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Electronic Supplementary Information

Co^{II}-catalyzed room-temperature growth of MnO_2 on the skeleton of carbonized zeolitic imidazolate framework-67 crystals for boosting oxygen reduction reaction

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Koutecky-Levich equation:

$$\frac{1}{j}=\frac{1}{j_L}+\frac{1}{j_K}=\frac{1}{B\omega^{0.5}}+\frac{1}{j_K}$$

$$B=0.2nFc_0D_0^{2/3}\nu^{-1/6}$$

where j is the measured current density, j_K is the kinetic current density, j_L is the diffusion limiting current density, ω is electrode rotation rate, n is transferred electron number, F is the Faraday constant (96485 $C\cdot mol^{-1}$), c_0 is the bulk concentration of O_2 (1.2×10^{-6} $mol\cdot cm^{-3}$ for 0.10 mol/L KOH), D_0 is the diffusion coefficient of O_2 (1.9×10^{-5} $cm^2\cdot s^{-1}$ in 0.10 mol/L KOH), and ν is the kinematic viscosity of the electrolyte (0.010 $cm^2\cdot s^{-1}$ for 0.10 mol/L KOH solution).

In the RRDE experiments, the apparent number of electrons transferred during ORR and H_2O_2 yield were calculated from the following equation:

$$H_2O_2(\%)=200\times\frac{\frac{j_R}{N}}{\frac{j_R}{N}+j_D}$$

$$n=\frac{4j_D}{\frac{j_R}{N}+j_D}$$

where j_D is the current density at the disk, j_R is the current density at the ring, and N is the collection coefficient of H_2O_2 at the ring (~0.25).

Supplementary Figures, Captions and Tables

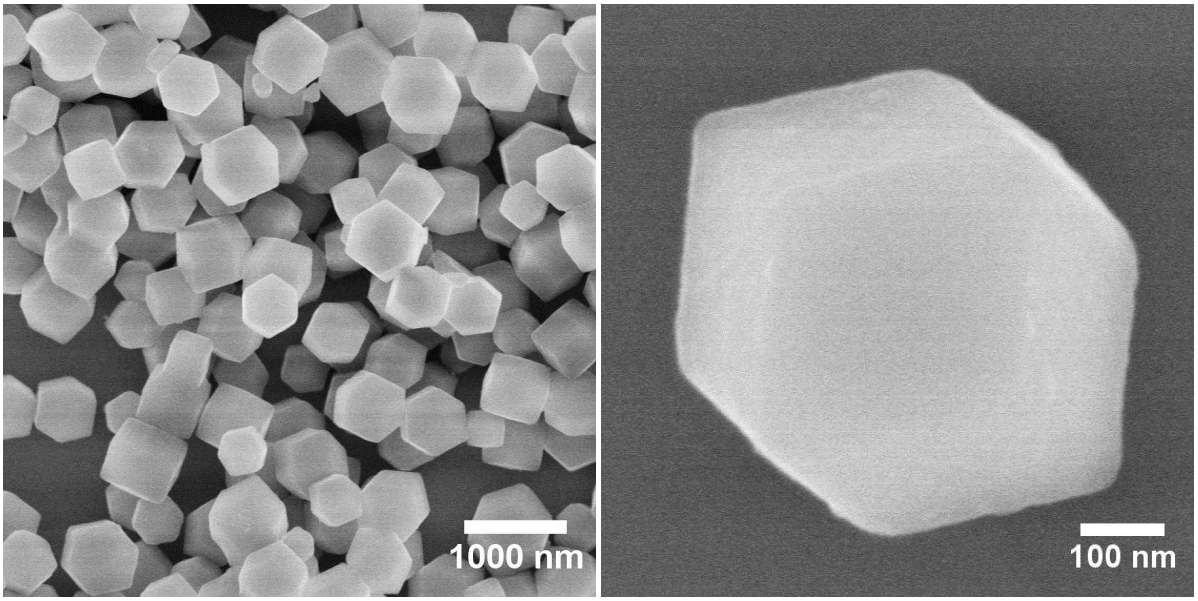

Figure S1. SEM images of ZIF-67 crystals with different magnifications.

