

## **Activating Hematite Nanoplates *via* Partial Reduction for Electrocatalytic Oxygen Reduction Reaction**

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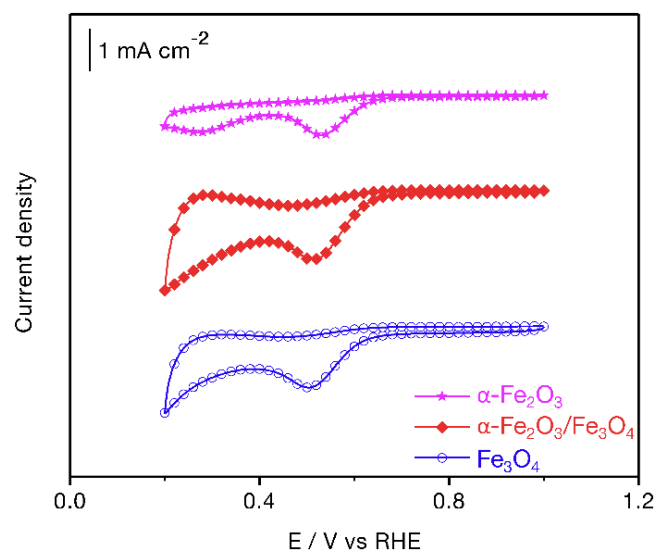
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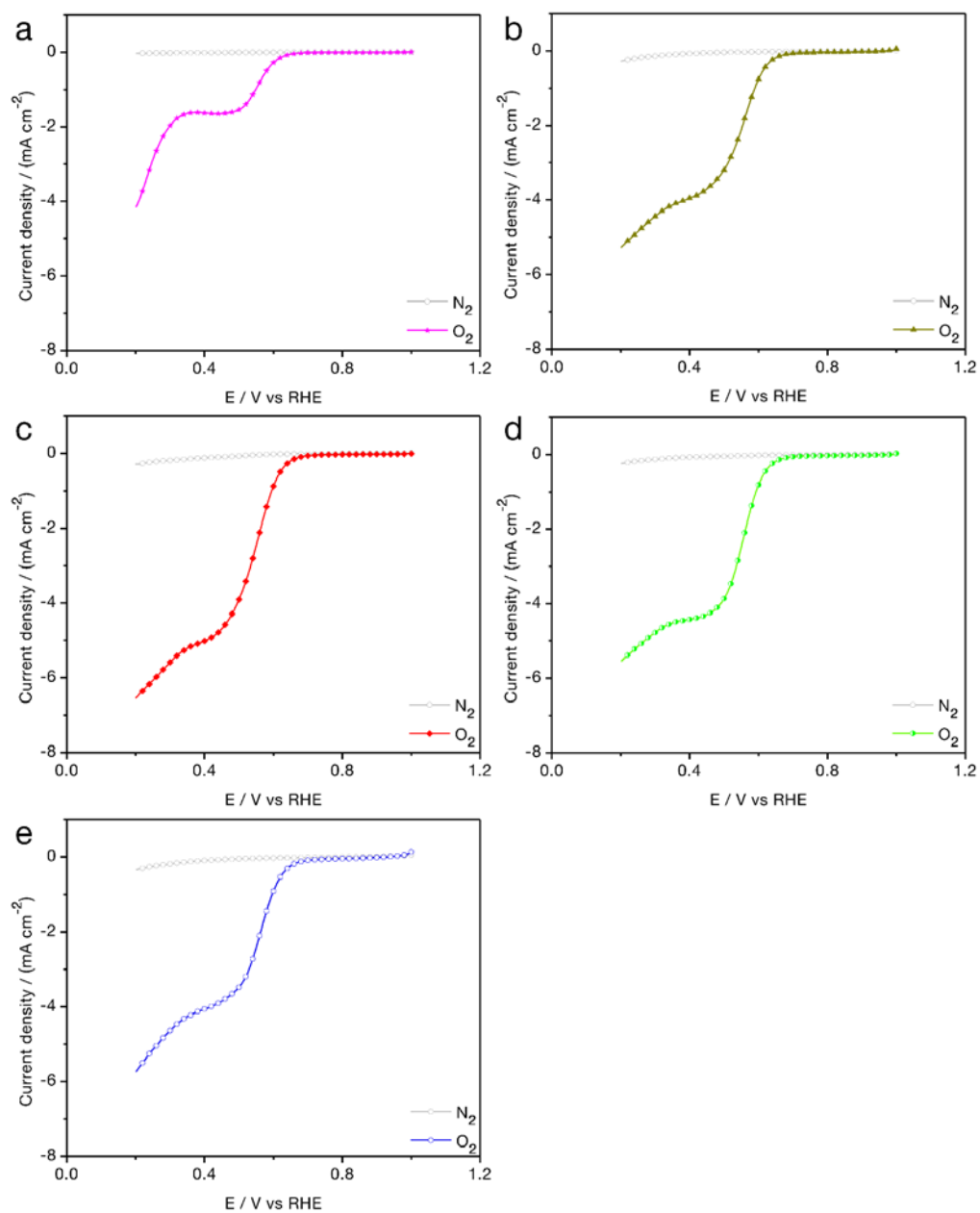
