Electronic Supplementary Information

Raisin Bread-like Iron Sulfides/Nitrogen and Sulfur Dual-doped Mesoporous Graphitic Carbon Spheres: A Promising Electrocatalyst for the Oxygen Reduction Reaction in Alkaline and Acidic Media

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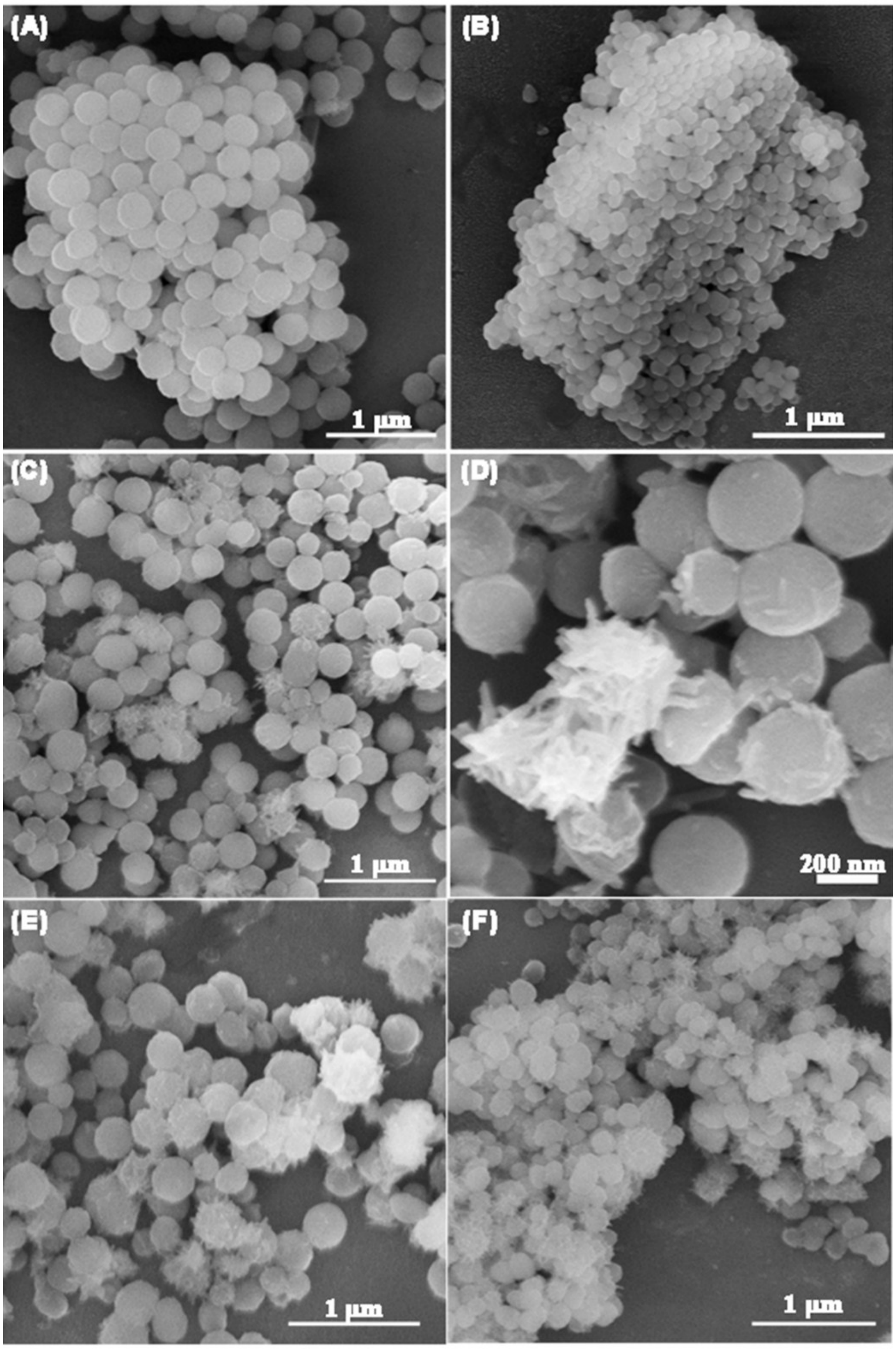

Figure S1. SEM images of (A) $(Fe^{2+}\text{-PDA})_{0.1}$, (B) $(Fe^{2+}\text{-PDA})_{0.2}$, (C, D) $(Fe^{2+}\text{-PDA})_{0.3}$, (E) $(Fe^{2+}\text{-PDA})_{0.4}$, and (F) $(Fe^{2+}\text{-PDA})_{0.5}$.

