**Supporting information:**

# Magnetic properties in α-$MnO_2$ doped with alkaline elements

*Li-Ting Tseng[1], Yunhao Lu[2] , Hai Ming Fan[3] , Yiren Wang[1], Xi Luo[1], Tao Li[4], Paul Munroe[1], Sean Li[1], and Jiabao Yi*[1]*

[1]*School of Materials Science and Engineering, University of New South Wales, Kensington, 2052, NSW, Australia*
[2]*Department of Materials Science and Engineering, Zhejiang University, China*
[3]*Shanxi Key Laboratory of Degradable Biomedical Materials, School of Chemical Engineering, Northwest University, Xi'an, Shanxi 710069, China.*
[4]Institute for Synchrotron Radiation. Karlsruhe Institute of Technology, Karlsruhe, Germany

Email: Jiabao.yi@unsw.edu.au; Tel: 61-293854837; Fax: 61-293856565

Table SI: Coordinate numbers and atomic distance of $MnO_2$ doped with alkaline elements.

| samples | Mn-O | | | Mn-Mn | | |
|---|---|---|---|---|---|---|
| | CN | R | DW | CN | R | DW |
| Li:Mn | 5.8 | 1.90 | 0.0043 | 4.3 | 2.86 | 0.0051 |
| Na:Mn | 5.9 | 1.90 | 0.0045 | 4.4 | 2.86 | 0.0053 |
| K1:Mn | 4.6<br>2.2 | 1.90<br>1.76 | 0.0008<br>0.001 | 4.8 | 2.87 | 0.0076 |
| K3:Mn | 8.6<br>2.9 | 1.86<br>1.66 | 0.0038<br>0.0013 | 5.7 | 2.89 | 0.0079 |
| K4:Mn | 7.5<br>3.4 | 1.86<br>1.67 | 0.001<br>0.001 | 4.5 | 2.86 | 0.0062 |
| K60:Mn | 4.5 | 1.90 | 0.001 | 6.7 | 2.82 | 0.0114 |

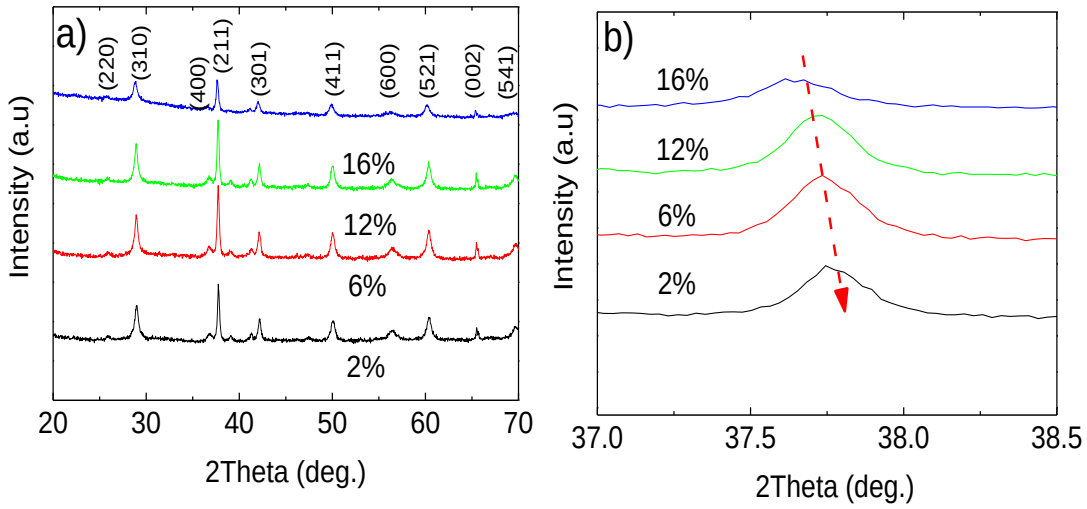


**Figure S1**: XRD spectra of K doped MnO2 with different doping concentrations. (a) XRD patterns of K-$MnO_2$ in full range; (b) Zoom in of (a) at the index of (211).