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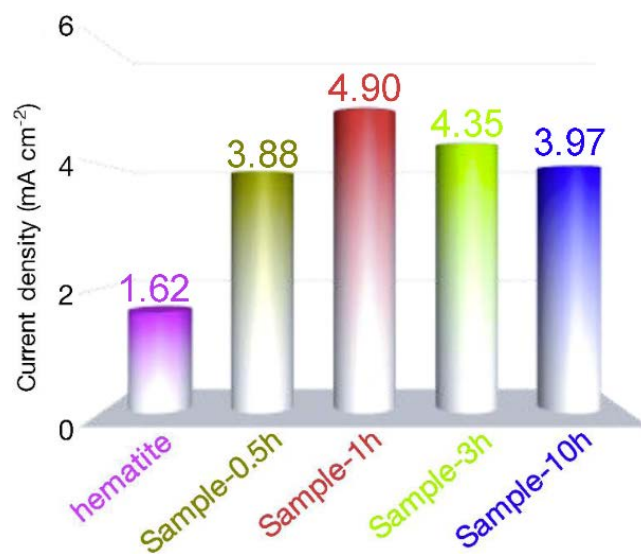
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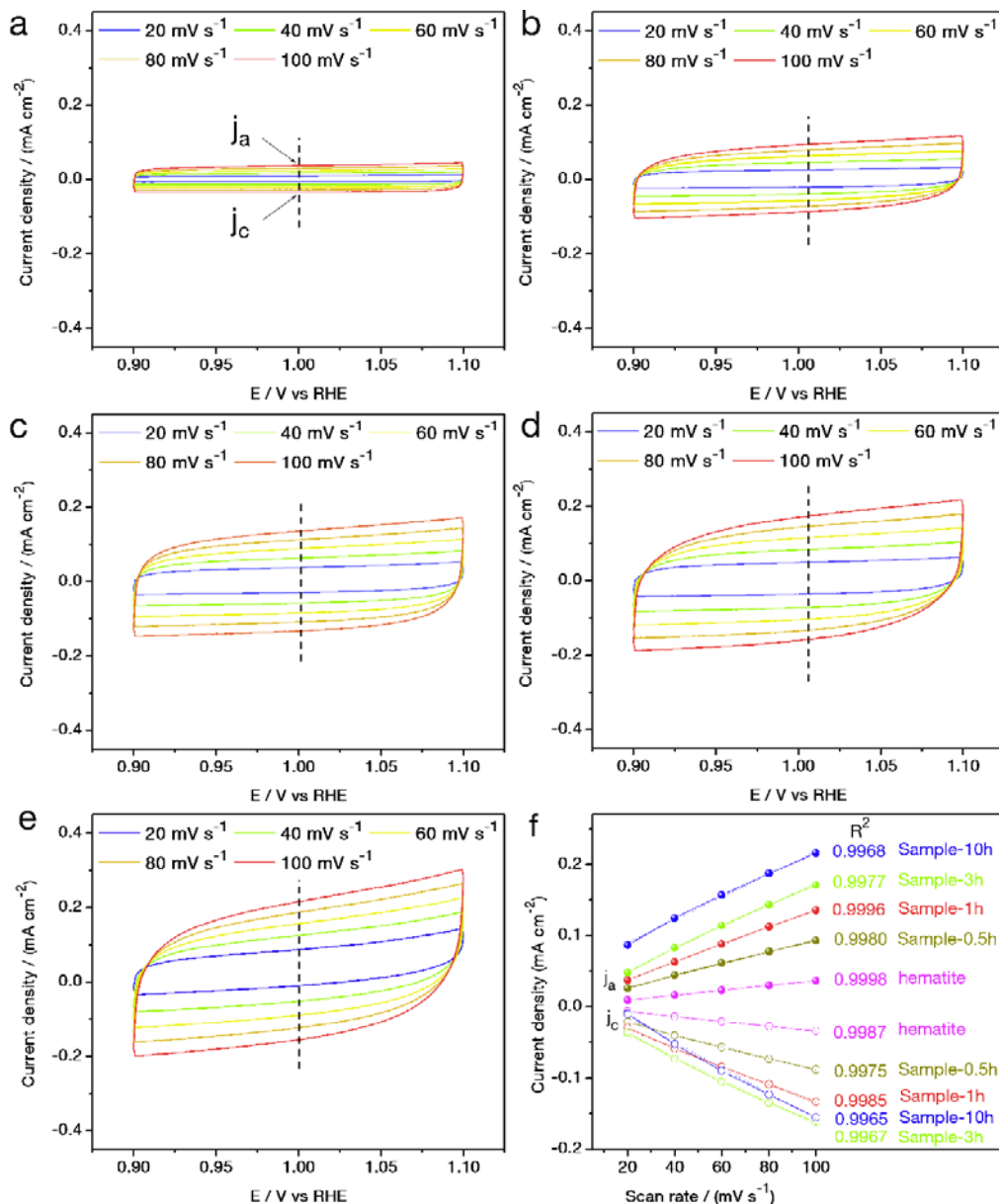
**Figure S1.** CV curves of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  products. Here,  $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  composite corresponds to Sample-1h.