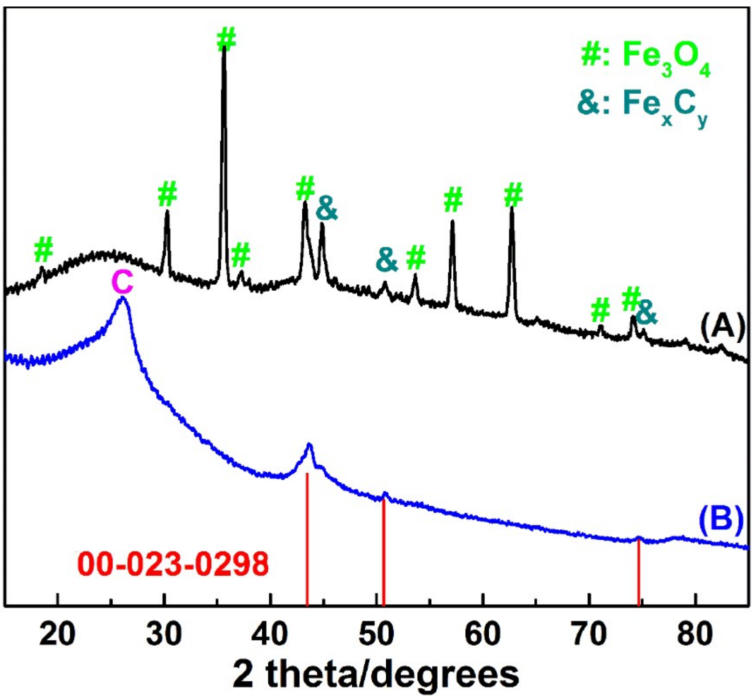

Figure S2. XRD patterns of (A) (Fe_3O_4/Fe_xC_y/N-GCS)$_{0.2}$ and (B) (Fe_xC_y/N-MGCS)$_{0.2}$, of which the diffraction peaks are in accordance with the standard patterns of Fe_3O_4 (JCPDS 00-001-1111) and Fe_xC_y (JCPDS 00-023-0298).

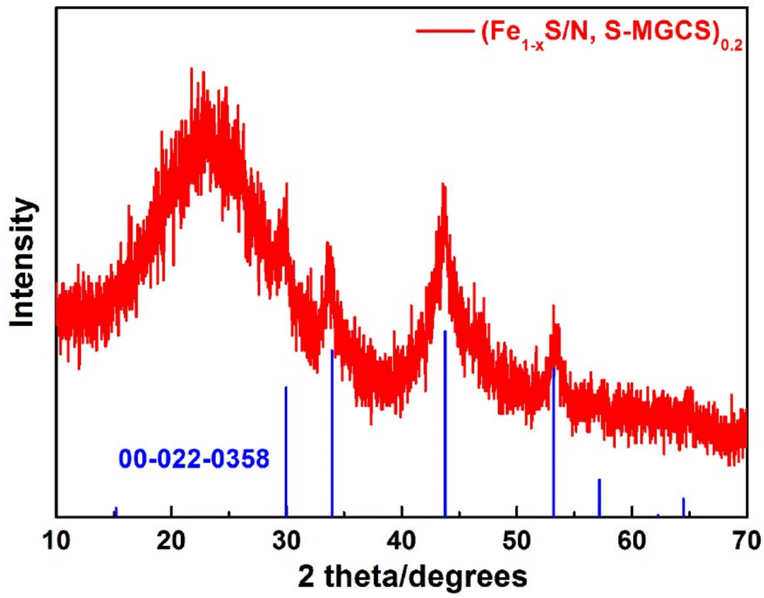

Figure S3. XRD patterns of $(Fe_{1-x}S/N, S\text{-}MGCS)_{0.2}$ pyrolyzed from $(Fe_xC_y/N\text{-}MGCS)_{0.2}$ in the presence of thiourea, of which the diffraction peaks are in consistent with the standard pattern of $Fe_{1-x}S$ (JCPDS: 00-022-0358).

