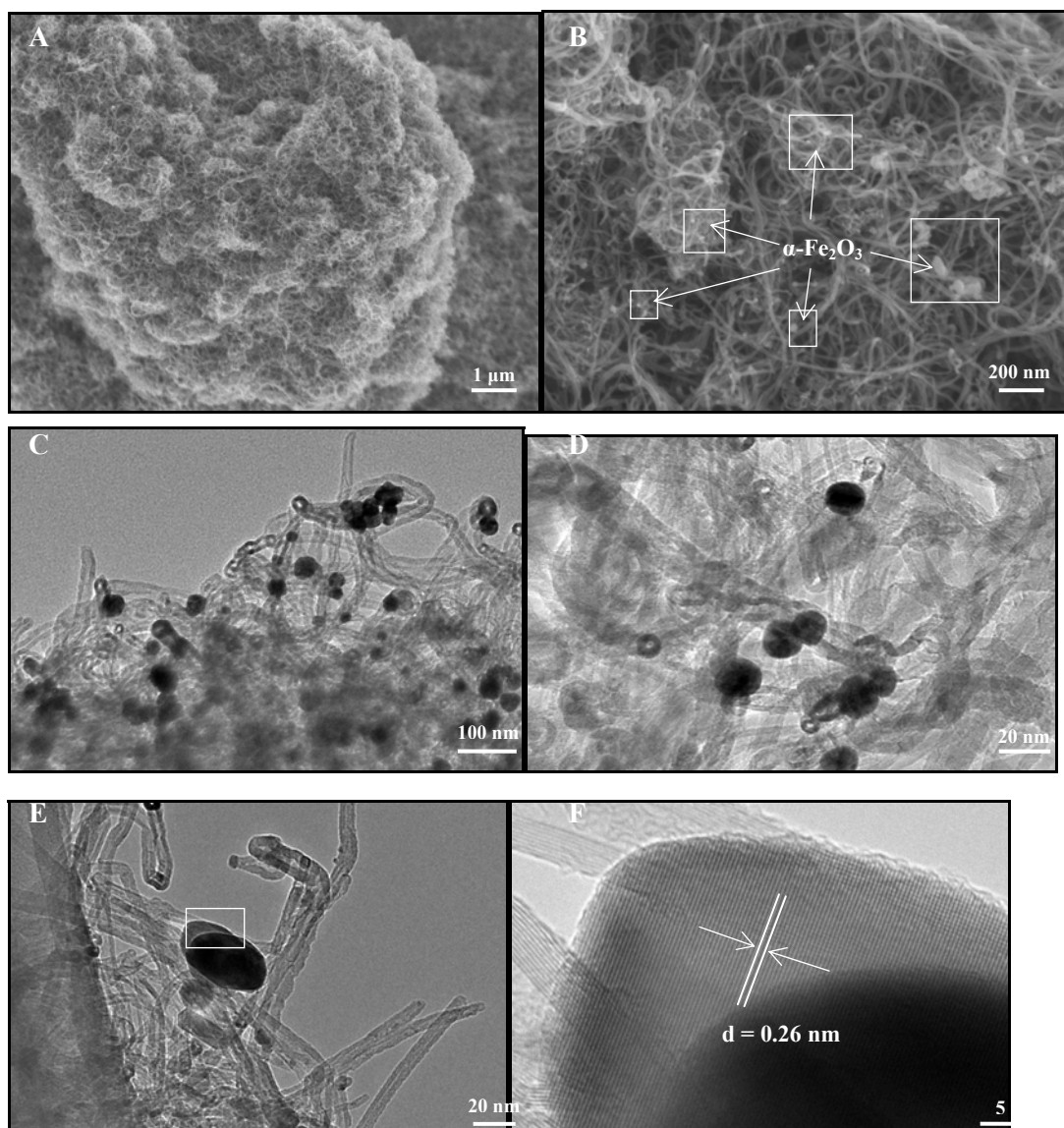


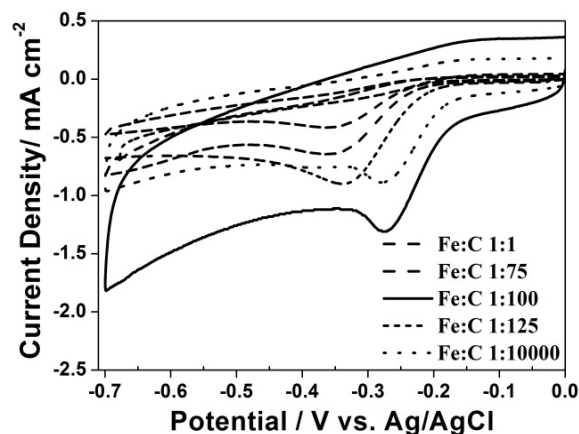
## Electronic support information

### $\alpha\text{-Fe}_2\text{O}_3$ spherical nanocrystals supported on CNTs as efficient non-noble electrocatalyst for oxygen reduction reaction