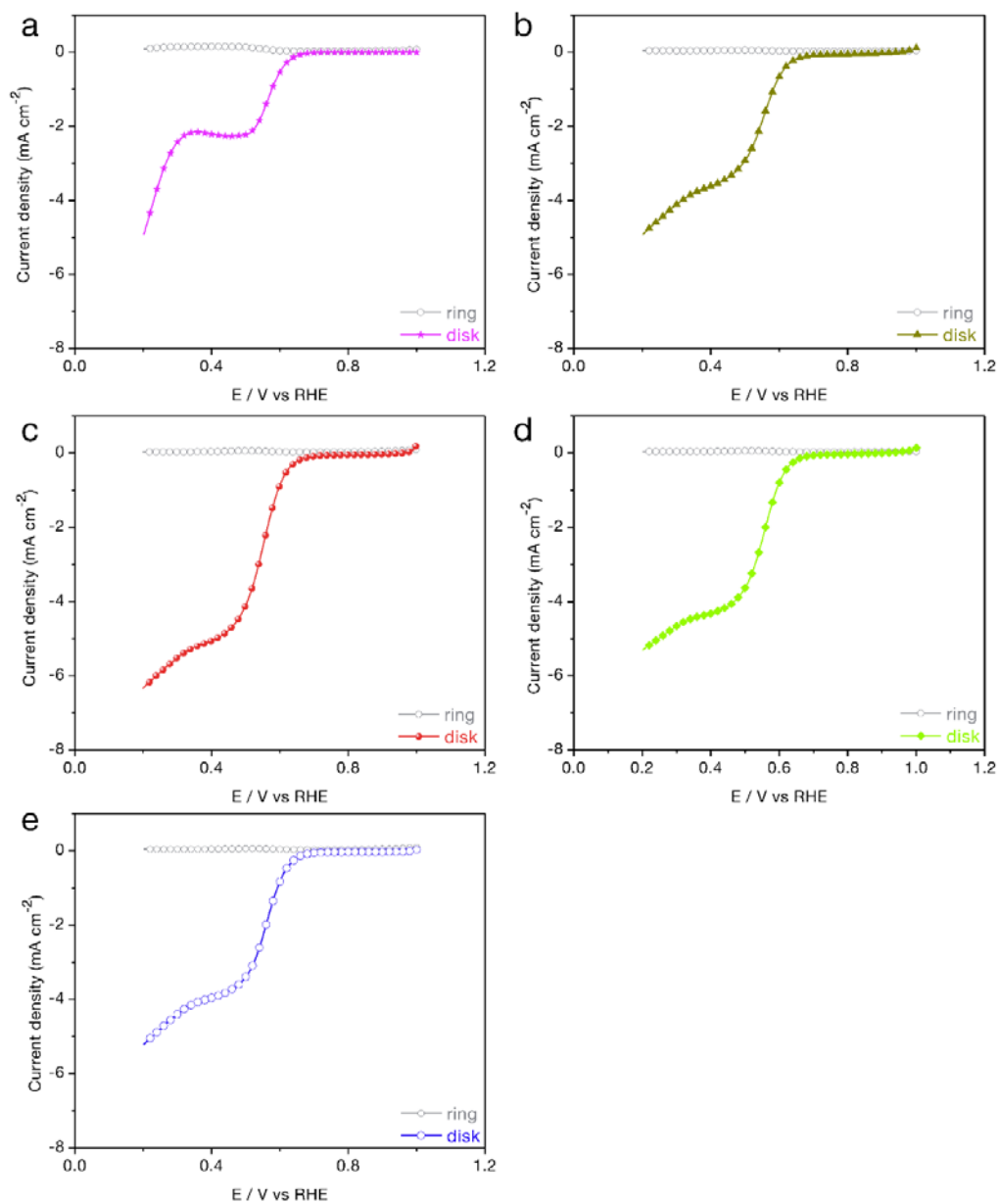
**Figure S2.** Polarization curves in N<sub>2</sub>- or O<sub>2</sub>-saturated KOH electrolyte. (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates, (b) Sample-0.5h, (c) Sample-1h, (d) Sample-3h and (e) Sample-10h.



