

Supporting Information

Sensing Nitrogen Mustard Gas Simulant at the ppb-Scale via Selective Dual-Site Activation at Au/Mn₃O₄ Interfaces

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Alla fine, ricontrollare tutti i numeri delle figure sia qui che nel main paper

§ S-1. Materials and methods

§ S-1.1 Synthesis

Mn₃O₄ nanodeposits were synthesized using a previously described cold-wall horizontal chemical vapor deposition (CVD) reactor equipped with a quartz chamber and an external precursor reservoir.¹⁻² The Mn(hfa)₂•TMEDA precursor (hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; TMEDA = *N,N,N',N'*-tetramethylethylenediamine), synthesized following a recently reported procedure,³ was vaporized in a glass vessel at a temperature of 60°C throughout each experiment. Precursor vapors were transported towards the growth substrate by an electronic grade O₂ flow (rate = 100 standard cubic centimeters per minute (SCCM)). An auxiliary 100 SCCM oxygen flow was separately introduced into the reactor. Gas lines between the precursor reservoir and the reaction chamber were maintained at 100°C in order to prevent condensation phenomena.

Radio frequency (RF) sputtering for the functionalization of manganese oxide deposits with noble metal nanoparticles was performed using a custom-built two-electrode plasmochemical apparatus equipped with a RF generator (ν = 13.56 MHz).⁴⁻⁵ Depositions were carried out from electronic grade Ar plasmas using Ag or Au targets (BALTEC AG, 99.99%). On the basis of previous results,⁶⁻⁷ silver or gold sputtering was performed using the following optimized experimental conditions: Ar flow rate = 10 SCCM; RF-power = 5 W. The use of higher RF-powers or longer deposition times was discarded to prevent the formation of compact systems with an excessive Ag/Au loading and a reduced active area.

§ S-1.2 Characterization

Field emission-scanning electron microscopy (FE-SEM) images were recorded using in-lens or backscattered (BSE) electron signals. The mean deposit thickness and nanoaggregate dimensions were evaluated through the ImageJ[®] software (<https://imagej.nih.gov/ij/>, accessed November 2018), averaging over various independent measurements.

Atomic force microscopy (AFM) characterization was carried out using an NT-MDT SPM solver P47H-PRO apparatus equipped with an anti-noise table, operating in tapping mode and in air. Root

mean square (RMS) roughness values were obtained from $5 \times 5 \mu\text{m}^2$ images after plane fitting.

As regards photoelectron spectroscopy analyses, for Mn_3O_4 -Ag samples silver α_1 and α_2 Auger parameters were calculated as previously reported.⁸⁻⁹ For Mn_3O_4 -Au systems, quantitative analyses were conducted following a recently reported procedure,^{6,10} which involved the use of the $\text{Au}4d_{5/2}$ signal instead of the most intense Au 4f one due to $\text{Mn}2p/\text{Au}4p_{1/2}$ and $\text{Mn}3s/\text{Au}4f$ photopeak overlaps.^{6,11} After a Shirley-type background subtraction,¹² atomic percentages (at. %) were determined by peak area integration using Φ V5.4A sensitivity factors. Gold and silver molar fractions were calculated as $X_M = ((M \text{ at.}\%) / (M \text{ at.}\% + \text{Mn at.}\%)) \times 100$, with $M = \text{Ag, Au}$.¹³⁻¹⁴ Whenever necessary, peak fitting was performed by a least-squares procedure with Gaussian–Lorentzian peak shapes, using the XPS peak software (<https://xpspeak.software.informer.com/4.1/>, accessed September 2018).

Secondary ion mass spectrometry (SIMS) measurements were carried out in beam blanking mode, to improve the depth resolution, as well as in high-mass resolution configuration, to prevent mass interference artefacts. The nominal rastered area was $150 \times 150 \mu\text{m}^2$, whereas ion detection was performed from a $8 \times 8 \mu\text{m}^2$ sub-region in order to avoid crater effects.

