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Supporting Information

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Mn_3O_4 Nanomaterials Functionalized with Fe_2O_3 and ZnO: Fabrication, Characterization, and Ammonia Sensing Properties

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S-1. Characterization

S-1.1. Field emission-scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDXS)

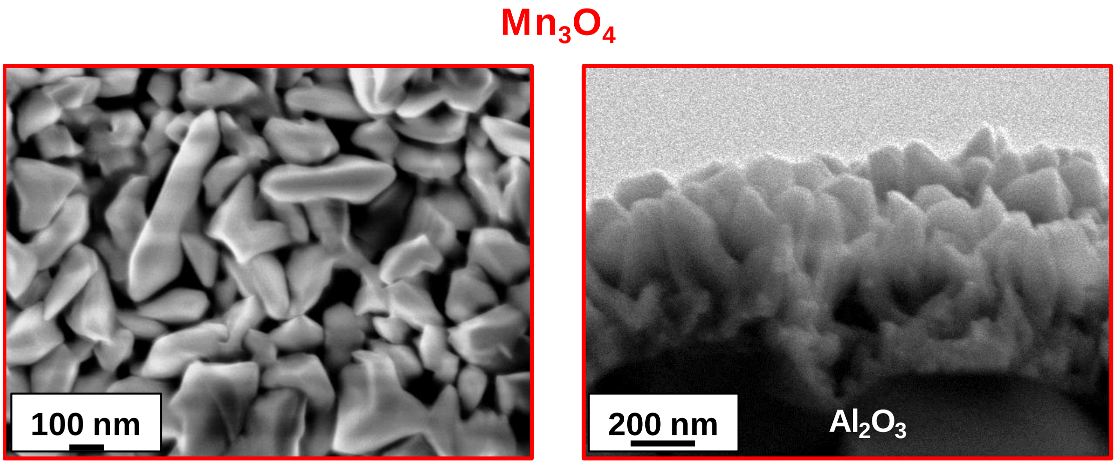

Figure S1. Plane-view and cross-sectional field emission-scanning electron microscopy (FE-SEM) micrographs of a bare Mn_3O_4 sample.

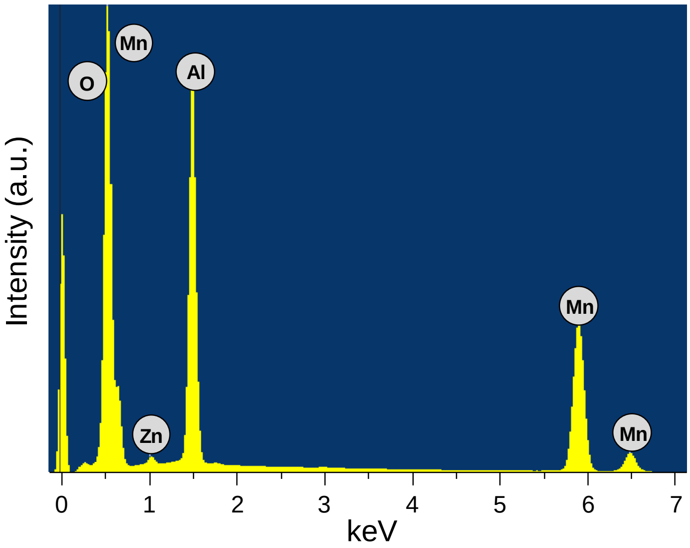

Figure S2. EDXS spectrum for a Mn_3O_4/ZnO specimen.