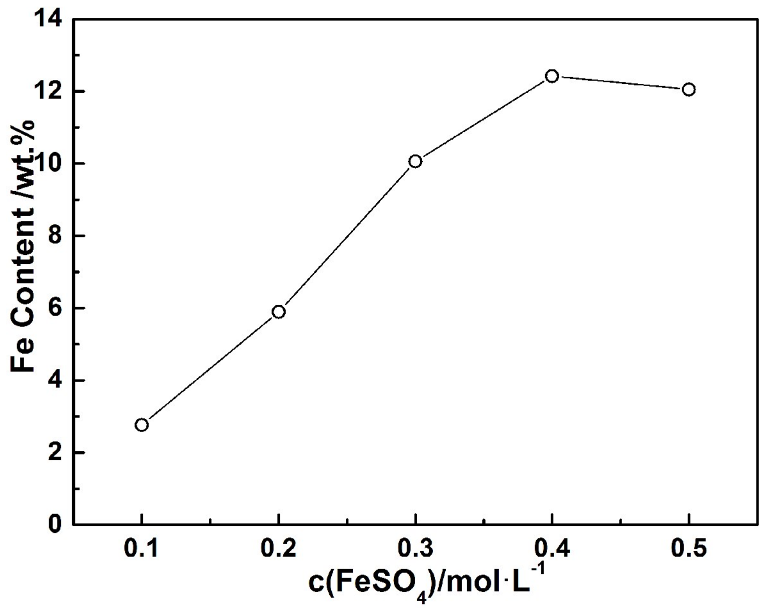

Figure S4. The iron contents in the $Fe_{1-x}S$/N, S-MGCS determined by MP-AES.

