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-Supporting information-



Figure S1 XPS survey spectrum of MnO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>.



**Figure S2** High-resolution Mn 2p (a) and O 1s (b) spectra and XPS survey spectrum (c) of pure MnO<sub>2</sub>.



Figure S3 High-resolution Fe 2p (a) and XPS survey spectra (b) of pure Fe<sub>2</sub>O<sub>3</sub>.



**Figure S4** (a) LSV curves of pure  $MnO_2$  measured at different rotating rates; (b) Corresponding K-L plots of pure  $MnO_2$  in various potential range (vs. RHE, the inset gives the calculated electron transfer number at various potentials).



**Figure S5** (a) LSV curves of pure  $Fe_2O_3$  measured at different rotating rates; (b) Corresponding K-L plots of pure  $Fe_2O_3$  in various potential range (vs. RHE, the inset gives the calculated electron transfer number at various potentials).



**Figure S6** (a) LSV curves of  $MnO_2/Fe_2O_3$ -400 measured at different rotating rates; (b) Corresponding K-L plots of  $MnO_2/Fe_2O_3$ -400 in various potential range (vs. RHE, the inset gives the calculated electron transfer number at various potentials).



**Figure S7** (a) LSV curves of  $MnO_2/Fe_2O_3$ -600 measured at different rotating rates; (b) Corresponding K-L plots of  $MnO_2/Fe_2O_3$ -600 in various potential range (vs. RHE, the inset gives the calculated electron transfer number at various potentials).



**Figure S8** High-resolution Mn 2p (a) and Fe 2p (b) and O 1s spectra (c) and XPS survey spectrum (d) of  $MnO_2/Fe_2O_3$ -400.



Figure S9 High-resolution Mn 2p (a) and Fe 2p (b) and O 1s spectra (c) and XPS survey spectrum (d) of  $MnO_2/Fe_2O_3$ -600.



**Figure S10** (a) LSV curves of  $MnO_2/Fe_2O_3$ -3.2 measured at different rotating rates; (b) Corresponding K-L plots of  $MnO_2/Fe_2O_3$ -3.2 in various potential range (vs. RHE, the inset gives the calculated electron transfer number at various potentials).



**Figure S11** (a) LSV curves of  $MnO_2/Fe_2O_3-1.7$  measured at different rotating rates; (b) Corresponding K-L plots of  $MnO_2/Fe_2O_3-1.7$  in various potential range (vs. RHE, the inset gives the calculated electron transfer number at various potentials).



Figure S12 Current-time chronoamperometric responses of  $MnO_2/Fe_2O_3/N$ ,P-C and Pt/C.



Figure S13 FTIR spectrum of MnO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>/PANI.





Figure S15 (a) CV curves of  $MnO_2/Fe_2O_3/N$ ,P-C in  $N_2$  and  $O_2$  saturated 0.1 M KOH.



**Figure S16** XPS survey spectrum (a) and high-resolution Mn 2p (b), Fe 2p (c), O 1s (d), C 1s (e), N 1s (f) and P 2p (g) spectra of  $MnO_2/Fe_2O_3/N$ ,P-C.