§ S-1.3 Gas sensing tests

Conductometric device working principle is based on the variation of the electrical resistance in presence of the target analyte. Gas sensing measurements were performed in the 200–300°C temperature (T) interval. In fact, lower temperatures did not enable the obtainment of appreciable responses, whereas for $T > 300^\circ\text{C}$ undesired Mn_3O_4 alterations resulted in a detrimental performance degradation.¹⁵ Prior to measurements, sensors were maintained at the desired working temperature for 8 h in order to attain material stabilization before functional tests. Analyses were carried out using a standard configuration with interdigitated Pt contacts.¹⁶ IDEs and a Pt heater were deposited by DC sputtering on the top of the sensing material and on the back of Al_2O_3 substrates, respectively (Ar plasma, 7 SCCM gas flow, 70 W, 5×10^{-3} mbar, room temperature). All tests were performed using gaseous analytes from certified bottles with known concentration. To achieve the desired concentration during gas sensing tests, the analyte was diluted further with

synthetic air by mass flow controllers (MKS, Germany, resolution 0.1% full scale), and then introduced into the chamber. Humidity was controlled by generating a water-saturated synthetic air flow, which was mixed with the desired analyte in each experiment.

For a *p*-type semiconductor like Mn_3O_4 in the presence of reducing analytes [like acetone, ethanol and di(propyleneglycol) monomethyl ether (DPGME)], the sensor response was defined as:^{15,17-18}

$$\text{Response} = (R_G - R_a) \times 100 / R_a = \Delta R / R_a \times 100 \quad (\text{S1})$$

where R_a and R_G are the air resistance and the corresponding steady state value reached after analyte exposure.

Experimental data were fitted by the relation:^{15,19-21}

$$\text{Response} = A \times C^B \quad (\text{S2})$$

where A is a constant, C is the concentration of the gaseous analyte in ppm, and B is an exponent dependent on the reaction stoichiometry.²² Upon assuming the validity of equation (S2) even at low analyte concentration, detection limits were extrapolated for a fixed response value of 30.¹⁵

The response time (τ_{resp}) was calculated as the time requested for the sample resistance to reach 90% of the equilibrium value after exposure to the analyte,^{18,23-26} whereas the recovery time (τ_{rec}) was the one necessary to return to 70% of the original resistance in air.^{20,23,27} The maximum uncertainty on these values was estimated to be $\pm 10\%$.

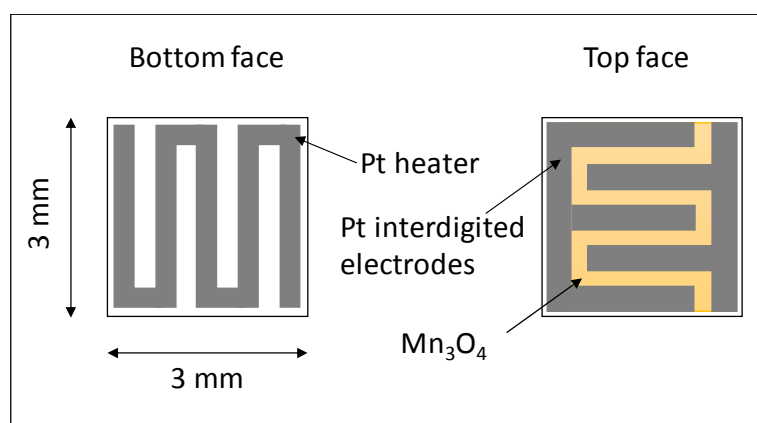


Figure S1. Sketch of the sensor device structure utilized in the present work.

§ S-2. Material characterization

§ S-2.1 Atomic force microscopy (AFM)