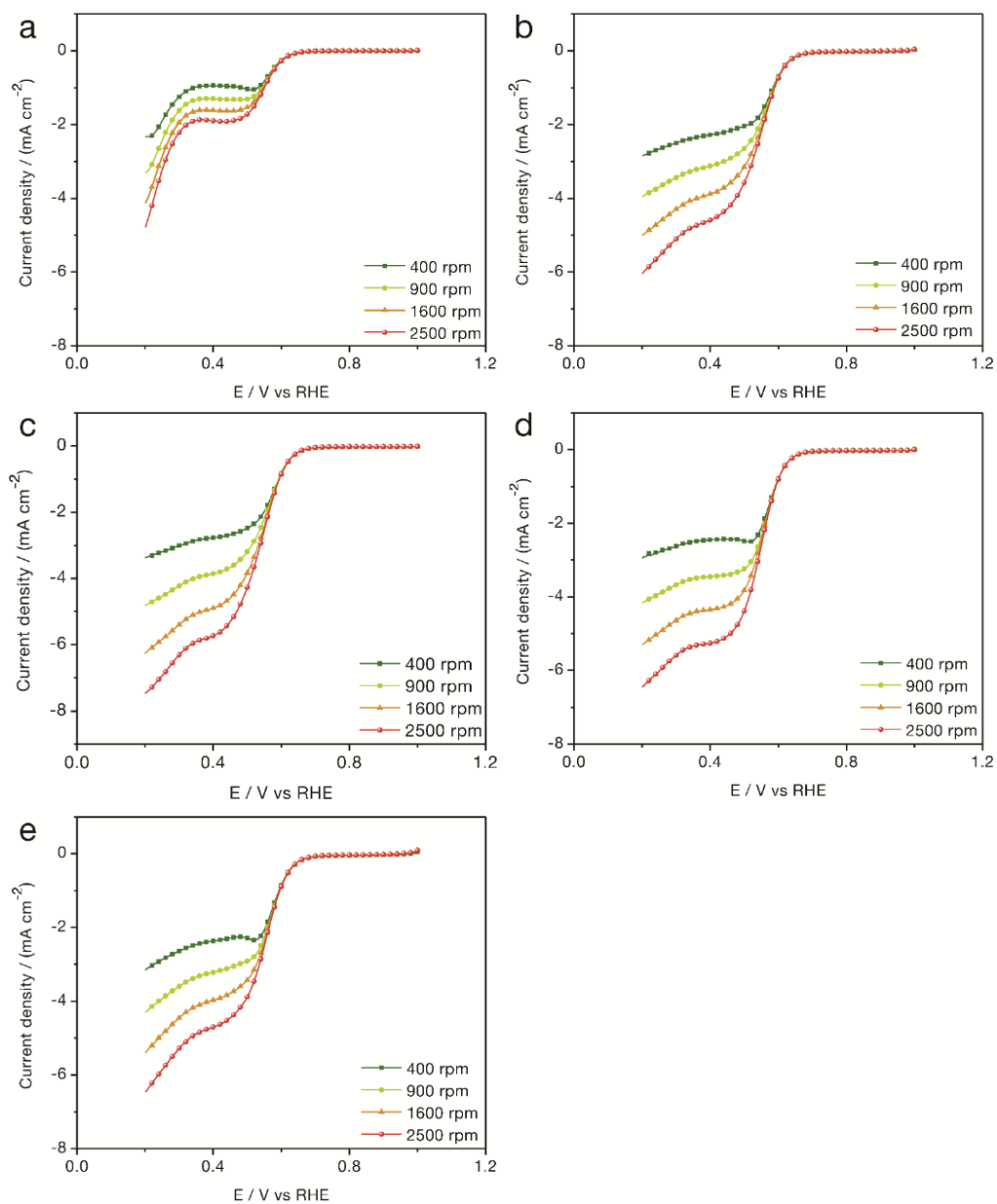
**Figure S3.** The current densities achieved by the as-prepared electrocatalysts at the potential of 0.4 V vs RHE.