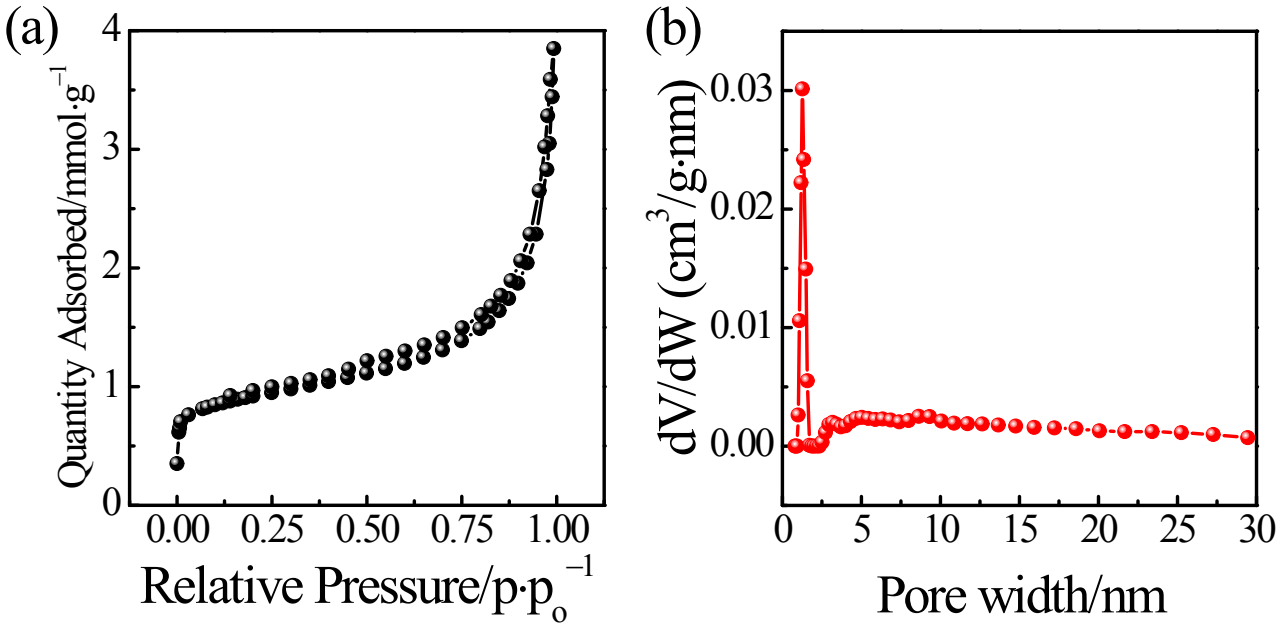

Figure S2. (a) N_2 adsorption-desorption Brunauer-Emmett-Teller isotherms and (b) pore size distribution of $MnO_2/C_{ZIF\text{-}67}$.

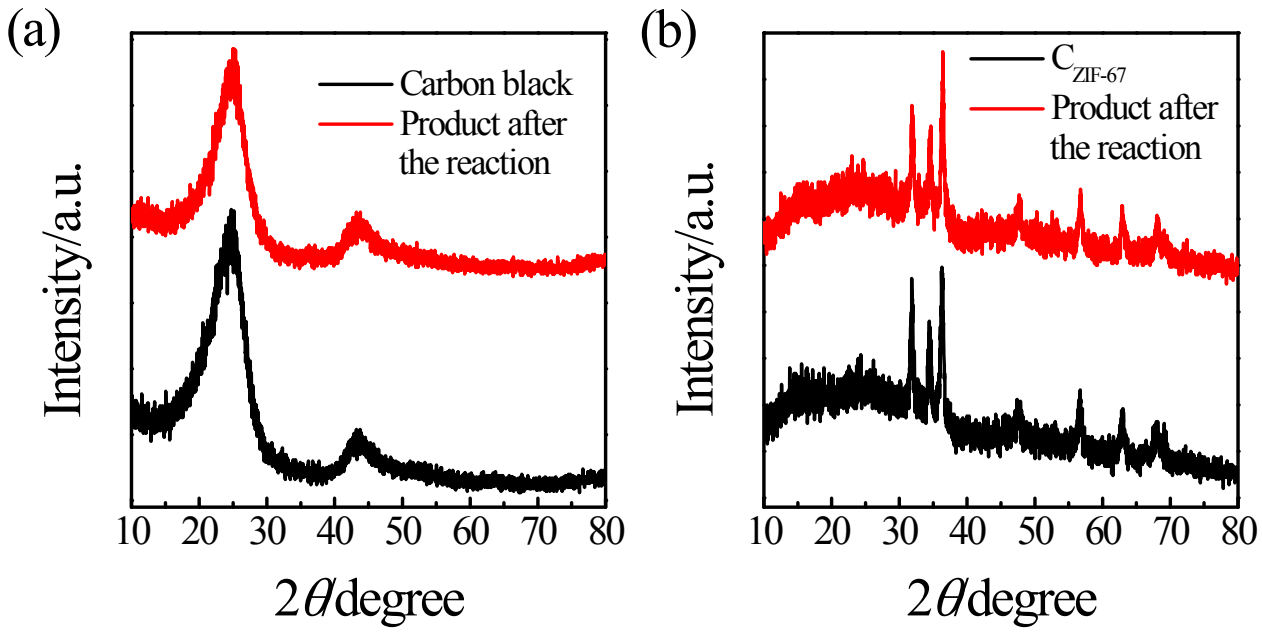

Figure S3. XRD patterns of carbon black (a), C_{ZIF-8} (b) and products obtained after 12-h reaction between $KMnO_4$ and carbon black (a), and between $KMnO_4$ and C_{ZIF-8} (b).

