Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2018

Electronic Supplementary Information

Controllable vapor phase fabrication of F:Mn_3O_4 thin films functionalized with Ag and TiO_2

Lorenzo Bigiani,[a] Davide Barreca,*[b] Alberto Gasparotto,[a]

Cinzia Sada,[c] Sara Martí-Sanchez,[d] Jordi Arbiol[d,e] and Chiara Maccato*[a]

[a] *Department of Chemical Sciences, Padova University and INSTM, Via F. Marzolo 1, 35131 Padova, Italy*

[b] *CNR-ICMATE and INSTM, Department of Chemical Sciences, Padova University, Via F. Marzolo 1, 35131 Padova, Italy*

[c] *Department of Physics and Astronomy, Padova University and INSTM, Via F. Marzolo 8, 35131 Padova, Italy*

[d] *Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Bellaterra, 08193 Barcelona, Catalonia, Spain*

[e] *ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Catalonia, Spain*

* Authors to whom correspondence should be addressed; e-mail: davide.barreca@unipd.it (D.B.); chiara.maccato@unipd.it (C.M.).

S-2. Characterization

S-2.1 X-ray diffraction (XRD)

The texture coefficient (TC_{hkl}) has been calculated as:[1-4]

$$TC_{hkl} = (I_{hkl}/I^0_{hkl}) / \{(1/N)*[\Sigma(I_{hkl}/I^0_{hkl})]\} \quad (S1)$$

where I_{hkl} and I^0_{hkl} are the diffracted intensities corresponding to the (hkl) planes for the target sample and the reference *haussmannite* Mn_3O_4 pattern, and N is the number of reflections observed in the XRD pattern.[5]

The average crystallite sizes D were estimated from the patterns presented in Fig. 1 by using the Scherrer formula:[1, 6-10]

$$D = 0.9[\lambda/(FWHM*\cos\theta)] \quad (S2)$$

where λ is the excitation wavelength (0.15418 nm), whereas 2θ and FWHM are the angular position and the full width at half maximum of the observed diffraction peaks.

The dislocation density (δ) and microstrain (ε) values have been estimated from the (211) peak, the most intense in the reference α-Mn_3O_4 powder spectrum, through the following equations:[1, 3, 6, 9]

$$\delta = 1/D^2 \quad (S3)$$

$$\varepsilon = FWHM/(4*\mathrm{tg}\theta) \quad (S4)$$

S-2.2 Secondary ion mass spectrometry (SIMS)

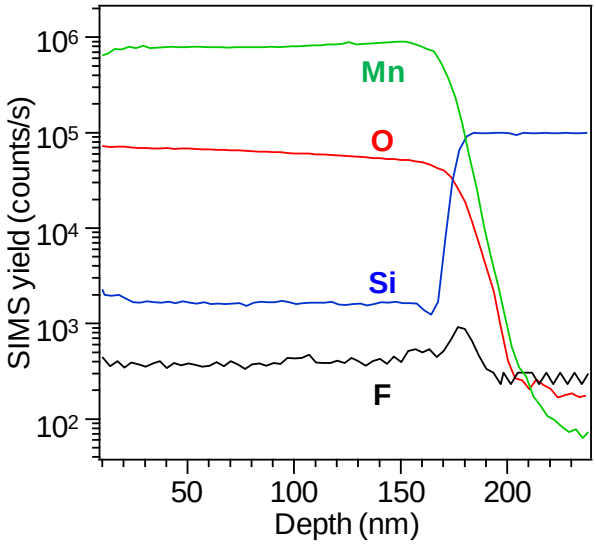

Fig. S1 SIMS depth profile for a F:Mn_3O_4 thin film deposited at 400°C. The increase in F signal detected at the interface between the deposit and the Si substrate can be related to variations in fluorine sputtering upon passing from the Mn3O4 nanodeposit to silicon.

