

Supplementary information

Table S1 Surface Areas, Pore Sizes, and Pore Volumes of the MnO₂ samples

Samples	Surface area [*] (m ² g ⁻¹)	Average pore diameter(nm)	Pore volume(cm ³ g ⁻¹)
	1)	**	***
α-MnO ₂	78.3	7.11	0.122
γ-MnO ₂	70.7	6.75	0.104

Noted: * the surface area is based on the BET method.

** the pore diameter is based on the BJH desorption average pore diameter

*** the pore volume is based on the BJH desorption cumulative volume of pores

Table S2 Some recently reported MnO₂ catalysts for ORR

Samples	E_{onset} (V)	E_{half} (V)	Ref
α -MnO ₂ 3D microscopic spheres	0.85	0.72	This work
α -MnO ₂ nanorods	0.89	0.71	[1]
Cu- α -MnO ₂ NWs	0.85	0.71	[2]
β -MnO ₂ nanorods with vacancies	0.86	0.72	[3]
α -MnO ₂ nanoparticles	0.71	0.57	[4]
α -MnO ₂ NWs	0.89	0.64	[5]
MnO ₂ nanoflakes	0.82	0.67	[6]

Reference:

- 1) W. Xiao, D. Wang and X. W. Lou, *J. Phys. Chem. C*, 2010, **114**, 1694.
- 2) D. J. Davis, T. N. Lambert, J. A. Vigil, M. A. Rodriguez, M. T. Brumbach, E. N. Coker and S. J. Limmer, *J. Phys. Chem. C*, 2014, **118**, 17342.
- 3) F. Cheng, T. Zhang, Y. Zhang, J. Du, X. Han and J. Chen, *Angew. Chem., Int. Ed.*, 2013, **52**, 2474.
- 4) C. Shi, G.-L. Zang, Z. Zhang, G.-P. Sheng, Y.-X. Huang, G.-X. Zhao, X.-K. Wang and H.-Q. Yu, *Electrochim. Acta*, 2014, **132**, 239.
- 5) K. Selvakumar, S. M. Senthil Kumar, R. Thangamuthu, K. Ganesan, P. Murugan, P. Rajput, S. N. Jha and D. Bhattacharyya, *J. Phys. Chem. C*, 2015, **119**, 6604.
- 6) C. Wei, L. Yu, C. Cui, J. Lin, C. Wei, N. Mathews, F. Huo, T. Sritharan and Z. Xu, *Chem. Commun.*, 2014, **50**, 7885.

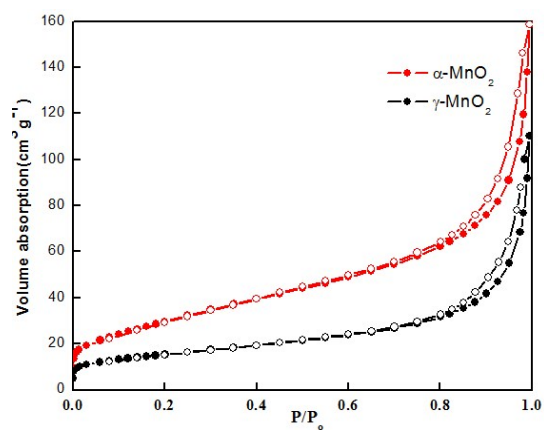


Fig. S1 Nitrogen adsorption-desorption isotherms of MnO₂ samples

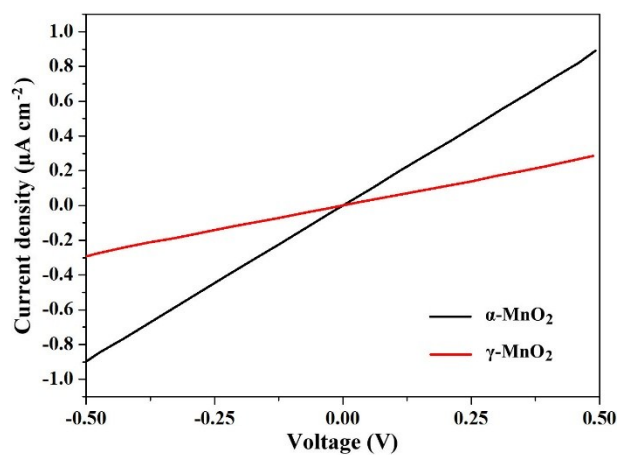


Fig. S2 Comparison of the I-V curves of the two MnO₂ samples.

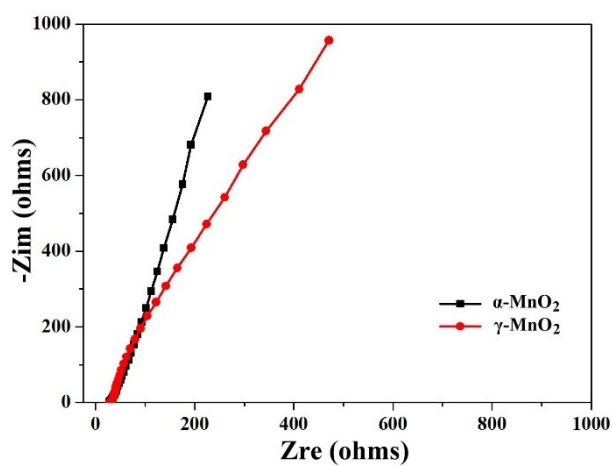


Fig. S3 Nyquist plots of EIS for the ORR at 0.7 V in O₂ saturated 0.1 M KOH.