Electronic Supplementary Information

$ZnMn_2O_4$ Nanorods: An Effective Fenton-like Heterogeneous Catalyst with $t_{2g}^3 e_g^1$ Electronic Configuration

Maoqin Qiu, [a] Zhangxian Chen,*[a] Zeheng Yang,*[a] Wenming Li, [a] Yuan Tian, [a] Weixin Zhang,*[a] Yishu Xu [a] and Hansong Cheng [b]

a School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei, China 230009

b Sustainable Energy Laboratory, Faculty of Material Science and Chemistry, China University of Geosciences (Wuhan), 388 Lumo Road, Wuhan, China 430074

Corresponding authors: Tel.:+86 0551 62901450; fax:+86 0551 62901450. Email address: zehengyang@hfut.edu.cn (Z.H. Yang); zxchen@hfut.edu.cn (Z.X. Chen); wxzhang@hfut.edu.cn (W.X. Zhang)

EXPERIMENTAL AND COMPUTIONAL DETAILS

Characterizations

The crystal phases of the samples were determined by X-ray diffraction (XRD) on a Rigaku D/max-γB X-ray diffractometer (Cu Kα source, λ= 0.154178 nm), operating at 40 kV and 80 mA. Morphologies and structures were characterized by field-emission scanning electron microscopy (FESEM, Hitachi SU8020). The Raman spectra were recorded on a LabRam HR Evolution (HORIBA, France) equipped with a CCD detector using a laser source (λ_{ex} = 633 nm) at room temperature. N_2 adsorption-desorption isotherms were collected on a Quantachrome NOVA 2200e surface area and pore size analyzer at liquid nitrogen temperature. All samples were degassed at 120 °C for 2 h prior to the measurements. The specific surface area and the average pore diameter were calculated by the multi-point Brunauer-Emmett-Teller

(BET) equation and the Barrett-Joyner-Halenda (BJH) method, respectively.

Computational Details

Periodic density functional theory computations were performed using VASP code implemented with the projector augmented wave method to describe the electron-ion interactions.[1-4] The exchange-correlation potential was expressed using the Perdew-Burke-Ernzerhof functional incorporated in the generalized gradient approximation.[5] The Hubbard U correction for Mn 3d orbitals was applied to include the strong on-site Coulomb interaction.[6] A U-J value of 5 eV was found to be sufficient to give reasonable lattice constants and minority spin band gap of about 2.9 eV, in consistence with the reported work.[7] The geometric structures were optimized with the convergence criteria of total energy less than 10^{-5} eV and total force less than 0.01 eV/Å on each atom. The Brillouin zone was sampled using the Monkhorst-Pack k-point meshes of 7×7×5 for structural optimization and 13×13×9 for static calculation. The semi core 3p states of Mn were also treated as valence states.

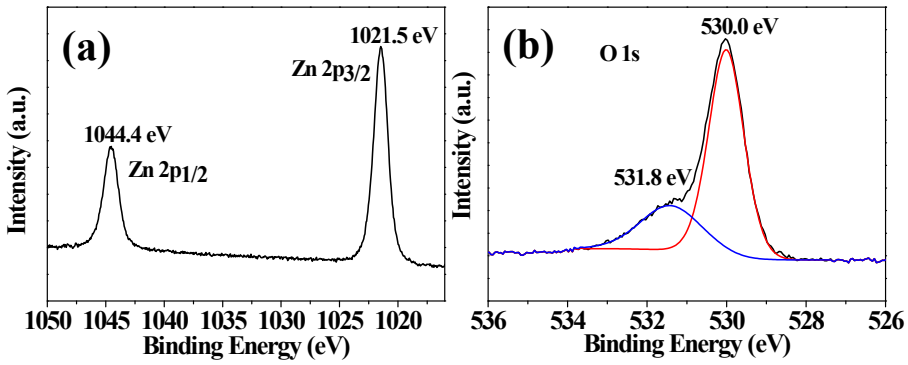

Fig. S1 XPS spectra of $ZnMnO_3$ nanorods: (a) Zn 2p; (b) O 1s.

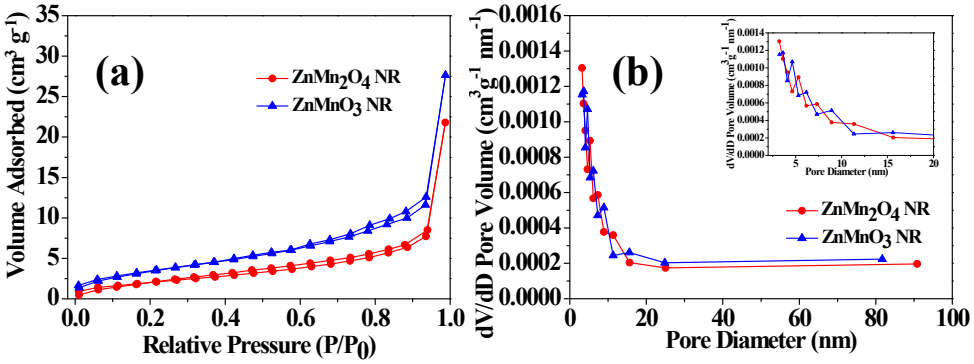

Fig. S2 (a) N_2 absorption-desorption isothermal curves and (b) the corresponding pore size distributions of different catalysts.

Table S1 The specific surface area and average pore size of as-prepared catalysts.

Sample	Specific Surface Area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})
$ZnMn_2O_4$ nanorods	17.3	0.22
$ZnMnO_3$ nanorods	10.6	0.11

References

1 G. Kresse, J. Furthmüller, *Comp. Mater. Sci.*, 1996, **6**, 15-50.

2 G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.

3 P.E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.

4 G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.

5 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

6 S. L. Dudarev, G. A. Botton, S. Y. Savrasov and C. J. Humphreys, *Phys. Rev. B*, 1998, **57**, 1505-1509.

7 H. C. Choi, J. H. Shim and B. I. Min, *Phys. Rev. B*, 2006, **74**, 172103.