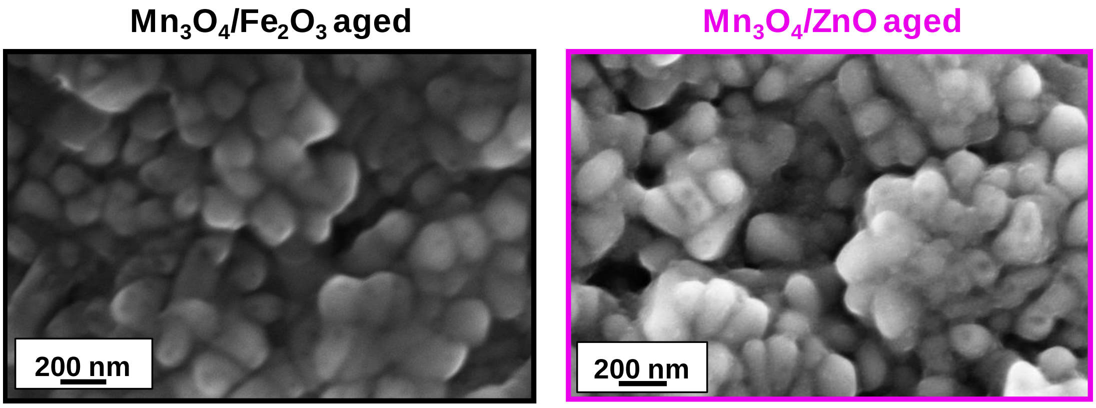

Figure S3. Plane-view FE-SEM micrographs for Mn_3O_4/Fe_2O_3 and Mn_3O_4/ZnO samples after cycled gas sensing tests for one year (average dimensions = (180±40) nm and (170±40) nm for Mn_3O_4/Fe_2O_3 and Mn_3O_4/ZnO, respectively).

S-1.2. X-ray photoelectron spectroscopy (XPS)

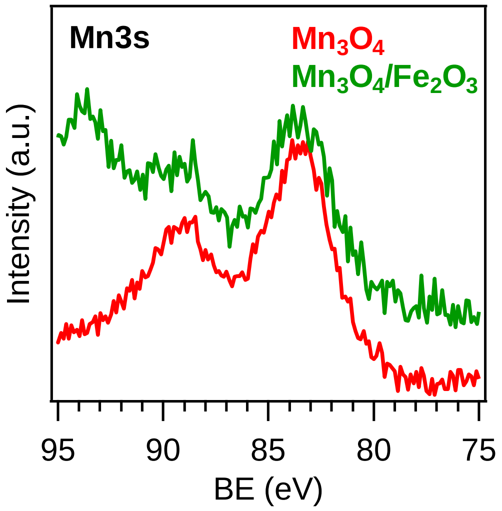

Figure S4. Surface Mn3s photoelectron peaks for Mn_3O_4 and Mn_3O_4/Fe_2O_3 samples. In the case of Mn_3O_4/ZnO specimen, the signal is not reported since it is superimposed with the Zn3p one (http://srdata.nist.gov/xps).

S-1-3. Gas sensing tests and data analysis

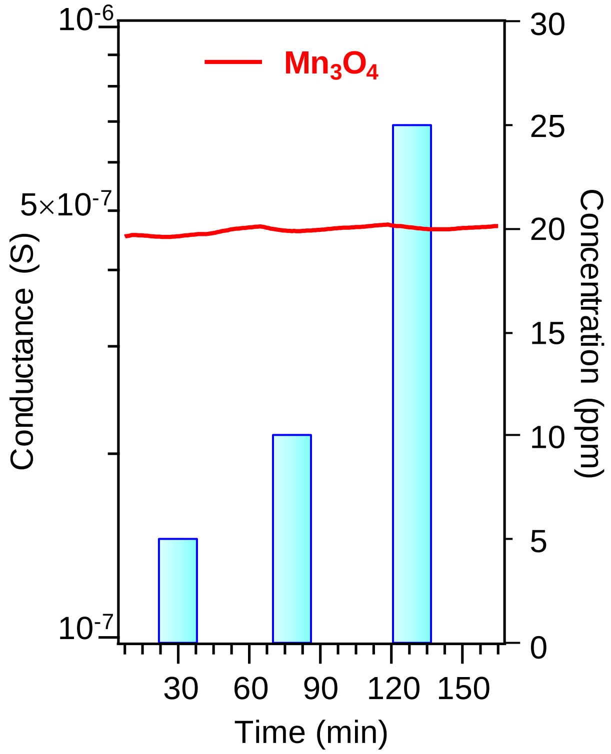

Figure S5. Dynamic response for a Mn_3O_4 specimen upon exposure to ammonia concentration pulses. Working temperature = 300 °C.

sample	*K*	*B*
Mn_3O_4/Fe_2O_3	4.9	0.83
Mn_3O_4/ZnO	5.4	0.83

Table S1. Parameters obtained by best fitting of the calibration curves (Response = $K \times C^B$) at a working temperature of 300 °C.