S-2.3 X-ray photoelectron spectroscopy (XPS)

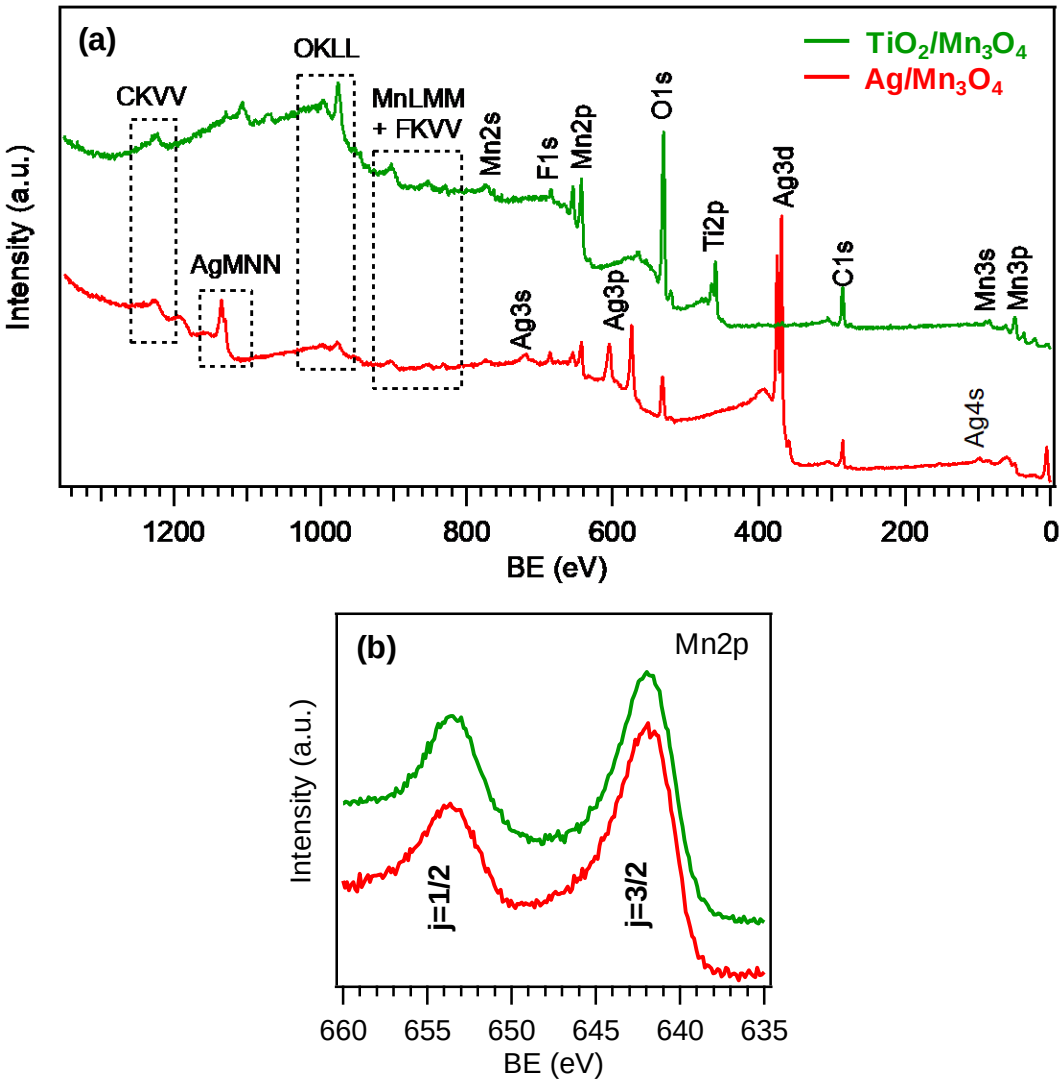

Fig. S2 (a) Surface wide-scan XP spectra of Ag/F:Mn_3O_4 and TiO_2/F:Mn_3O_4 samples, along with the corresponding detailed Mn2p photopeaks (b).