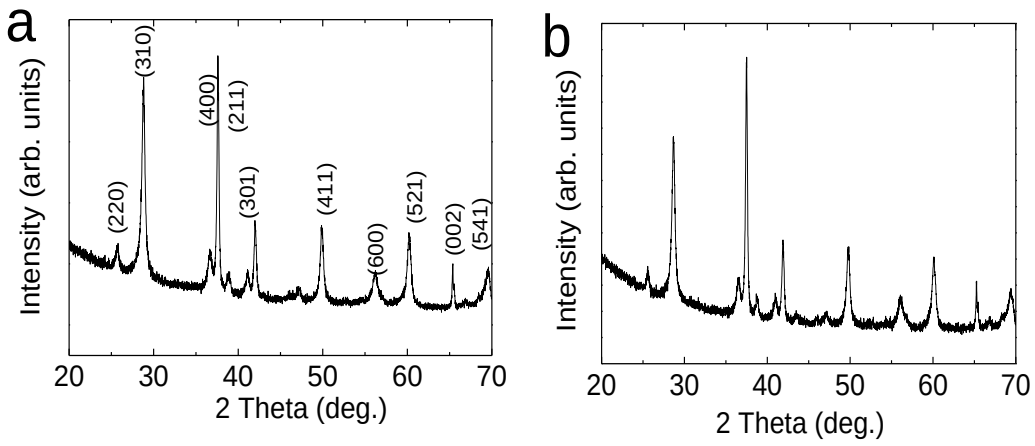


**Figure S2**: XRD spectrum. (a) 6 % Na doped $MnO_2$; (b) 6 % Li doped $MnO_2$.

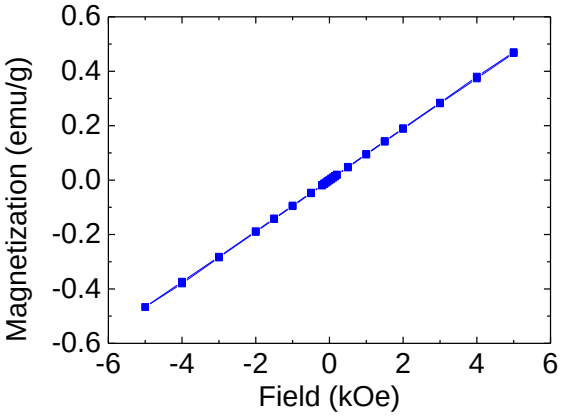


**Figure S3**: M-H curve of 12% Na doped $MnO_2$ taken at 5 K.

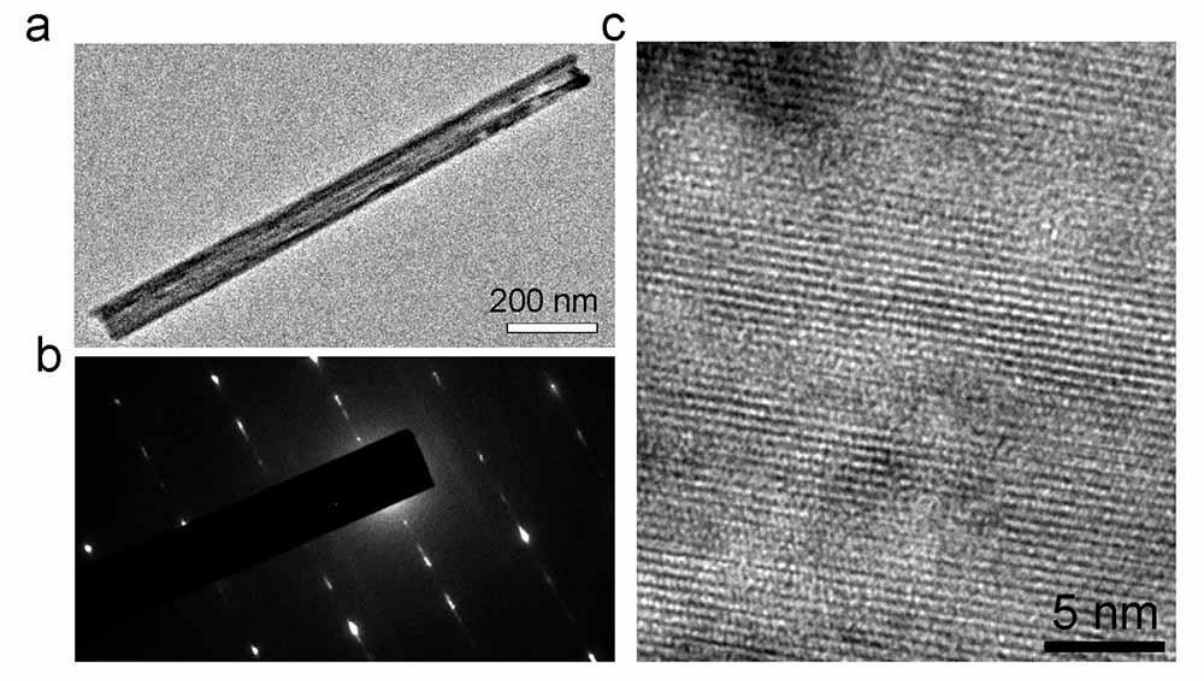


**Figure S4**: TEM image and SAED of 16% K-$MnO_2$ nanotubes. (a) TEM image of $MnO_2$ nanotubes at low magnification; (b) SAED; (c) High resolution TEM image.