The width of the hole accumulation layer (HAL) in pure *p*-type Mn_3O_4 can be estimated by the following relation:[1]

$$W_{\mathrm{Mn3O4}} = \left[\frac{2\varepsilon_{\mathrm{Mn3O4}} V_0}{q N_{\mathrm{Mn3O4}}}\right]^{1/2}$$

(S1)

where $\varepsilon_{\mathrm{Mn3O4}}$ is the Mn_3O_4 permittivity ($7.94\times\varepsilon_0$, where ε_0 is the vacuum dielectric permittivity = 8.854×10^{-12} $C^2\times N^{-1}\times m^{-2}$),[2] V_0 is the height of the potential barrier established by oxygen adsorption (1.1 eV),[3] q is the electron charge (1.602×10^{-19} C), and N_{Mn3O4} is the hole density in Mn_3O_4 (2.25×10^{24} m^{-3}).[4] The calculated W_{Mn3O4} value is 20.6 nm.

When M_xO_y = Fe_2O_3 or ZnO are loaded onto Mn_3O_4, the HAL thickness is tuned due to the formation of *p–n* Mn_3O_4/M_xO_y junctions, according to the equation:[1]

$$W'_{\mathrm{Mn3O4}} = \left[\frac{2\varepsilon_{\mathrm{Mn3O4}}\varepsilon_{\mathrm{MxOy}} V_{\mathrm{C}} N_{\mathrm{MxOy}}}{q N_{\mathrm{Mn3O4}}\left(\varepsilon_{\mathrm{Mn3O4}} N_{\mathrm{Mn3O4}} + \varepsilon_{\mathrm{MxOy}} N_{\mathrm{MxOy}}\right)}\right]^{1/2}$$

(S2)

where $\varepsilon_{\mathrm{MxOy}}$ and N_{MxOy} denote M_xO_y permittivity and majority carrier concentration, respectively ($\varepsilon_{\mathrm{Fe2O3}} = 12.0\times\varepsilon_0$,[5] $N_{\mathrm{Fe2O3}} = 5.62\times10^{25}$ m^{-3};[6] $\varepsilon_{\mathrm{ZnO}} = 9.67\times\varepsilon_0$,[7] $N_{\mathrm{ZnO}} = 6.50\times10^{25}$ m^{-3}),[8] and V_{C} is the contact potential variation between M_xO_y and Mn_3O_4, calculated as the difference between the corresponding work function values (Φ_{Mn3O4} = 4.4 eV,[9] Φ_{Fe2O3} = 5.4 eV,[10] Φ_{ZnO} = 5.3 eV[8]).

The calculation yields W'_{Mn3O4} = 19.5 nm and 18.5 nm for Mn_3O_4/Fe_2O_3 and Mn_3O_4/ZnO junctions, respectively.

