Electronic support information

**α-Fe$_2$O$_3$ spherical nanocrystals supported on CNTs as efficient non-noble electrocatalyst for oxygen reduction reaction**

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

Fig. SI-2 CV curves of $\alpha$-Fe$_2$O$_3$/CNTs with different mole ratios of Fe and C from 1:10000 to 1:1 in O$_2$-saturated 0.1 M KOH solutions. Scan rate: 50 mV s$^{-1}$.

Fig. SI-3 RDE curves of (A) Pt/C and $\alpha$-Fe$_2$O$_3$/CNTs with different mole ratios of Fe and C from (B) 1:125, (C) 1:75 and (D) 1:1 in O$_2$-saturated 0.1 M KOH solution at various rotation rates. Sweep rate: 5 mV s$^{-1}$. The insets of (A), (B), (C) and (D) are the corresponding Koutecky–Levich plots of Pt/C and $\alpha$-Fe$_2$O$_3$/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) α-Fe$_2$O$_3$ and (C) CNTs in N$_2$ and O$_2$-saturated 0.1 M KOH solutions as well as O$_2$-saturated 0.1 M KOH solution with 3 M methanol. Scan rate: 50 mV s$^{-1}$.

Fig. SI-5 TGA measurements of α-Fe$_2$O$_3$/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 α-Fe$_2$O$_3$/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 α-Fe$_2$O$_3$/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 μm ptfe 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 μg/ml Fe³⁺ suggests an approximate actual loading of α-Fe₂O₃ 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 α-Fe₂O₃ on CNTs.

![Graph](image)

Fig.SI-6 RRDE curves of CNTs, α-Fe₂O₃ and α-Fe₂O₃/CNTs nanocomposites in O₂-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm. Sweep rate: 5 mV s⁻¹.

Rotating ring-disk electrode (RRDE) measurements is an additional way to estimate $n$ and to evaluate the generated H₂O₂ in ORR pathways.¹ The disk current from oxygen reduction was much larger than the ring current from peroxide oxidation towards CNTs, α-Fe₂O₃, α-Fe₂O₃/CNTs nanocomposites, respectively (Fig. SI-6). As obtained from Fig. SI-6, the measured H₂O₂ yield for α-Fe₂O₃ 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 H₂O₂ percentage produced by α-Fe₂O₃/CNTs was 17.2 % and $n$ was calculated to be 3.65, which implied its notable ORR activity. Likewise, the $n = 3.41–3.83$ for α-Fe₂O₃/CNTs over the whole potential range from -0.2 to -0.7 V, emphasizing a nearly four-electron ORR proceeds of α-Fe₂O₃/CNTs.
References: