Supporting Information

Al_2O_3/ZnO Composite-Based Sensors for Battery Safety Applications: An Experimental and Theoretical Investigation

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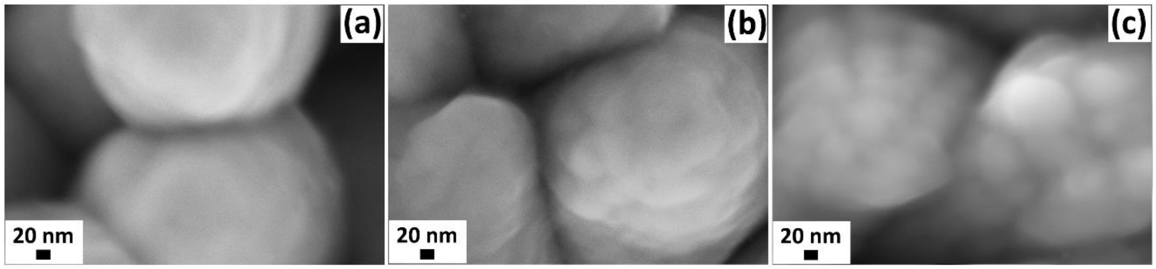

Figure S1. Scanning electron microscopy (SEM) images of the Al_2O_3/ZnO heterostructures at high magnification after the ALD process and deposition of the Al_2O_3, overlayer with thicknesses of: (a) 7 nm; (b) 10 nm; and (c) 12 nm.

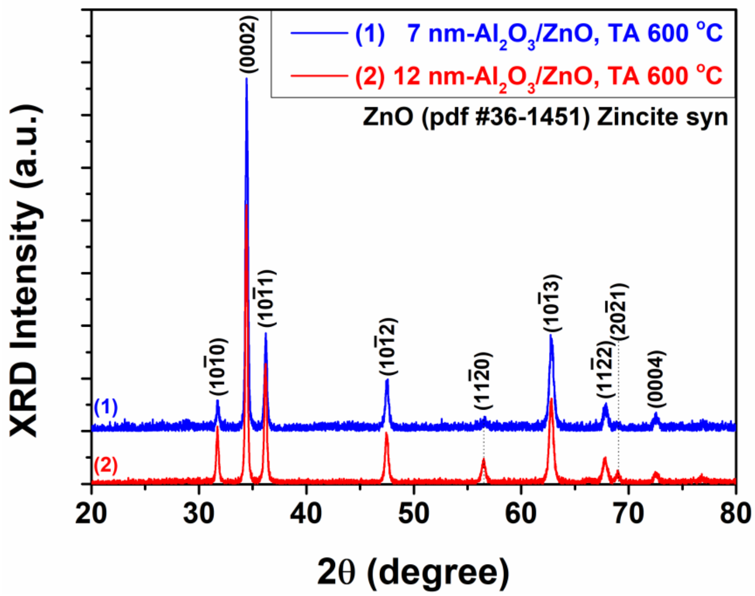

Figure S2. X-ray diffraction (XRD) patterns of the Al_2O_3/ZnO heterostructures thermally annealed at 600 °C for 30 min with different thicknesses of the Al_2O_3 overlayer: 7 nm – curve 1 and 12 nm – curve 2.

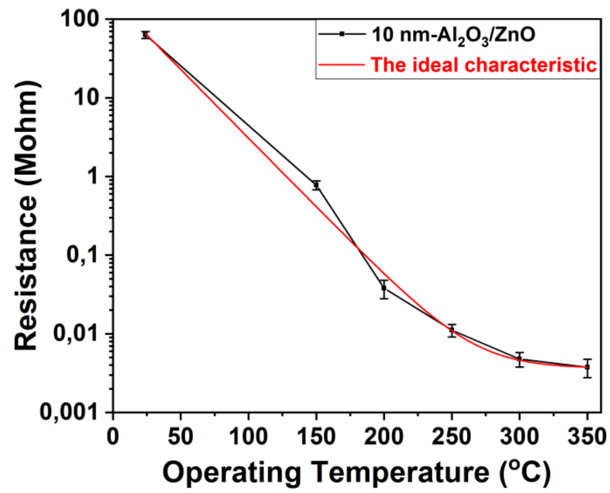

Figure S3. Electrical resistance as a function of the operating temperature.