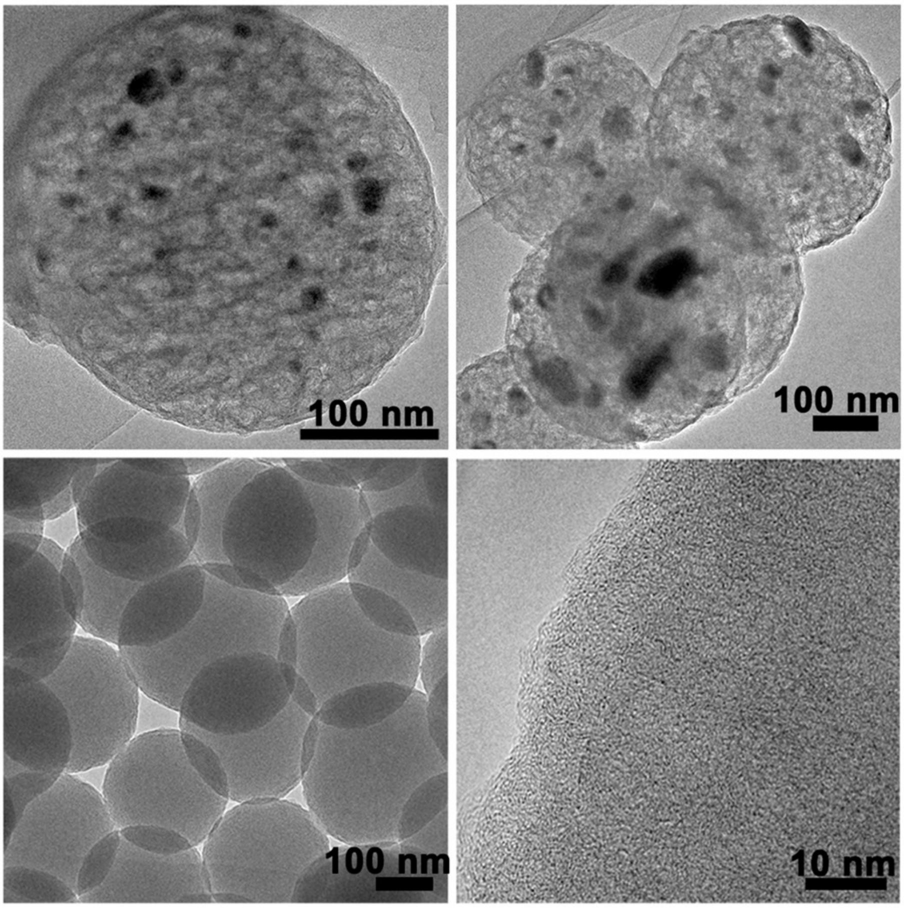

Figure S5. TEM images of (A) ($Fe_{1-x}S$/N, S-MGCS)$_{0.3}$, (B) ($Fe_{1-x}S$/N, S-MGCS)$_{0.4}$ and (C, D) N, S-CS.

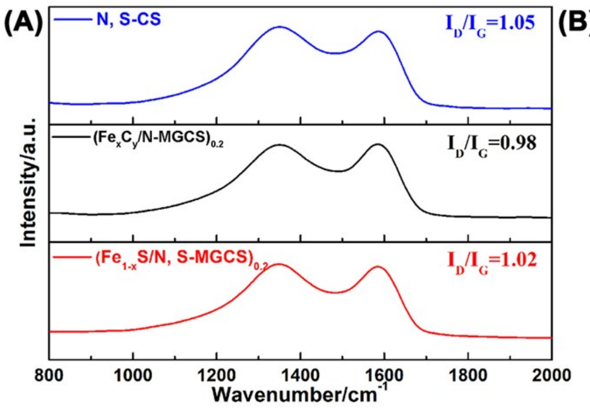

Figure S6. Raman spectra of (A) N, S-CS, $(Fe_xC_y/N\text{-}MGCS)_{0.2}$ and $(Fe_{1-x}S/N, S\text{-}MGCS)_{0.2}$ in the wavenumber region of 800 ~ 2000 cm^{-1}, and (B) $(Fe_{1-x}S/N, S\text{-}MGCS)_{0.2}$ in the wavenumber region of 150 ~ 650 cm^{-1}.

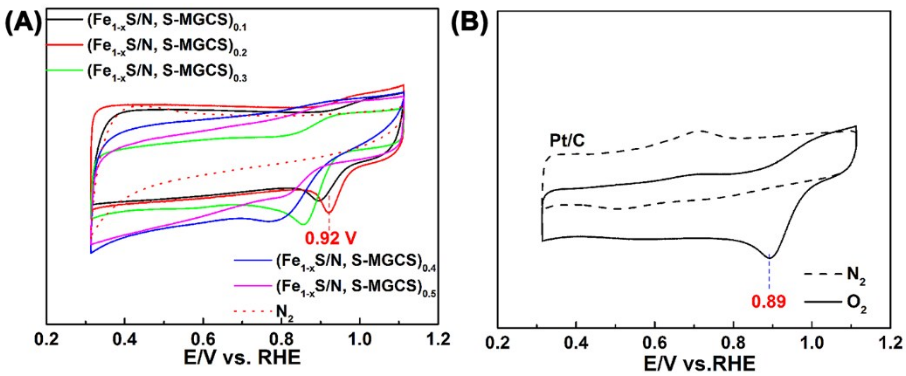

Figure S7. (A) CV curves of (A) the ($Fe_{1-x}S$/N, S-MGCS)$_{0.1\sim0.5}$ and (B) commercial Pt/C catalysts in N_2-saturated (dash line) or O_2-saturated (solid line) 0.1 M KOH at a scan rate of 10 mV s^{-1}.