S-2.4 Atomic force microscopy (AFM)

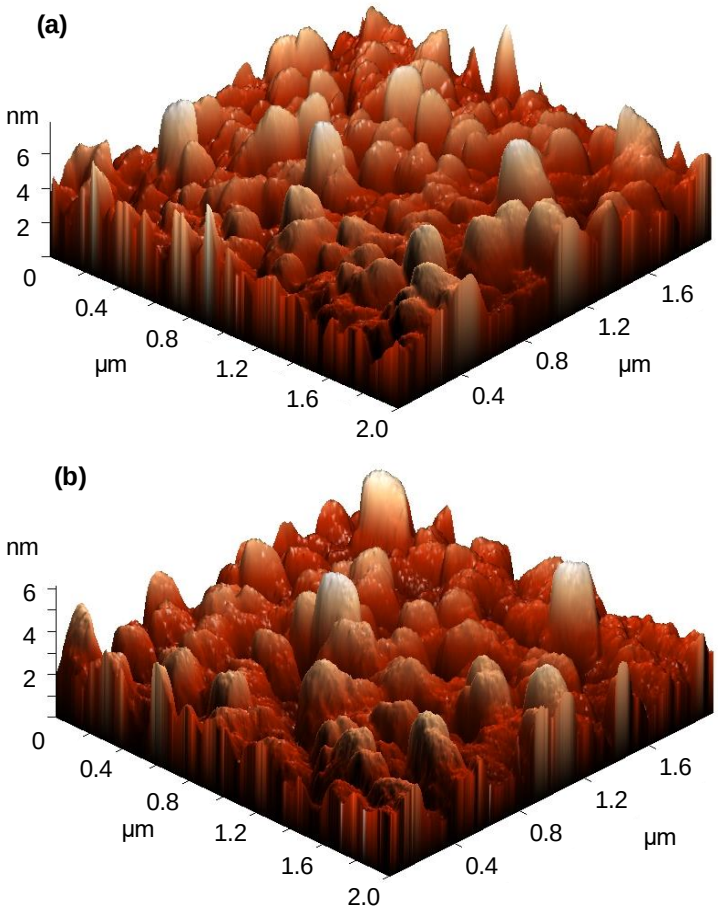

Fig. S3 Representative AFM micrographs for: (a) Ag/F:Mn_3O_4; (b) TiO_2/F:Mn_3O_4 samples. RMS roughness values are close to 1.0 nm for both specimens.

S-2.5 Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDXS)