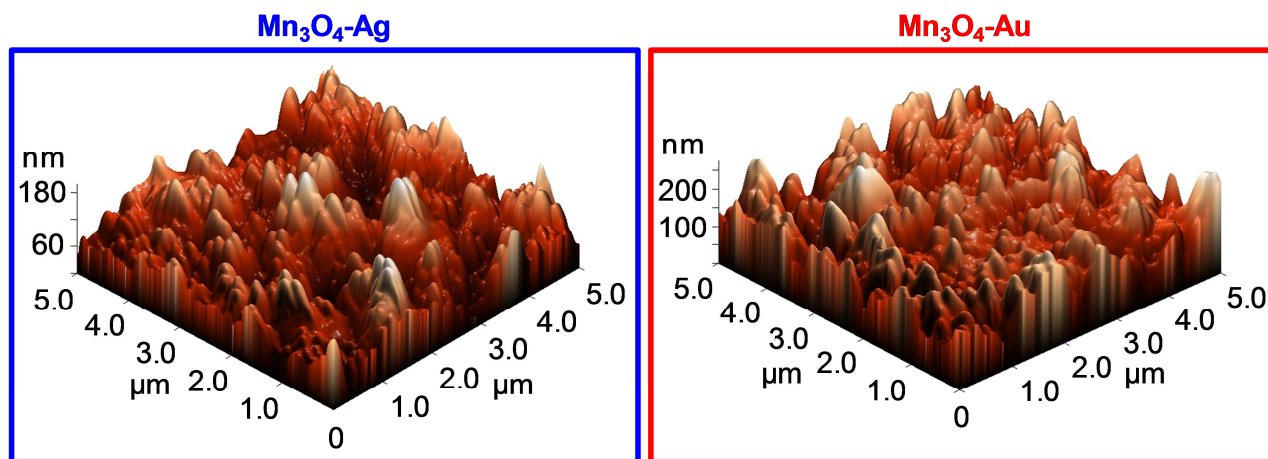


Figure S2. Representative AFM micrographs for $\text{Mn}_3\text{O}_4\text{-Ag}$ and $\text{Mn}_3\text{O}_4\text{-Au}$ specimens.

AFM analyses evidenced a uniform surface topography with a granular-like texture and enabled to estimate a RMS roughness of ≈ 27 nm for all the target specimens, irrespective of Ag or Au functionalization.

§ S-2.2 Energy dispersive X-ray spectroscopy (EDXS)