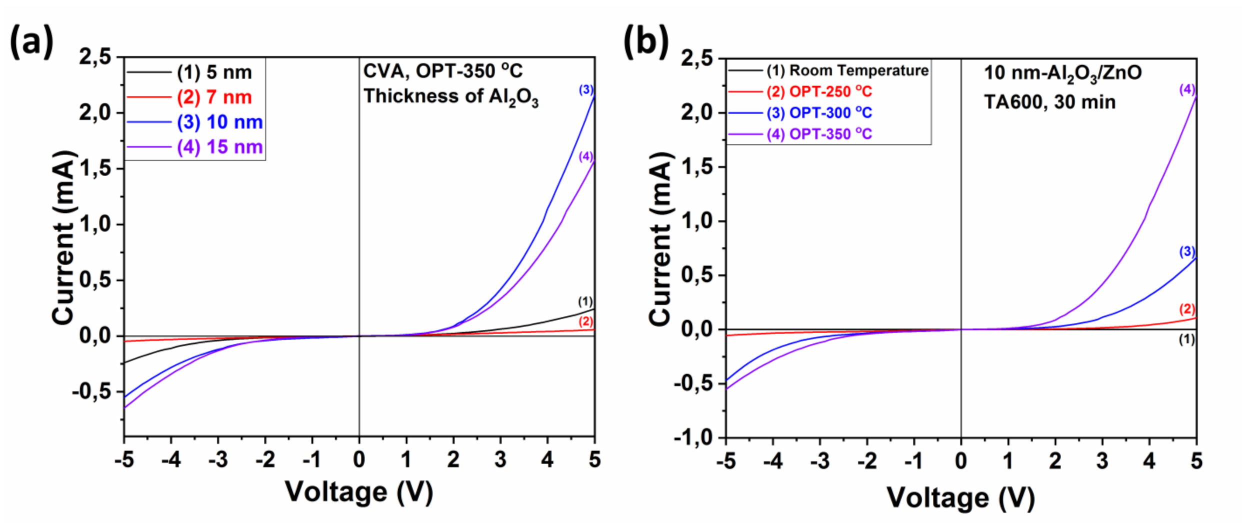

Figure S4. (a) Current-voltage characteristics of the Al_2O_3/ZnO heterostructures with different thicknesses of the Al_2O_3 overlayer. (b) The current-voltage characteristics of the Al_2O_3/ZnO heterostructures with an Al_2O_3 thickness of 10 nm is shown at different operating temperatures.

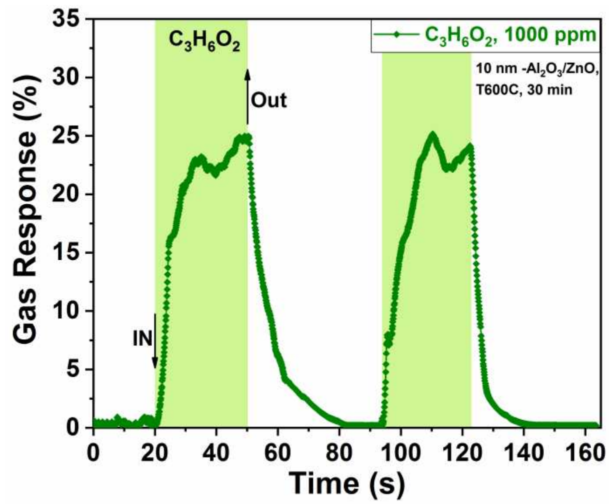

Figure S5. (a) Dynamic response to 1000 ppm of $C_3H_6O_2$ vapors for the Al_2O_3/ZnO heterostructures thermally annealed at 600 °C for 30 min with an Al_2O_3 thickness of 10 nm.