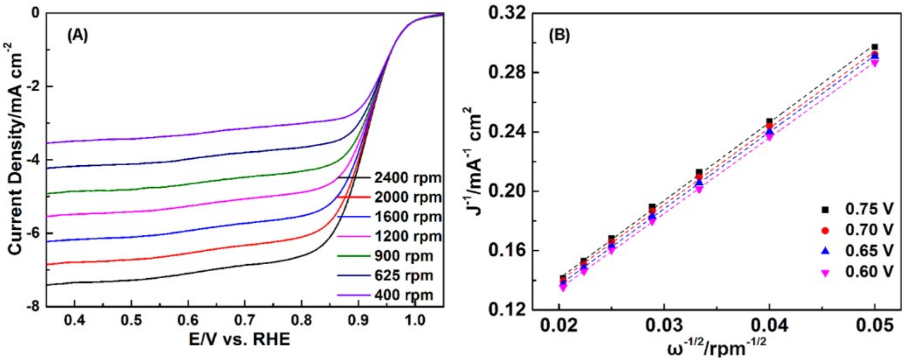

Figure S8. (A) Linear scan voltammogram (LSVs) curves of (Fe_{1-x}S/N, S-MGCS)$_{0.2}$ in O_2-saturated 0.1 M KOH at the rotating rates of 2400 ~ 400 rpm and a scan rate of 5 mV s^{-1}, and (B) corresponding Koutecky-Levich plots (J^{-1} versus $\omega^{-1/2}$) at the potentials of 0.75 ~ 0.60 V versus RHE.

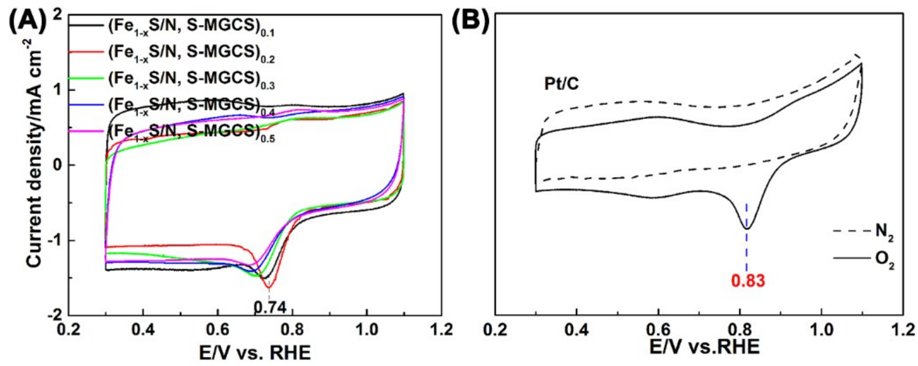

Figure S9. CV curves of (A) the (Fe$_{1-x}$S/N, S-MGCS)$_{0.1\sim0.5}$ and (B) commercial Pt/C catalysts in N_2 (dash line) or O_2 (solid line) saturated-0.1 M $HClO_4$ solution with a scan rate of 10 mV s^{-1}.

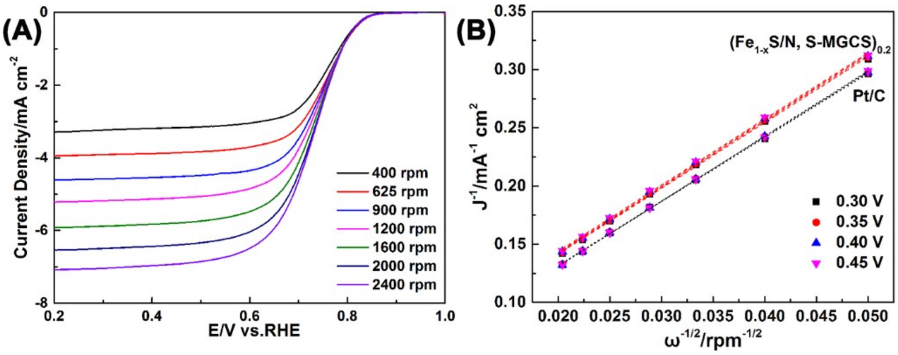

Figure S10. (A) Linear scan voltammograms (LSVs) of the ($Fe_{1-x}S$/N, S-MGCS)$_{0.2}$ in O_2-saturated 0.1 M $HClO_4$ at the rotating rates of 2400 ~ 400 rpm, and (B) corresponding Koutecky-Levich plots (J^{-1} versus $\omega^{-1/2}$) in the potential range of 0.30-0.45 V versus RHE.