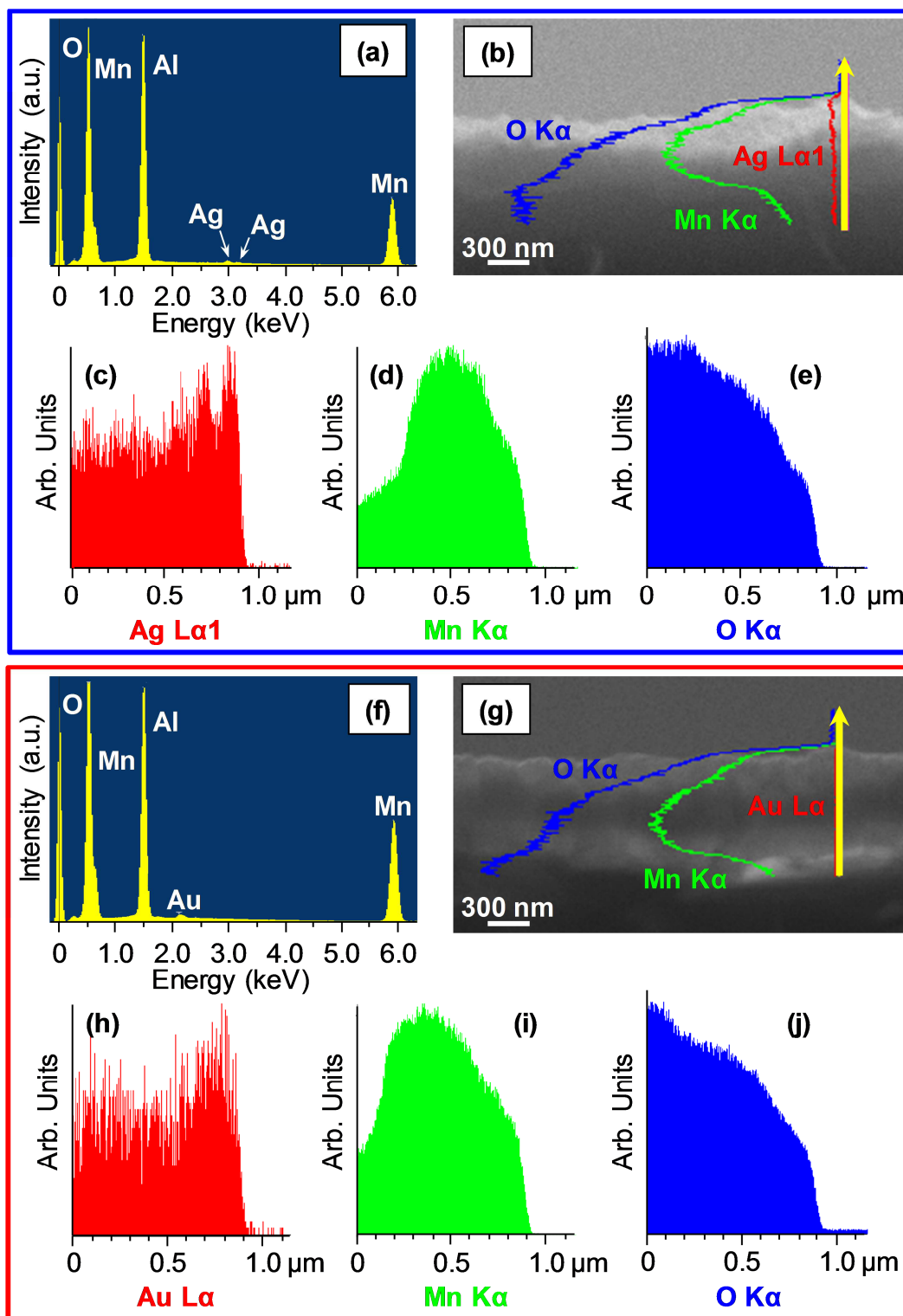


Figure S3. EDXS spectra and cross-sectional line scan data for $\text{Mn}_3\text{O}_4\text{-Ag}$ (a→e) and $\text{Mn}_3\text{O}_4\text{-Au}$ (f→j) specimens, recorded along the yellow lines marked in cross-sectional FE-SEM images. Arrows indicate the

direction of abscissa increase.

§ S-2.3 X-ray diffraction (XRD)

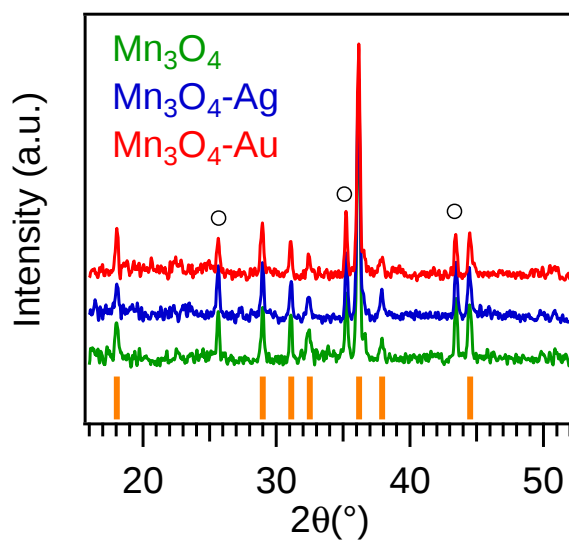


Figure S4. (a) XRD patterns of Mn_3O_4 , $\text{Mn}_3\text{O}_4\text{-Ag}$ and $\text{Mn}_3\text{O}_4\text{-Au}$. Reflections pertaining to tetragonal $\alpha\text{-Mn}_3\text{O}_4$ are marked by vertical orange bars,²⁸ whereas the circles indicate the reflections related to the Al_2O_3 substrate.

§ S-2.4 X-ray photoelectron spectroscopy (XPS)