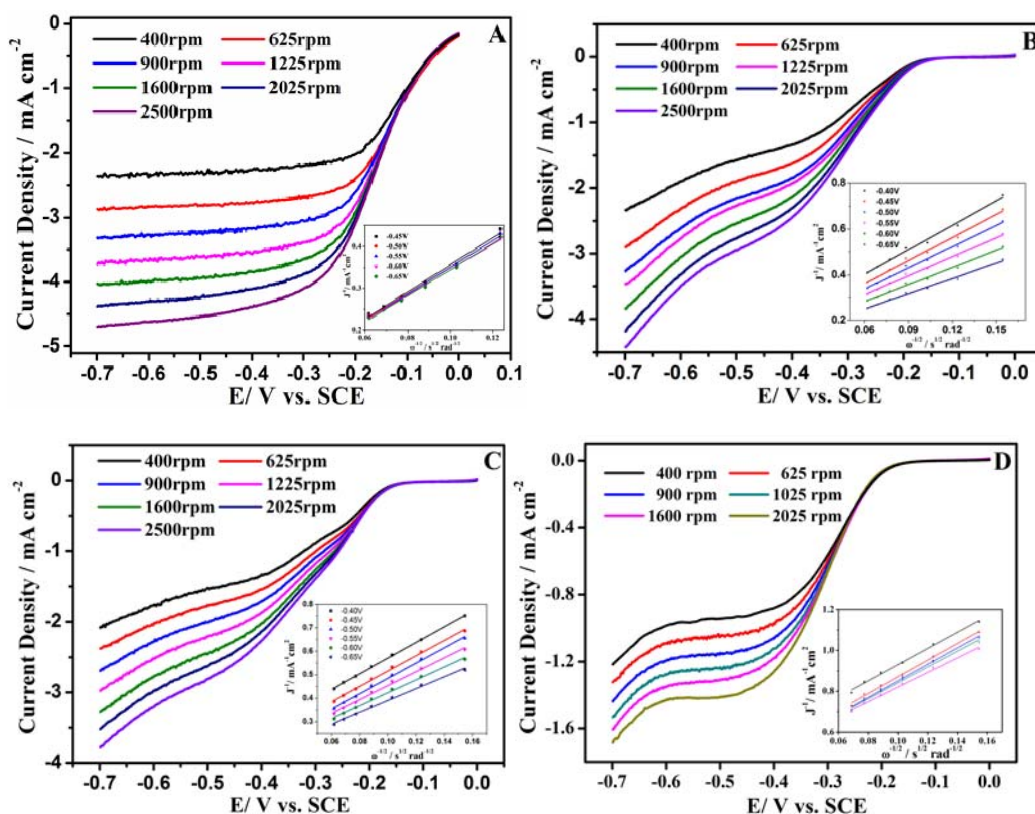
Meng Sun,<sup>ac</sup> Youzhen Dong,<sup>b</sup> Gong Zhang,<sup>ac</sup> Jiuhui Qu,<sup>\*a</sup> and Jinghong Li,<sup>\*b</sup>