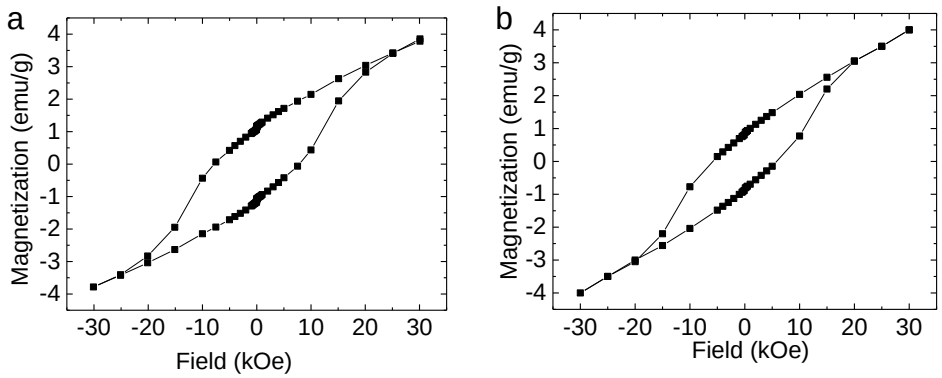


**Figure S5**: M-H loops taken at 5 K. (a) 6% Li-$MnO_2$; (b) 6% Na-$MnO_2$.

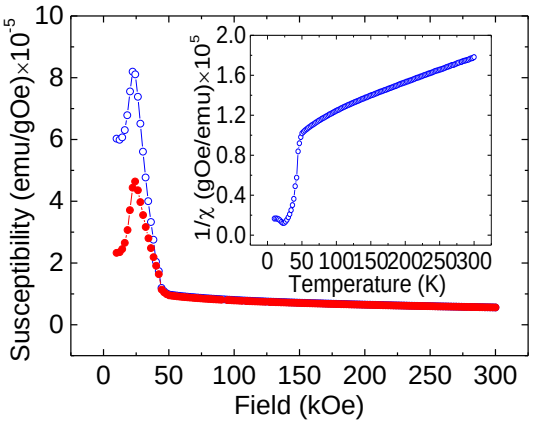


**Figure S6**: ZFC and FC curves of 16% K doped $MnO_2$ nanotubes.

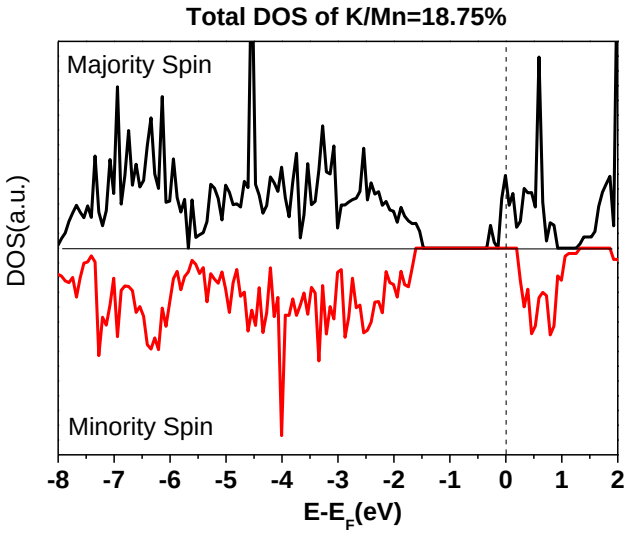


**Figure S7:** DOS of 18.5% K doped $MnO_2$, indicating half-metallic behaviour.

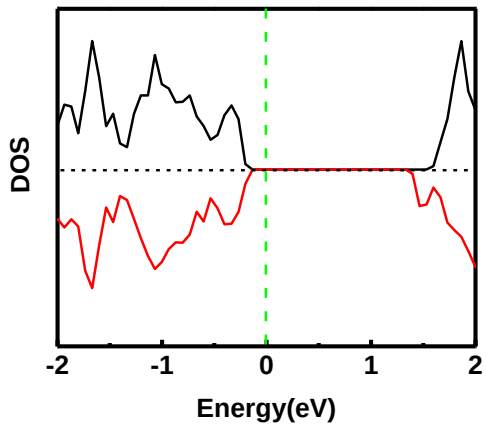


**Figure S8**: DOS of K doped $MnO_2$ without charge transfer. From the calculation, it can be seen that the Fermi level is inside the bandgap. Although the spin up and spin down in the conduction band is asymmetric, there are no filled states close to the Fermi level. Hence, the overall system is non-magnetic. This calculation has demonstrated that charge transfer is indispensable for the formation of ferromagnetic ordering.