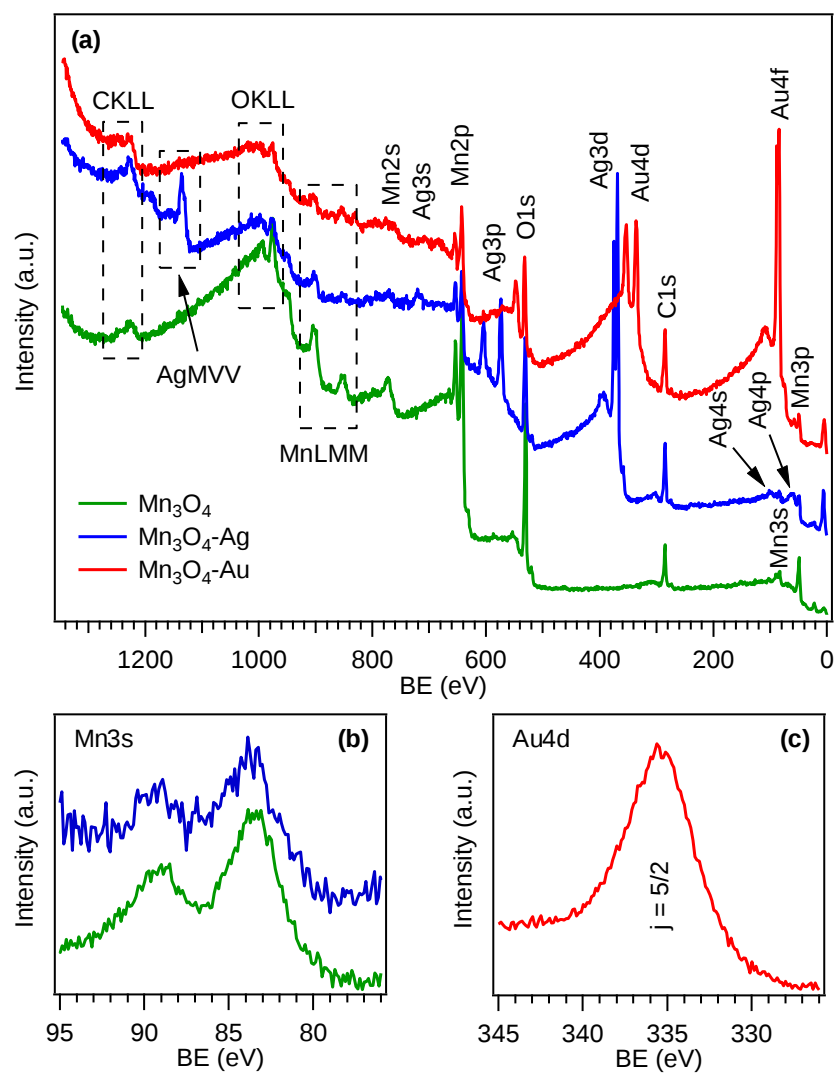


Figure S5. Surface XPS analysis of the samples fabricated in the present work: (a) wide-scan spectra; (b) Mn3s and (c) Au4d photopeaks.

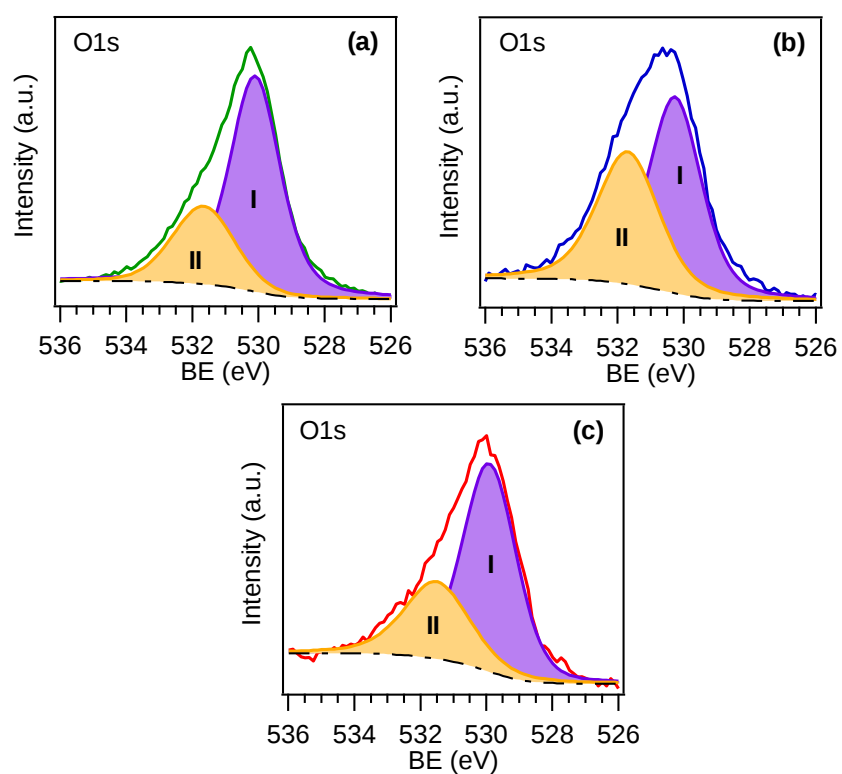


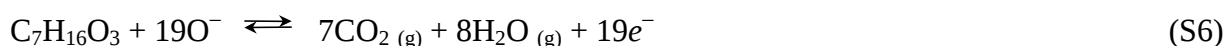
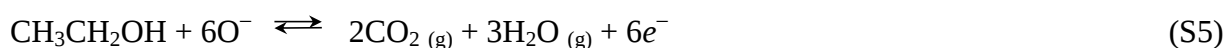
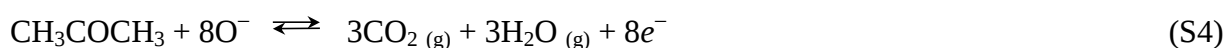
Figure S6. Surface O1s signals, along with the resulting fitting components, for Mn_3O_4 (a), $\text{Mn}_3\text{O}_4\text{-Ag}$ (b) and $\text{Mn}_3\text{O}_4\text{-Au}$ (c) specimens.