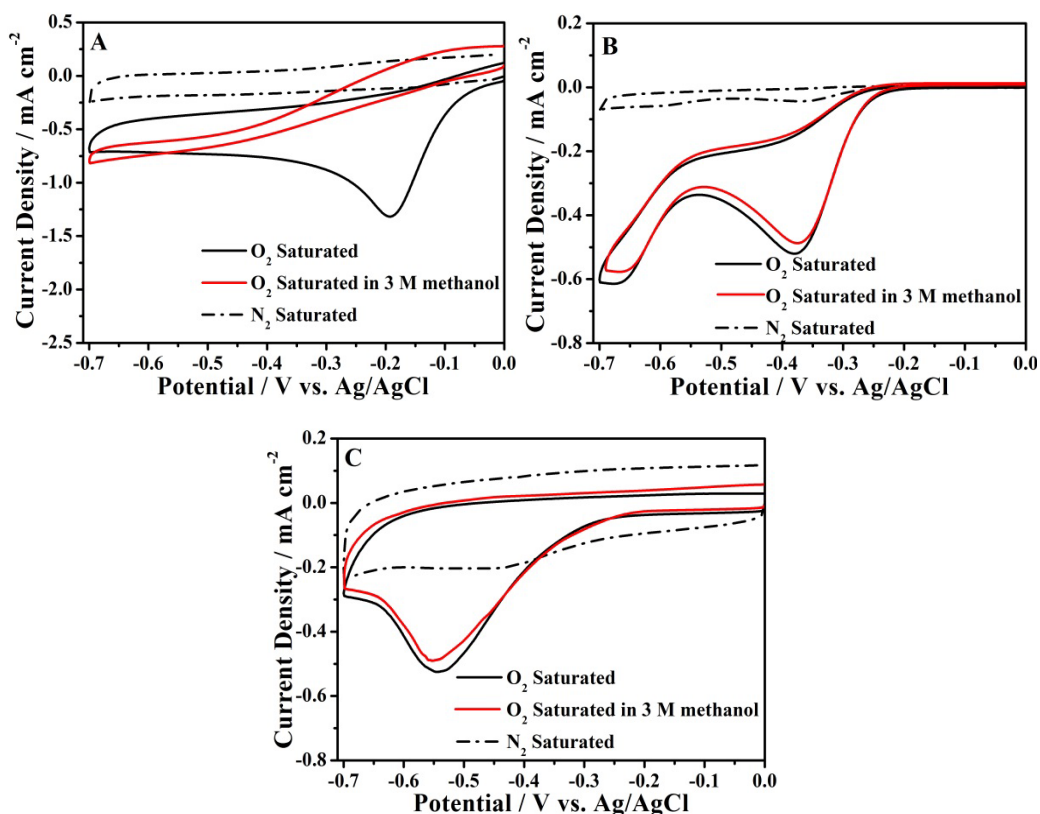
**Fig. SI-1** SEM images (A, B) of  $\alpha\text{-Fe}_2\text{O}_3/\text{CNTs}$  nanocomposites. The inserted white blocks of (B) indicate some  $\alpha\text{-Fe}_2\text{O}_3$  nanocrystals (white arrows) on CNTs. TEM images (C, D, E) of  $\alpha\text{-Fe}_2\text{O}_3/\text{CNTs}$  nanocomposites. The corresponding HRTEM image (F) shows a well-structured  $\alpha\text{-Fe}_2\text{O}_3$  nanocrystal with a lattice spacing of 0.26 nm.



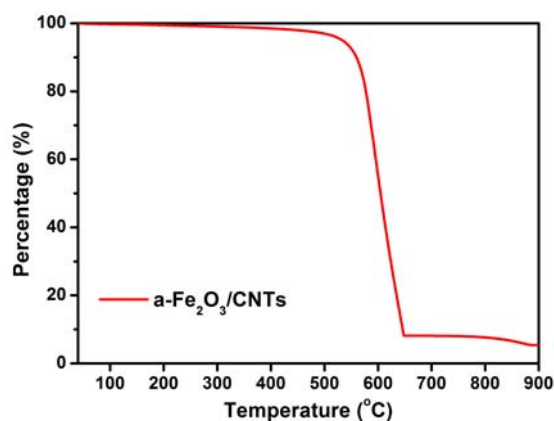
**Fig. SI-2** CV curves of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CNTs with different mole ratios of Fe and C from 1:10000 to 1:1 in O<sub>2</sub>-saturated 0.1 M KOH solutions. Scan rate: 50 mV s<sup>-1</sup>.



**Fig. SI-3** RDE curves of (A) Pt/C and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CNTs with different mole ratios of Fe and C from (B) 1:125, (C) 1:75 and (D) 1:1 in O<sub>2</sub>-saturated 0.1 M KOH solution at various rotation rates. Sweep rate: 5 mV s<sup>-1</sup>. The insets of (A), (B), (C) and (D) are the corresponding Koutecky–Levich plots of Pt/C and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CNTs nanocomposites with different mole ratios of Fe and C at different potentials derived from the RDE measurements.