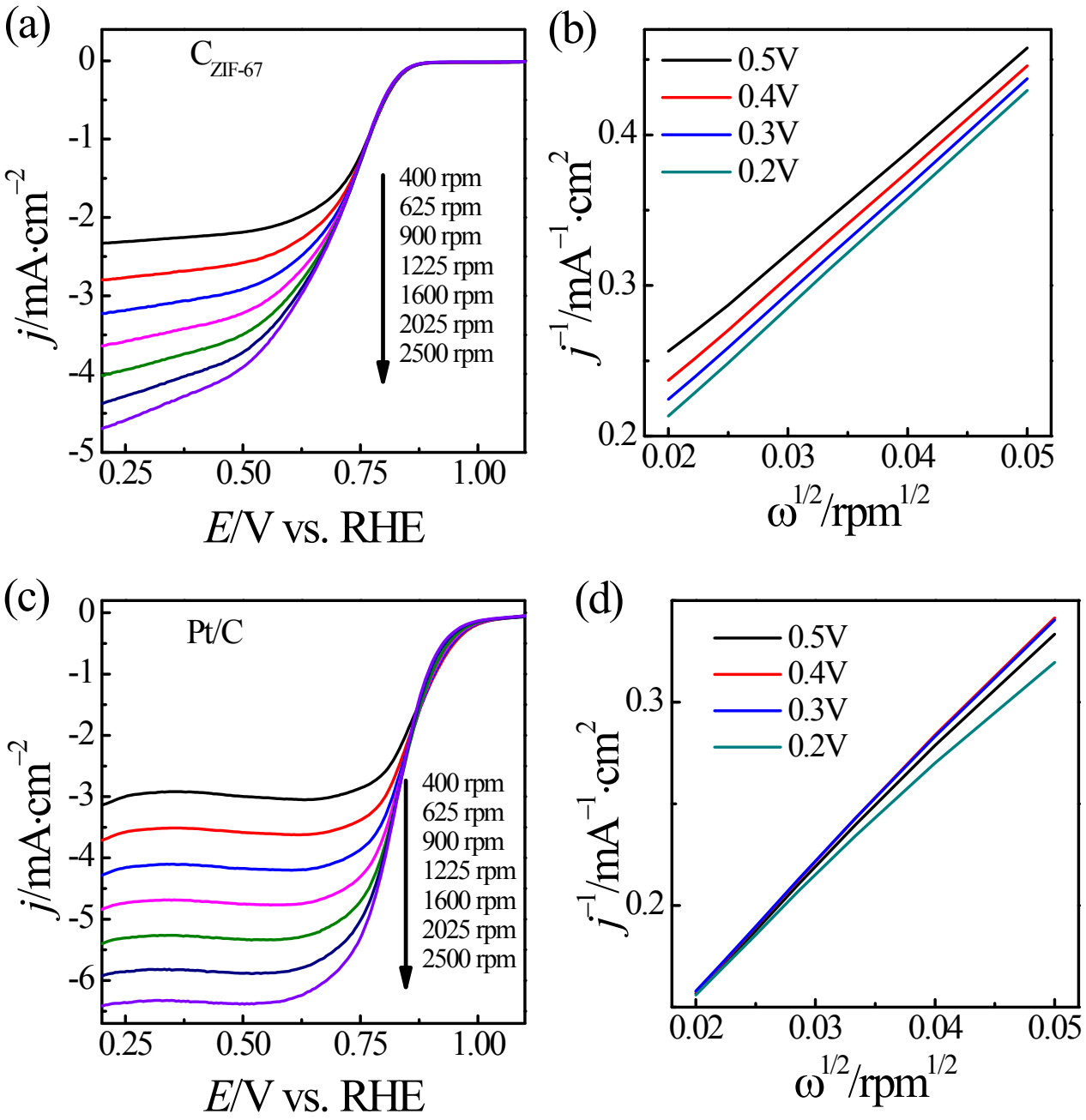

Figure S4. Linear sweep votammograms of C_{ZIF-67} (a) and Pt/C (c) in O_2-saturated 0.10 mol/L KOH solution at different rotating speeds with a scan rate of 5 mV·s^{-1}. K–L plots of C_{ZIF-67} (b) and Pt/C (d) in the potential range from 0.20 V to 1.10 V

Table S1. Summary of electrochemical parameters of ORR on MnO_2 materials reported previously and the results in this work.

Sample	Onset potential/V vs. RHE	Half-wave potential/V	Measured current/mA·cm^{-2}	*n*	Reference
C_{ZIF-67}	0.80	0.67	–3.98[a]	3.23	This work
MnO_2/C_{ZIF-67}	0.88	0.79	–5.92[a]	3.66	This work
Pt/C	0.97	0.82	–5.40[a]	3.89	This work
Ag-MnO_2/carbon nanotube	0.73	0.57	--	3.82	[1]
α-MnO_2 nanoflake	~0.8	--	~5.0[a]	~4	[2]
α-MnO_2	0.76	--	~4.8[a]	4.2	[3]
α-MnO_2	0.75	--	~4.2[a]	3.7	[3]
β-MnO_2	0.52	--	~3.4[a]	2.4	[3]
δ-MnO_2	0.56	--	~3.2[a]	1.7	[3]
ε-MnO_2/C	0.84	0.79	4.0[b]	3.8	[4]

[a]Limiting current at the rotating speed of 1600 rpm.

[b]Limiting current at the rotating speed of 2500 rpm.

Reference

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