§ S-2.5 Gas sensing tests

After Mn₃O₄ contact with air, active oxygen generated upon O₂ chemisorption:^{21,26,29-31}



yield the formation of a near-surface hole-accumulation layer (HAL).^{24,31-35} The subsequent analyte chemisorption³⁶⁻³⁹, whose stoichiometry can be formally described as:



and the concomitant electron release^{24,40} produce a decrease in the hole concentration and in a parallel reduction of the material HAL width, accounting for the observed conductance drop-off.^{30,35}

Upon switching off gas pulses, the original air baseline is recovered.

Despite the gas-sensing mechanism of DPGME has never been reported in the literature, it is reasonable to suppose that under the adopted working conditions, DPGME decomposition might be also triggered by adsorbed water/hydroxyl surface groups, as well as by O₂ derived species on the sensor surface. In this regard, the former species could be responsible for the hydrolysis of DPGME methoxy group to form dipropylene glycol (C₆H₁₄O₃) and of the dipropylene glycol backbone of DPGME to form PGME (propylene glycol methyl ether, C₄H₁₀O₂) and propylene glycol (C₃H₈O₂). This partial hydrolysis might be caused by the humidity present in the gas flow, and is also supported at atomistic level by the very short hydrogen bond (1.86 Å) between a water proton and the methoxy oxygen of DPGME obtained from our calculations (see Figure 6, main text). In parallel, surface adsorbed oxygen species could promote the oxidation of DPGME and of the above by-products, virtually yielding to their final full oxidation to CO₂ and H₂O.

	Mn₃O₄		Mn₃O₄-Ag		Mn₃O₄-Au	
Analyte	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
Acetone	26	0.34	39	0.32	136	0.23
Ethanol	18	0.46	29	0.41	47	0.50
DPGME	98	0.40	67	0.22	346	0.33

Table S1. Representative parameters obtained by fitting the calibration curves $Response = A \times C^B$.^{15,21} The data are obtained at 300°C, apart for the detection of DPGME by Mn₃O₄-Au, for which the values are reported at 200°C, corresponding to the maximum recorded response.

	Response time (min)			Recovery time (min)		
	Mn ₃ O ₄	Mn ₃ O ₄ -Ag	Mn ₃ O ₄ -Au	Mn ₃ O ₄	Mn ₃ O ₄ -Ag	Mn ₃ O ₄ -Au
Acetone	12	11	11	13	10	8
Ethanol	8	7	5	9	8	4
DPGME	20	18	9	93	81	28

Table S2. Response and recovery times for acetone, ethanol, and DPGME detection by the target nanomaterials. Data are obtained at 300°C for the former two analytes, and at 200°C for DPGME, these temperatures yielding the best response values for the corresponding gases. The obtained response and recovery times clearly highlight the beneficial impact of Mn₃O₄ functionalization.

For Au-Mn₃O₄, response and recovery time values reported in Table S2 were of the same order of magnitude of metal-functionalized Co₃O₄⁴¹ and Fe₂O₃²⁵ sensors, and lower than those reported for commercially produced SnO₂ nanoparticles.³⁵

For DPGME detection, at the optimal working temperature of 200°C, typical τ_{resp} and τ_{rec} values by Mn₃O₄-Au sensors were estimated to be 9 and 28 min, respectively. At 300°C the corresponding values were $\tau_{\text{resp}} = 27$ min and $\tau_{\text{rec}} = 57$ min. The increase of τ_{resp} and τ_{rec} with temperature is in line with a decreased analyte adsorption, and possible poisoning effects, respectively. Nonetheless, the obtained values, and, especially, the very long recovery times, are consistent with other literature works on CWA simulant detection.²⁷ Nevertheless, given the importance of these parameters for a possible practical use of the developed sensors, the future minimization of these values undoubtedly deserves further attention and efforts.