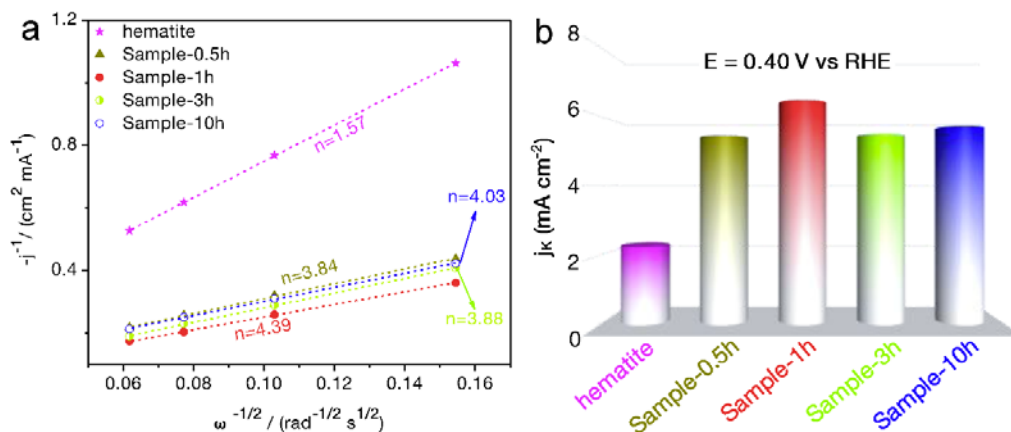
**Figure S4.** CV curves of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates, (b) Sample-0.5h, (c) Sample-1h, (d) Sample-3h and (e) Sample-10h at different scan rates. (f) Anodic and cathodic current densities (denoted as j<sub>a</sub> and j<sub>c</sub>, respectively) of iron oxide samples at the potential of 1.0 V vs RHE as a function of the scan rate. It can be seen that there exists a highly standard linear relationship between the current density and scan rate with all the coefficient of determinations (R<sup>2</sup>) over 0.9965 close to 1, revealing that in such a potential region, all of the iron oxides almost act as an ideal double-layer capacitor.



