Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information for

Toward Understanding The Active Site for Oxygen Reduction Reaction on Phosphorus-Encapsulated Single-Walled Carbon Nanotubes

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1. Supporting data

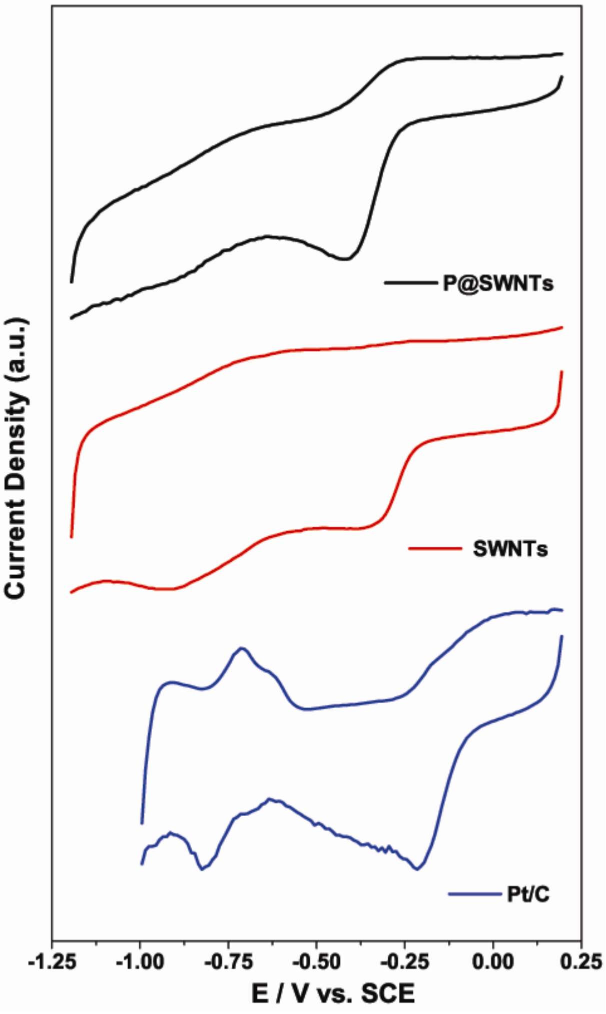

Fig. S1 CV curves of the pristine SWNTs, the P@SWNTs and commercial Pt/C catalysts in O_2-saturated 0.1 M NaOH electrolyte with scan rate 100 mVs^{-1})

The electrocatalytic capabilities of the SWNTs, P@SWNTs and the commercial Pt/C were evaluated by cyclic voltammetry (CVs, Figure S1). It clearly shows the ORR peaks at the region of 0 to -0.4 V for all samples. The readed maximum peak current follows the relationship: 3.8 I_{SWNTs} = 2.2 $I_{P@SWNTs}$ = $I_{Pt/C}$. The near one-time increase of peak current on the P@SWNTs indicates the considerable improved ORR electrocatalytic efficiency after phosphorus filling, which can be ascribed to the good electron-acceptor properties of the filled phosphorus that creates positively-charged sites in the nanotube carbon plane and facilitates the ORR process. Concerning the overpotential problem, the pristine SWNTs demonstrate the onset potential at about -0.22 V (versus SCE) and a cathodic reduction peaked at around -0.37 V, indicating a possible two-electron (2e) reduction process that is electrochemically mediated by the surface oxygen-containing groups on the SWNTs, with superoxide as an intermediate.[1] While at the P@SWNTs electrode, Both onset potential and the ORR peak negatively shift (-40 mV) with respect to those of the SWNTs, which are quite different from the well-known N-doped CNTs, resulted from the newly-created but weak catalytic active sites on the surface of the P@SWNTs. In a word, as compared to the pristine SWNTs, the P@SWNTs demonstrates a little-promoted ORR electrocatalytic activity.

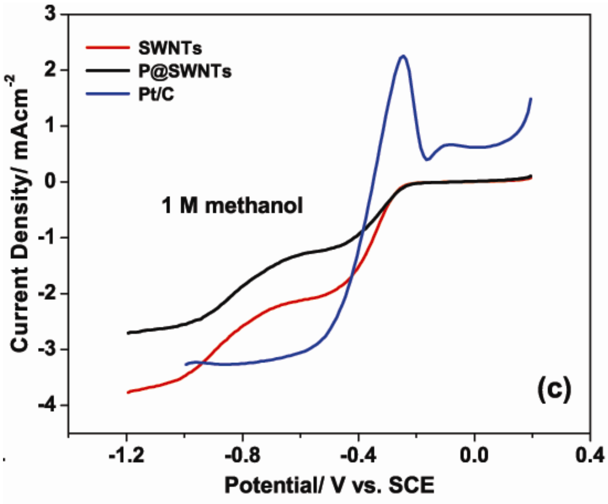

Fig. S2 Methanol tolerance test on the pristine SWNTs, the P@SWNTs and commercial Pt/C catalysts in O_2-saturated 0.1 M NaOH electrolyte with a ratation speed of 1600 rpm (scan rate 10 mVs^{-1})

2. Koutechy-Levich equations and the transfer electron number calcualtions

The transfer electron number per oxygen molecule involved in the oxygen reduction at both of the CNT electrodes was determined on the basis of the Koutechy-Levich equation given below:

$$I^{-1} = I_k^{-1} + (0.62nFCD^{2/3}\upsilon^{-1/6}\,\omega^{1/2})^{-1}$$

where I_k is the kinetics current density, I is the measured current density of the ORR, n represents the number of electrons transferred per oxygen molecule, F is the Faraday constant (F=96485 C mol^{-1}), C is the bulk concentration of O_2 (= 1.2 $\times 10^{-3}$ $mol \cdot L^{-1}$), D is the diffusion coefficient of O_2 in the KOH electrolyte ($=1.9*10^{-5}$ cm^2 S^{-1}), υ is the kinetic viscosity of the electrolyte (=0.01 cm_2 S^{-1}), and ω is the angular velocity of the the disk ($\omega = 2\pi N$, N is the linear rotation speed). The potential-dependence of n was provide in the table S1 below.

Table S1. The potential-dependence of electron-transfer number, n.

P@SWNTs	Potential (V)		-0.46	-0.55	-0.68	-0.81	-0.90	-0.95
	n		2.3	2.3	2.4	2.6	3.6	3.8
P-doped graphite [3]	Potential (V)	-0.40	-0.45	-0.51	-0.65	-0.83	-0.90	-0.95
	n	3.1	3	2.9	2.96	3.5	3.7	3.9

3. References

1. Z. W. Liu, F. Peng, H. J. Wang, H. Yu, W. X. Zheng and J. Yang, *Angew. Chem. Int. Ed.*, 2011, **50**, 3257.