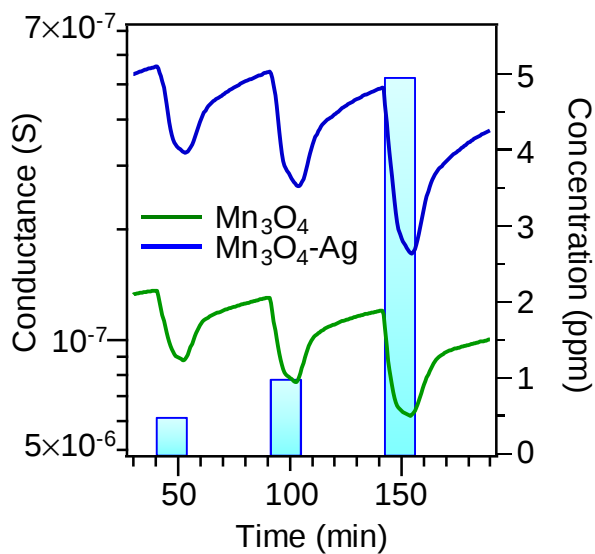


Figure S7. Dynamic responses at 300°C to different DPGME concentrations for Mn_3O_4 and $\text{Mn}_3\text{O}_4\text{-Ag}$ specimens.

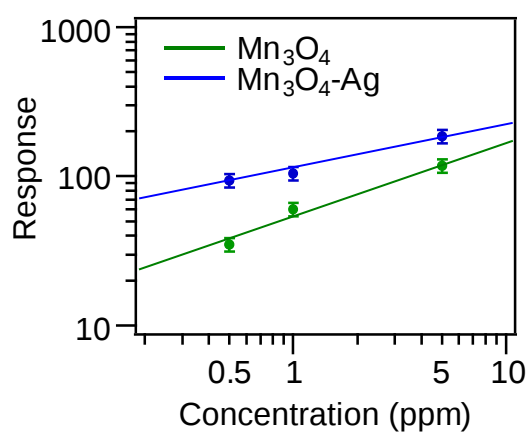


Figure S8. Dependence of response values on DPGME concentration for Mn_3O_4 and $\text{Mn}_3\text{O}_4\text{-Ag}$ samples. Working temperature = 300°C.

§ S-2.6 Computational Details

The Quantum Espresso suite of programs was adopted in all calculations.⁴² The stoichiometry of the resulting model slab is $\text{Mn}_{42}\text{Mn}^{\text{T}}_{16}\text{O}_{88}$ (Mn^{T} = tetrahedral Mn^{2+} cations). The slab was cut by leaving oxygen anions and octahedral Mn^{3+} cations on the surfaces.⁴³ The calculated magnetization was the same as reported for *hausmannite*,⁴⁴⁻⁴⁵ where the tetrahedral sites have spin-up arrangement, whereas the octahedral ones assume an antiferromagnetic ordering. The exposed surface area is $125.84 \text{ \AA}^2$ (see cell parameters in the caption for Figure 5). A vacuum layer of $15 \text{ \AA}$ was added in order to reduce the inter-slab interactions. Geometry optimizations were performed allowing all atoms to move, up to a convergence criterion of $0.5 \times 10^{-3} \text{ Hartree} \cdot \text{Bohr}^{-1}$. The active surface was modelled by adding an Au_8 cluster and two water molecules to one of the two free surfaces of the slab. The size of the cluster was chosen in order to match one of the so-called “magic numbers”—that is, the number of valence electrons for which gold nanoclusters are particularly stable.⁴⁶ Specifically, Au_8 corresponds to the smallest $-(\text{Au})_n$ cluster featuring a magic-number.

§ S-2.7 Structure comparison for the Mn_3O_4 -Au-ethanol and Mn_3O_4 -Au-DPGME systems

The investigation of the Mn_3O_4 -Au-ethanol system was performed by applying the same methodology adopted for the case of the Mn_3O_4 -Au-DPGME interaction. A careful comparison of the optimized geometries of the two models highlighted both similarities and differences between the two analytes. Significantly, the hydroxyl oxygen of ethanol is coordinated to a surface Mn^{3+} cation located close to the Au cluster, like in the case of DPGME. Specifically, the ethanol hydroxyl oxygen is at $2.09 \text{ \AA}$ from a Mn^{3+} cation, to be compared with $2.18 \text{ \AA}$ in the DPGME case. Similarly to DPGME, which forms hydrogen bonds with two water molecules, ethanol interacts with one water molecule, but the hydrogen bond is weaker ($\text{H}-\text{O}_{\text{water}}$ distance = $2.11 \text{ \AA}$), as depicted in Figure S9a, while the second water molecule is close to a gold atom.