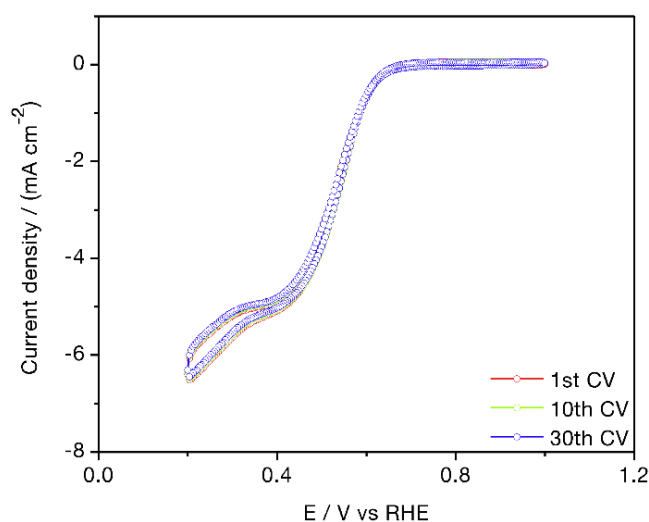
**Figure S5.** Polarization curves tested using RRDE method. (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates, (b) Sample-0.5h, (c) Sample-1h, (d) Sample-3h and (e) Sample-10h.



**Figure S6.** Polarization curves of as-prepared iron oxides tested at different rotating rates. (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates, (b) Sample-0.5h, (c) Sample-1h, (d) Sample-3h and (e) Sample-10h.

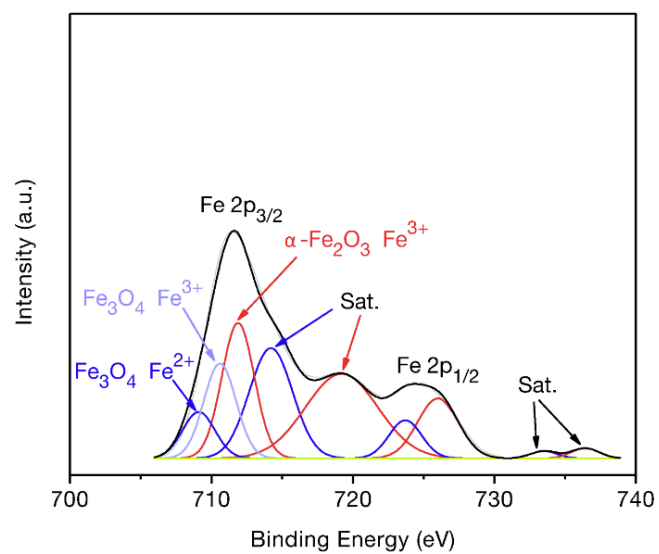


**Figure S7.** (a) Calculated electron transfer number using K-L method and (b)  $j_K$  of as-prepared iron oxide materials. Electron transfer number was estimated as 1.57, 3.84, 4.39, 3.88 and 4.03 for  $\alpha\text{-Fe}_2\text{O}_3$  nanoplates, Sample-0.5h, Sample-1h, Sample-3h and Sample-10h, respectively.