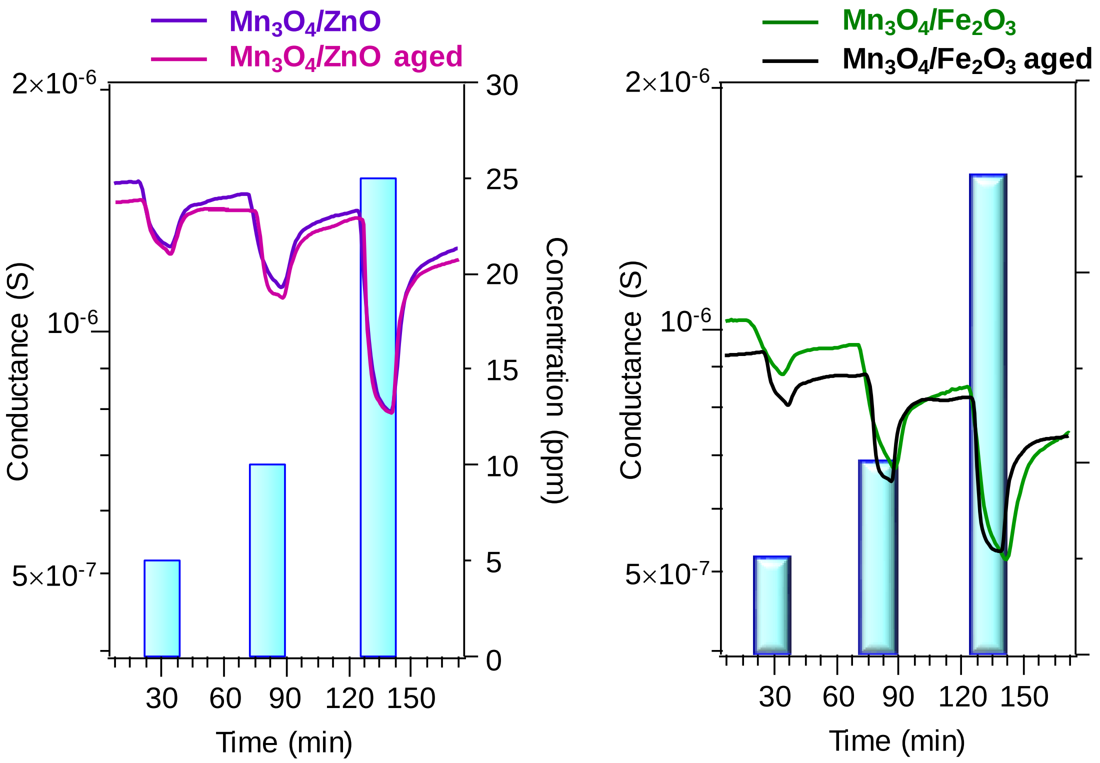

Figure S6. Dynamic responses of Mn_3O_4/ZnO and Mn_3O_4/Fe_2O_3 sensors to NH_3 concentration pulses after one year of cycled tests. Working temperature = 300 °C.

References

[1] S.-W. Choi, A. Katoch, J.-H. Kim, S. S. Kim, *ACS Appl. Mater. Interf.* **2015**, *7*, 647.

[2] L. Ben Said, R. Boughalmi, A. Inoubli, M. Amlouk, *Appl. Microsc.* **2017**, *47*, 131.

[3] T. Larbi, B. Ouni, A. Boukhachem, K. Boubaker, M. Amlouk, *Mater. Res. Bull.* **2014**, *60*, 457.

[4] T. Larbi, M. Haj Lakhdar, A. Amara, B. Ouni, A. Boukhachem, A. Mater, M. Amlouk, *J. Alloys Compd.* **2015**, *626*, 93.

[5] D. R. Lide, H. P. R. Frederikse, *Handbook of Chemistry and Physics*, 75th Ed., CRC Press, Inc.: Boca Raton,, 1995, pp. 12-53.

[6] H. K. Mulmudi, N. Mathews, X. C. Dou, L. F. Xi, S. S. Pramana, Y. M. Lam, S. G. Mhaisalkar, *Electrochem. Commun.* **2011**, *13*, 951.

[7] F. S. Mahmood, R. D. Gould, A. K. Hassan, H. M. Salih, *Thin Solid Films* **1995**, *270*, 376.

[8] T. Minami, T. Miyata, T. Yamamoto, *Surf. Coat. Technol.* **1998**, *108-109*, 583.

[9] G. Maniak, P. Stelmachowski, F. Zasada, W. Piskorz, A. Kotarba, Z. Sojka, *Catalysis Today* **2011**, *176*, 369.

[10] Z. Fan, X. Wen, S. Yang, J. G. Lu, *Appl. Phys. Lett.* **2005**, *87*, 013113.