For the ethanol case, the three shortest $\text{Au}-\text{O}_{\text{Mn}}$ distances are $2.09 \text{ \AA}$, $2.17 \text{ \AA}$ and $2.21 \text{ \AA}$. They are similar to the corresponding values found in the DPGME case – namely, $2.10 \text{ \AA}$, $2.13 \text{ \AA}$ and $2.24 \text{ \AA}$. Nevertheless, as can be seen in Figure S9a, the ethanol-Au distances are longer than the sum of the

respective van der Waals radii, whereas the DPGME ethereal oxygen is clearly in contact with the noble metal (Figure S9b).

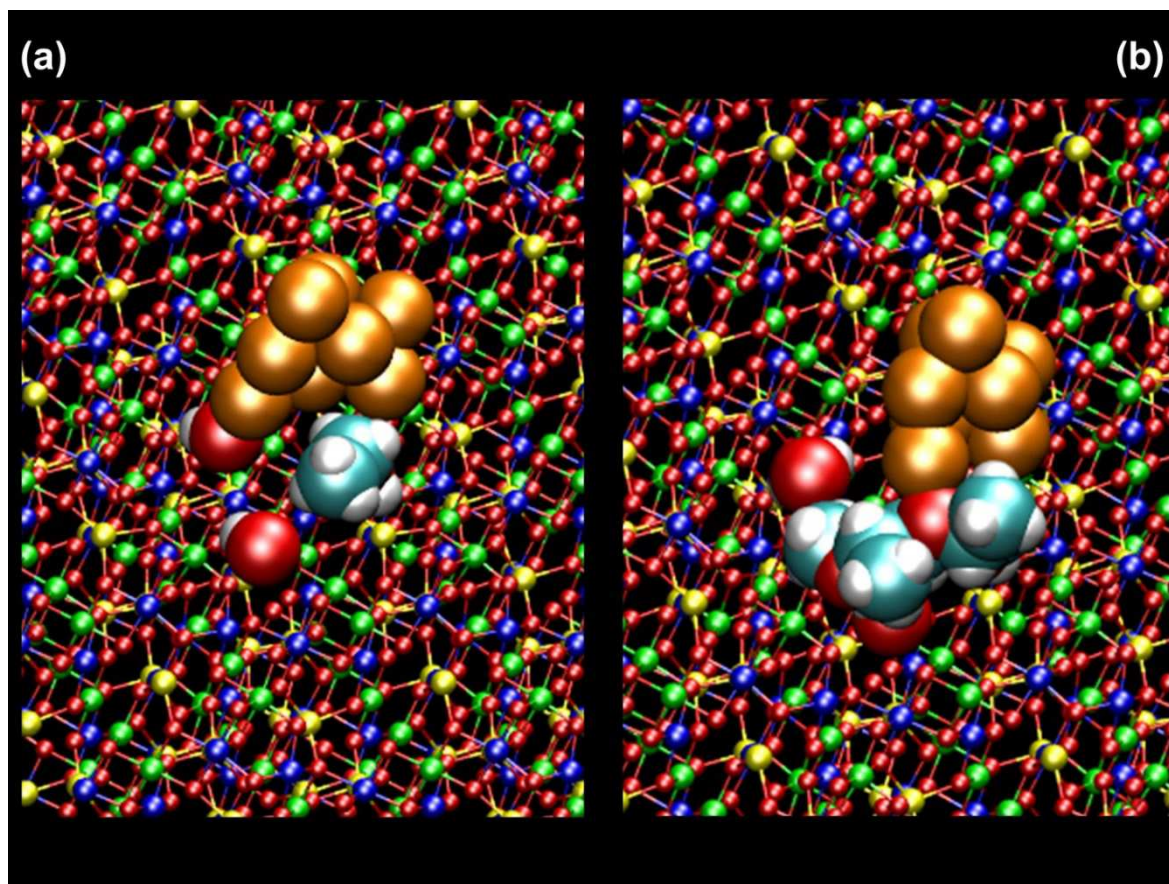


Figure S9. Graphical representations (top view) of the geometry optimized (a) Mn_3O_4 -Au-ethanol model and (b) Mn_3O_4 -Au-DPGME model. The Au cluster, the analytes and the water molecules are shown in van-der-Waals representation. Color codes: red, oxygen, yellow, tetrahedral Mn^{2+} ; blue (up-spin) and green (down-spin), octahedral Mn^{3+} ; orange, Au; cyan, C; white, H.

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