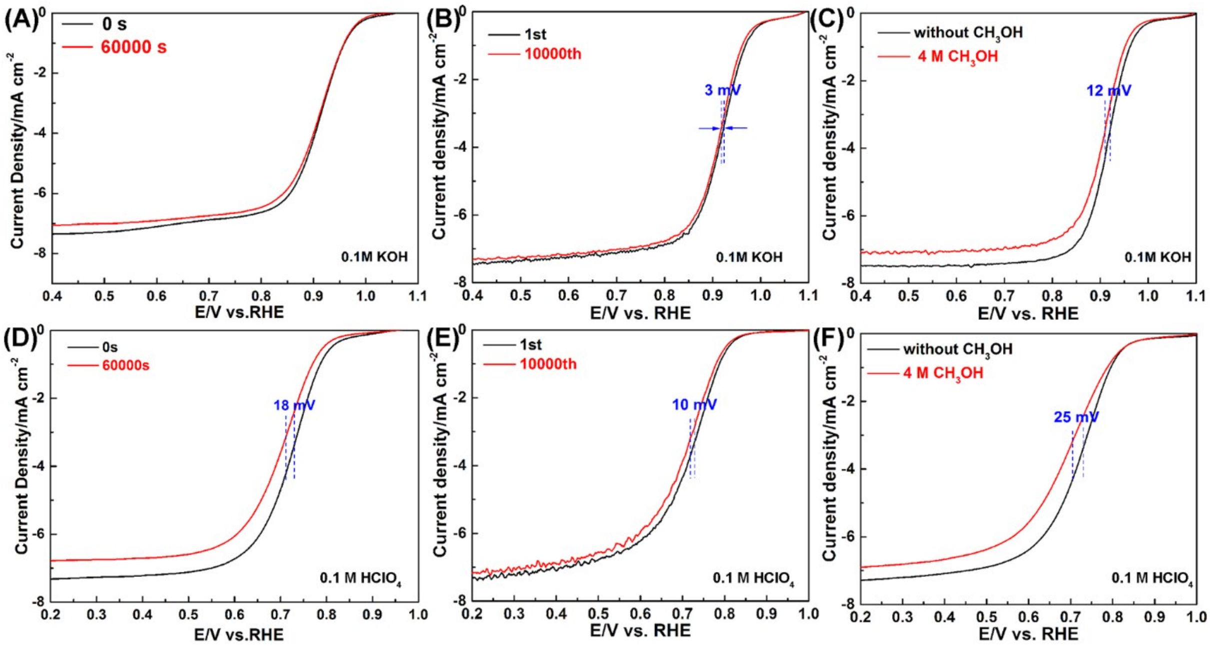

Figure S11. (A, D) The ORR polarization curves of ($Fe_{1-x}S$/N, S-MGCS)$_{0.2}$ in O_2-saturated 0.1 M KOH solution at 2400 rpm after 60000 s continuous operation at a constant cathode potential. (B, E) The ORR polarization curves of ($Fe_{1-x}S$/N, S-MGCS)$_{0.2}$ in O_2-saturated 0.1 M KOH solution at 2400 rpm after 10000 repetitive cycles. (C, F) The ORR polarization curves of ($Fe_{1-x}S$/N, S-MGCS)$_{0.2}$ in O_2-saturated 0.1 M KOH solution at 2400 rpm before and after the addition of 4.0 M methanol.

Table S1. Comparison of the onset potential (E_{onset} vs. RHE), half-wave potential ($E_{1/2}$ vs. RHE), diffusion-limited current density (mA cm^{-2}) of the Pt/C, N, S-CS, ($Fe_{1-x}S$/N, S-MGCS)$_{0.1\sim0.5}$, and as-reported NPMCs in O_2-saturated 0.1 M KOH electrolyte with a rotating speed of 1600 rpm.