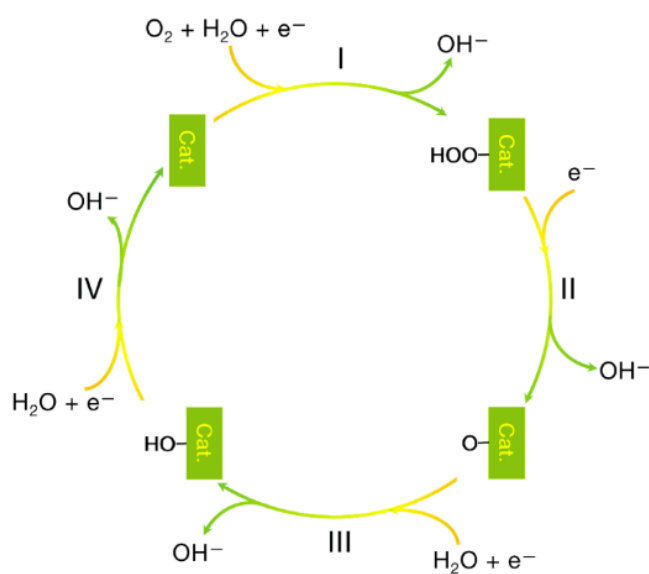


**Figure S8.** The 1st, 10th and 30th CV curves of Sample-1h.

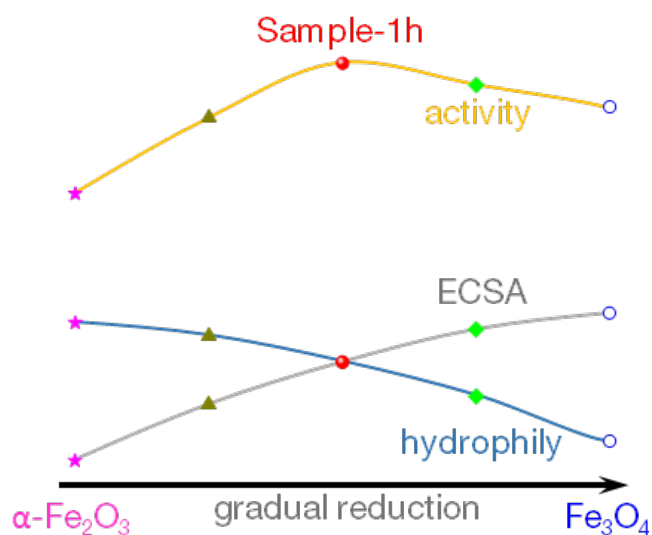




**Figure S9.** Fe 2p region of Sample-1h after a chronoamperometry measurement at 0.60 V vs RHE for 800 s.



**Figure S10.** Electrocatalytic oxygen reduction process of 4-electron pathway.



**Figure S11.** Plausible mechanism for the best performance of Sample-10h.

**Table S1.** Activity comparison of iron oxide materials for electrocatalytic oxygen reduction process in 0.1 M KOH electrolyte.

Materials	j (mA cm <sup>-2</sup> ) @ 0.4 V vs RHE	Tafel slope (mV dec <sup>-1</sup> )	Electron transfer number	Ref.
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	1.62	107	3.19 @ 0.4 V vs RHE	
Sample-0.5h	3.88	89	3.81 @ 0.4 V vs RHE	
Sample-1h	4.90	76	3.89 @ 0.4 V vs RHE	this work
Sample-3h	4.35	81	3.85 @ 0.4 V vs RHE	
Sample-10h	3.97	86	3.83 @ 0.4 V vs RHE	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /CNTs	3.72	–	3.45 @ 0.365 V vs RHE	S1
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Ppy/GO	1.23	–	3.91 @ 0.4 V vs RHE	S2
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /N-doped CNTs	3.82	–	3.37 @ 0.365 V vs RHE	S3

**Table S2.** Fitting parameters of the electronic components in the equivalent circuit as shown in the inset of Figure 6c.

Materials	R <sub>0</sub> (Ω)	R <sub>1</sub> (Ω)	R <sub>2</sub> (Ω)
α-Fe <sub>2</sub> O <sub>3</sub>	66.73	626.8	290.7
Sample-0.5h	70.85	455.6	141.7
Sample-1h	64.44	325.6	140.4
Sample-10h	64.66	392.5	132.2
Sample-10h	65.22	450.8	140.5

## References

- (S1) Sun, M.; Dong, Y.; Zhang, G.; Qu, L.; Li, J. α-Fe<sub>2</sub>O<sub>3</sub> spherical nanocrystals supported on CNTs as efficient non-noble electrocatalysts for the oxygen reduction reaction. *J. Mater. Chem. A* **2014**, 2(33), 13635–13640, DOI: 10.1039/c4ta02172j.
- (S2) Ren, S.; Ma, S.; Yang, Y.; Mao, Q.; Hao, C. Hydrothermal synthesis of Fe<sub>2</sub>O<sub>3</sub>/polypyrrole/graphene oxide composites as highly efficient electrocatalysts for oxygen reduction reaction in alkaline electrolyte. *Electrochim. Acta* **2015**, 178, 179–189, DOI: 10.1016/j.electacta.2015.07.181.
- (S3) Sun, M.; Zhang, G.; Liu, H.; Liu, Y.; Li, J. α- and γ-Fe<sub>2</sub>O<sub>3</sub> nanoparticle/nitrogen doped carbon nanotube catalysts for high-performance oxygen reduction reaction. *Sci. China Mater.* **2015**, 58(9), 683–692, DOI: 10.1007/s40843-015-0082-x.