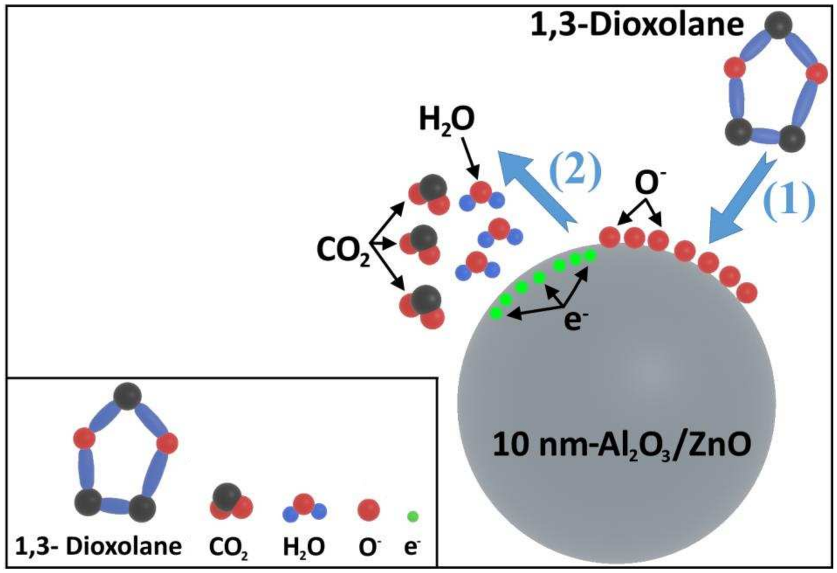

Figure S6. The interaction of the 1,3-Dioxolane molecule with oxygen ions on the surface of the Al_2O_3/ZnO heterostructure.

Table S1. Surface energies (γ_r) for the pristine α-$Al_2O_3(0001)$ and $ZnO(10\bar{1}0)$ surfaces as well as surface free energy (σ_{int}) for the $Al_2O_3/ZnO(10\bar{1}0)$ interface. The average atomic charges (q) and work function (Φ) are also indicated for each surface.

Surface	α-$Al_2O_3(0001)$		$ZnO(10\bar{1}0)$		$Al_2O_3/ZnO(10\bar{1}0)$	
		layer		layer		layer
γ_r/σ_{int} (meV Å^{-2})	110[a]		84[b]		99	
$q_{Al/Zn}$ (e$^-$ atom^{-1})	2.410	Al−1	1.152	Zn−O−1	1.148	Zn_3−O_4−1
	2.467	Al−3	1.155	Zn−O−2	1.199	Zn in Zn_2−Al_2−O_4−2
					2.415	Al in Zn_2−Al_2−O_4−2
q_O (e$^-$ atom^{-1})	−1.619		−1.154	Zn−O−1	−1.326	Zn_3−O_4−1
			−1.150	Zn−O−2	−1.264	Zn_2−Al_2−O_4−2
Φ (eV)	5.48		5.80[b]		5.35	

[a] Ref. [1], [b] Ref. [2]

Table S2. Adsorption energies (E_{ads}) and charge transfers (Δq) for $C_3H_6O_2$, $C_4H_{10}O_2$, NO_2, PF_5 and H_2O on the α-Al_2O_3(0001) and ZnO $(10\bar{1}0)$ surfaces as well as on the Al_2O_3/ZnO$(10\bar{1}0)$ interface. The adsorption site of the adsorbate is also indicated. A negative value of Δq denotes that the adsorbate gains electron charge.

Adsorbate	α-Al_2O_3(0001)		ZnO$(10\bar{1}0)$		Al_2O_3/ZnO$(10\bar{1}0)$		
	E_{ads} (eV)	Δq (e^-)	E_{ads} (eV)	Δq (e^-)	Site	E_{ads} (eV)	Δq (e^-)
$C_3H_6O_2$	−1.593	0.019	−1.034	0.048	Al	−0.608	−0.018
					Zn	−1.401	0.065
$C_4H_{10}O_2$	−1.531	0.019	−0.895	0.044	Al	−0.652	−0.022
					Zn	−1.279	0.040
NO_2	−0.859	−0.428	−0.674	−0.361	Al	−0.226	−0.041
					Zn	−0.861	−0.476
PF_5	−1.783	−0.228	−0.349	−0.016	Al	−0.326	−0.027
					Zn	−0.430	−0.023
H_2O	−1.297	0.011	−1.138	0.013	Al	−0.103	−0.005
					Zn	−1.226	0.034

References

[1] B. Ramogayana, D. Santos-Carballal, K.P. Maenetja, N.H. de Leeuw, P.E. Ngoepe, Density functional theory study of ethylene carbonate adsorption on the (0001) surface of aluminum oxide α-Al_2O_3, ACS Omega. 6 (2021) 29577–29587. https://doi.org/10.1021/acsomega.1c03771.

[2] V. Postica, A. Vahl, J. Strobel, D. Santos-Carballal, O. Lupan, A. Cadi-Essadek, N.H. De Leeuw, F. Schütt, O. Polonskyi, T. Strunskus, M. Baum, L. Kienle, R. Adelung, F. Faupel, Tuning doping and surface functionalization of columnar oxide films for volatile organic compounds sensing: experiments and theory, J. Mater. Chem. A. 6 (2018) 23669–23682. https://doi.org/10.1039/C8TA08985J.