Catalysts	E_{onset}/V	$E_{1/2}$/V	Current density	Ref.
Pt/C	0.93	0.87	~ 5.1 at 0.40 V	This work
N, S-CNS	0.89	0.81	~ 5.1 at 0.40 V	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.1}$	0.95	0.89	~ 5.4 at 0.40 V	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.2}$	0.97	0.91	~ 6.2 at 0.40 V	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.3}$	0.92	0.85	~ 5.3 at 0.40 V	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.4}$	0.90	0.80	~ 5.1 at 0.40 V	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.5}$	0.88	0.78	~ 4.2 at 0.40 V	This work
N, S-Fe/N/C-CNT	/	0.85	~ 6.7 at 0.20 V	Angew. Chem. Int. Ed. 2017, 56, 610
Co-TA-800	0.95	0.83	~ 4.4 at 0.30 V	Angew. Chem. Int. Ed. 2016, 55, 12470
Co SAs/N-C(900)	0.98	0.88	~ 5.6 at 0.40 V	Angew. Chem. Int. Ed. 2016, 55, 10800
FP-Fe-TA-N-850	0.98	0.83	~ 5.0 at 0.60 V	Angew. Chem. Int. Ed. 2016, 55, 1355
Fe-N/C-800	0.92	0.81	~ 6.1 at 0.40 V	J. Am. Chem. Soc. 2014, 136, 11027
Fe_3C/NG-800	1.03	0.86	~ 5.8 at 0.40 V	Adv. Mater. 2015, 27, 2521
Fe/Fe_3C@C	0.91	0.83	/	Adv. Energy Mater. 2014, 4, 1400337
Fe-NMCSs	1.03	0.86	~ 5.2 at 0.40 V	Adv. Mater. 2016, 28, 7948
N, P-CGHNs	0.94	0.82	/	Adv. Mater. 2016, 28, 4606
FeCo/C-800	1.00	0.85	~ 5.3 at 0.40 V	Adv. Mater. 2015, 27, 3431
Fe_3C/C-700	1.05	0.83	/	Angew. Chem. Int. Ed. 2014, 53, 3675
Fe-N-GC-900	1.01	0.86	~ 5.2 at 0.40 V	ACS Catal. 2014, 4, 1793

Table S2. Comparison of the onset potential (E_{onset} vs. RHE), half-wave potential ($E_{1/2}$ vs. RHE), and the difference between $E_{1/2,\ Pt/C}$ and $E_{1/2,\ catalysts}$ (ΔE) for the Pt/C, N, S-CS, ($Fe_{1-x}S$/N, S-MGCS)$_{0.1\sim0.5}$, and as-reported NPMCs in O_2-saturated 0.1 M $HClO_4$ electrolyte with a rotating speed of 1600 rpm.

Catalysts	E_{onset}/V	$E_{1/2}$/V	ΔE/mV	Ref.
Pt/C	0.90	0.81	/	This work
N, S-CNS	0.70	0.56	~ 250	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.1}$	0.80	0.71	~ 100	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.2}$	0.81	0.73	~ 80	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.3}$	0.80	0.70	~ 110	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.4}$	0.79	0.69	~ 120	This work
($Fe_{1-x}S$/N, S-MCNS)$_{0.5}$	0.77	0.67	~ 140	This work
Fe_3C/C-700	0.90	0.73	~ 100	Angew. Chem. Int. Ed. 2014, 53, 3675
Fe_3C/NG-800	0.90	0.77	~ 100	Adv. Mater. 2015, 27, 2521
PpPD-Fe-C	0.826	0.718	~ 89	Angew. Chem. Int. Ed. 2014, 53, 10673
N, P-CGHNs	0.90	0.68	~ 70	Adv. Mater. 2016, 28, 4606
FeCo/C-800	0.88	0.74	/	Adv. Mater. 2015, 27, 3431
Fe-N-GC-900	/	0.71	~ 70	ACS Catal. 2014, 4, 1793
Fe-NMCSs	/	/	~ 59	Adv. Mater. 2016, 28, 7948