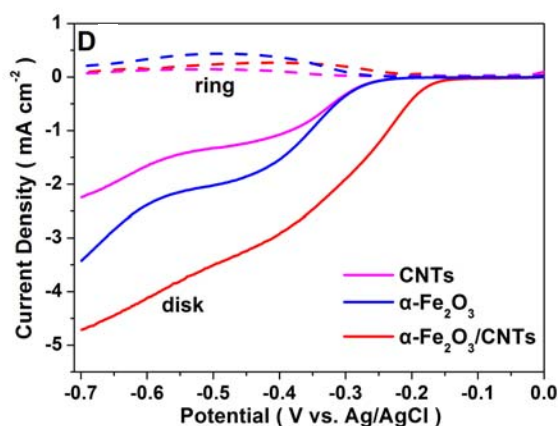
**Fig. SI-4** CV curves of (A) commercial Pt/C, (B)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (C) CNTs in N<sub>2</sub> and O<sub>2</sub>-saturated 0.1 M KOH solutions as well as O<sub>2</sub>-saturated 0.1 M KOH solution with 3 M methanol. Scan rate: 50 mV s<sup>-1</sup>.



**Fig. SI-5** TGA measurements of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CNTs with a heating rate of 10 °C/min range from 40 to 900 °C under air condition.

As seen from Fig. SI-5, the TGA measurements of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CNTs nanocomposites with theoretical mole ratios of Fe and C 1:100 taken in air in a temperature range from 40 to 900 °C illustrates that CNTs completely oxidize in air at the temperatures above 650 °C, resulting in a 5.39 % of original  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/CNTs at 900 °C (only 0.40 mg iron oxides residues in total 7.41 mg originals). The residues were dissolved by 2ml aqua regia under ultrasonic,

diluted to 50 ml by ultrapure water, and then filtered by 0.45  $\mu\text{m}$  ptfе membrane. Concentrations of total iron ions in the resulting solution were measured using a 700 series inductively coupled plasma optical emission spectrometer (ICP–OES, Agilent Technology). The obtained concentration of 5.5  $\mu\text{g}/\text{ml}$   $\text{Fe}^{3+}$  suggests an approximate actual loading of  $\alpha\text{-Fe}_2\text{O}_3$  on CNTs with mole ratios of Fe and C was 1:106. It is acceptable that the actual loading is slightly lower than theoretical loading owing to the effects of impurities and errors on this low-loaded operation. Therefore, in consideration of the convenient expression, the theoretical mole ratios Fe and C are adopt to specifically define different loading of  $\alpha\text{-Fe}_2\text{O}_3$  on CNTs.



**Fig.SI-6** RRDE curves of CNTs,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3/\text{CNTs}$  nanocomposites in  $\text{O}_2$ -saturated 0.1 M KOH solution at a rotation rate of 1600 rpm. Sweep rate: 5  $\text{mV s}^{-1}$ .

Rotating ring-disk electrode (RRDE) measurements is an additional way to estimate  $n$  and to evaluate the generated  $\text{H}_2\text{O}_2$  in ORR pathways.<sup>1</sup> The disk current from oxygen reduction was much larger than the ring current from peroxide oxidation towards CNTs,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3/\text{CNTs}$  nanocomposites, respectively (Fig. SI-6). As obtained from Fig. SI-6, the measured  $\text{H}_2\text{O}_2$  yield for  $\alpha\text{-Fe}_2\text{O}_3$  and CNTs at -0.6 V were 54.0 and 32.3 %, while those calculated  $n$  values were 2.92 and 3.35, respectively. In contrast, the accumulated  $\text{H}_2\text{O}_2$  percentage produced by  $\alpha\text{-Fe}_2\text{O}_3/\text{CNTs}$  was 17.2 % and  $n$  was calculated to be 3.65, which implied its notable ORR activity. Likewise, the  $n = 3.41\text{--}3.83$  for  $\alpha\text{-Fe}_2\text{O}_3/\text{CNTs}$  over the whole potential range from -0.2 to -0.7 V, emphasizing a nearly four-electron ORR proceeds of  $\alpha\text{-Fe}_2\text{O}_3/\text{CNTs}$ .

**References:**

1. Y. Y. Jiang, Y. Z. Lu, X. Y. Lv, D. X. Han, Q. X. Zhang, L. Niu, W. Chen, *ACS Catal.*, 2013, 3, 1263–1271.