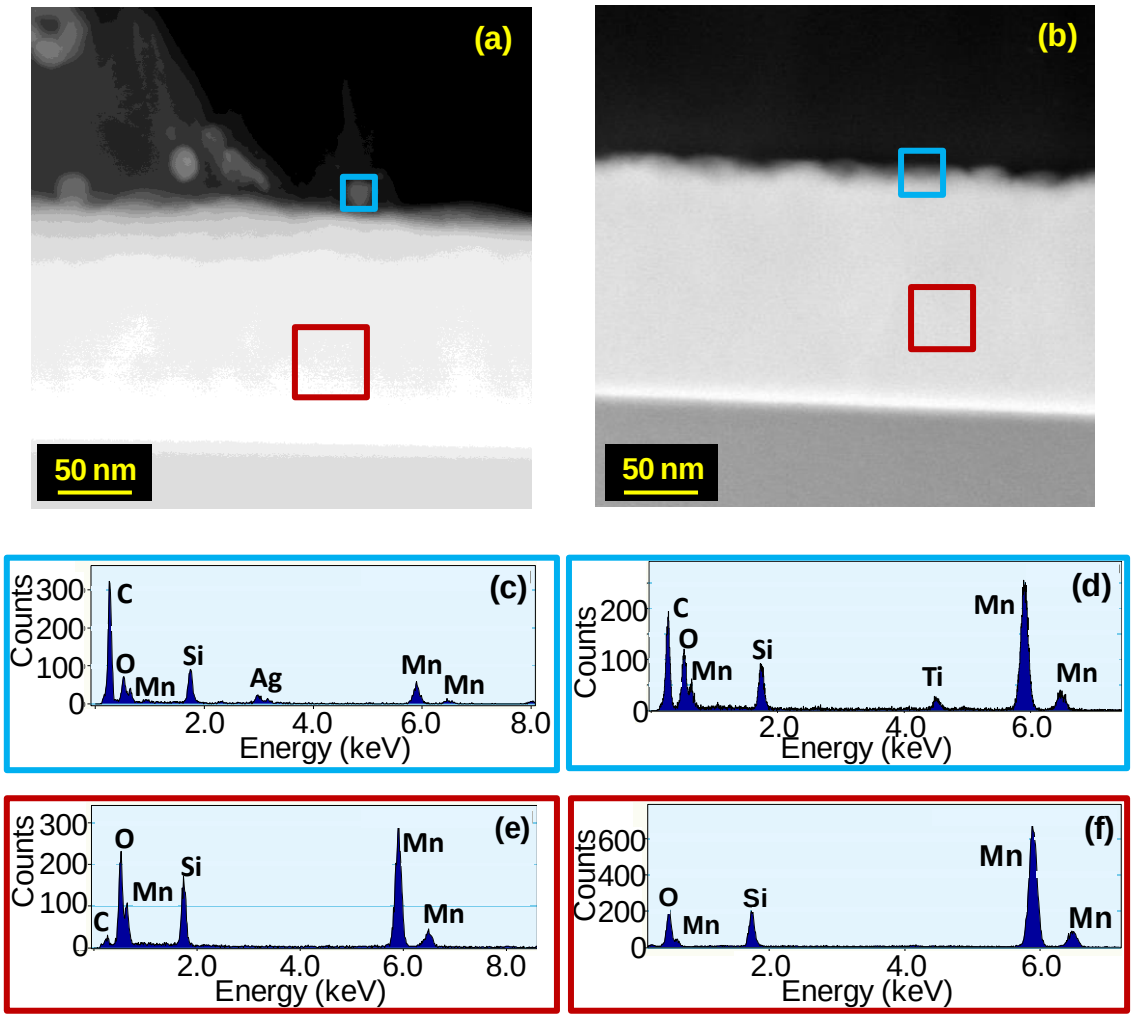

Fig. S4 Cross-sectional low magnification HAADF-STEM micrographs for (a) Ag/F:Mn_3O_4 and (b) TiO_2/F:Mn_3O_4 specimens. Corresponding EDXS spectra recorded in the marked areas for (c,e) Ag/F:Mn_3O_4 and (d,f) TiO_2/F:Mn_3O_4 samples.

References

1. T. Larbi, B. Ouni, A. Boukhachem, K. Boubaker and M. Amlouk, *Mater. Res. Bull.*, 2014, **60**, 457-466.
2. P. K. K. Kumarasinghe, A. Dissanayake, B. M. K. Pemasiri and B. S. Dassanayake, *J. Mater. Sci. - Mater. Electron.*, 2017, **28**, 276-283.
3. S. Dias, B. Murali and S. B. Krupanidhi, *Sol. Energy Mater. Sol. Cells*, 2015, **143**, 152-158.
4. S. Gangopadhyay, R. Acharya, A. K. Chattopadhyay and S. Paul, *Vacuum*, 2010, **84**, 843-850.
5. Pattern N° 024-0734, JCPDS (2000).
6. M. A. Amara, T. Larbi, A. Labidi, M. Karyaoui, B. Ouni and M. Amlouk, *Mater. Res. Bull.*, 2016, **75**, 217-223.
7. D. P. Dubal, D. S. Dhawale, R. R. Salunkhe, V. J. Fulari and C. D. Lokhande, *J. Alloys Compd.*, 2010, **497**, 166-170.
8. D. P. Dubal, D. S. Dhawale, R. R. Salunkhe, S. M. Pawar and C. D. Lokhande, *Appl. Surf. Sci.*, 2010, **256**, 4411-4416.
9. T. Larbi, M. H. Lakhdar, A. Amara, B. Ouni, A. Boukhachem, A. Mater and M. Amlouk, *J. Alloys Compd.*, 2015, **626**, 93-101.
10. M. R. Belkhedkar and A. U. Ubale, *Jo. Mol. Struct.*, 2014, **1068**, 94-100.