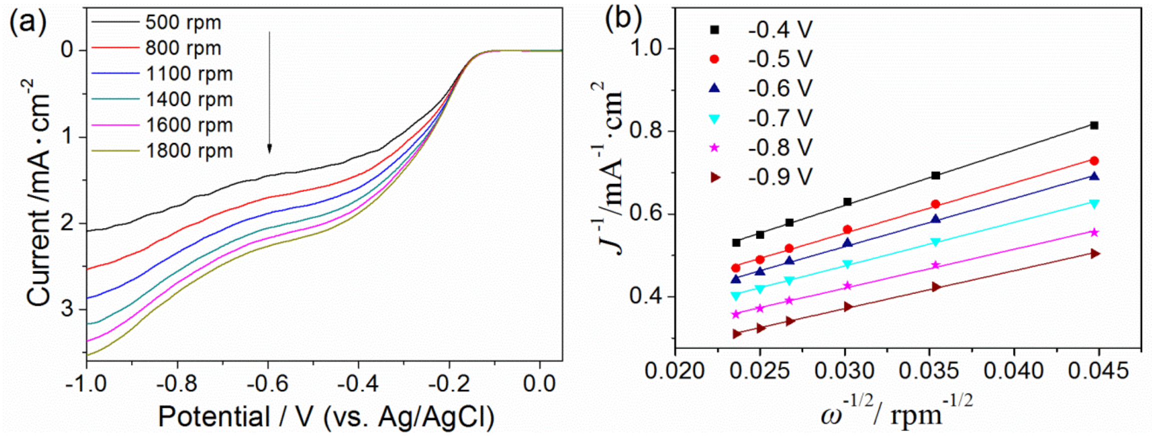

Fig. S11. (a) LSVs curves of Co_xP-CNTs-1000E at various rotating rates in O_2 saturated 0.1 M KOH and (b) the corresponding Kouteckye Levich plots recorded at selected potentials.

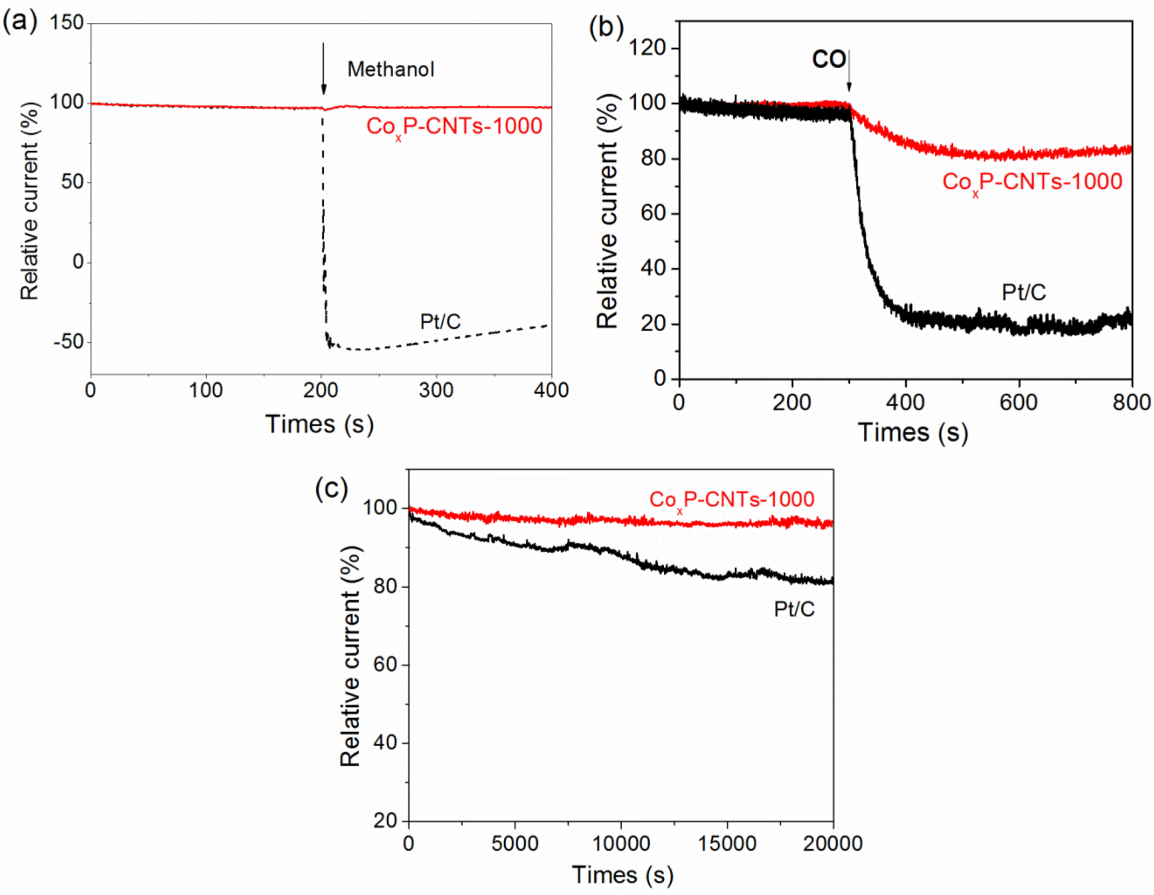

Fig. S12. Chronoamperometric responses of Co_xP-CNTs-1000 and Pt/C in 0.1 M KOH solution at -0.3 V (vs. Ag/AgCl) upon the introduction of 3 M methanol (a) and CO (b). (c)The durability testing curves of Co_xP-CNTs-1000 and Pt/C catalysts for 20000 s in 0.1 M KOH solution at -0.3 V (vs. Ag/AgCl) with a rotation rate of 1400 rpm.

References

1. R. De Jaeger and M. Gleria, *Progress in Polymer Science*, 1998, 23, 179-276.
2. L. Zhu, Y. Xu, W. Yuan, J. Xi, X. Huang, X. Tang and S. Zheng, *Advanced Materials*, 2006, 18, 2997-3000.