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Supporting Information

Al₂O₃/ZnO Composite-Based Sensors for Battery Safety Applications: An Experimental and Theoretical Investigation

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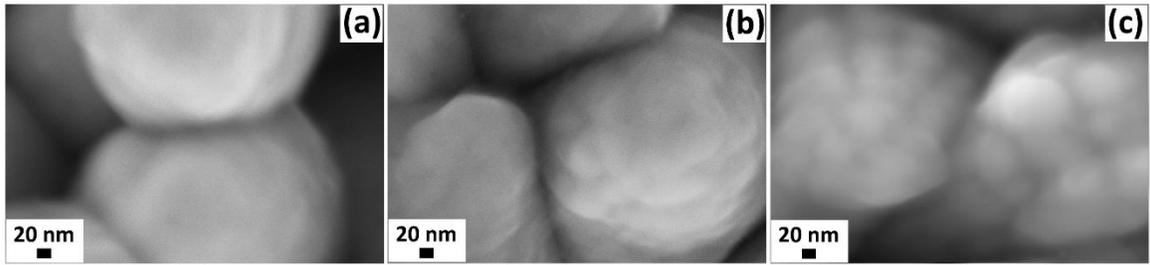


Figure S1. Scanning electron microscopy (SEM) images of the Al₂O₃/ZnO heterostructures at high magnification after the ALD process and deposition of the Al₂O₃ overlayer with thicknesses of: (a) 7 nm; (b) 10 nm; and (c) 12 nm.

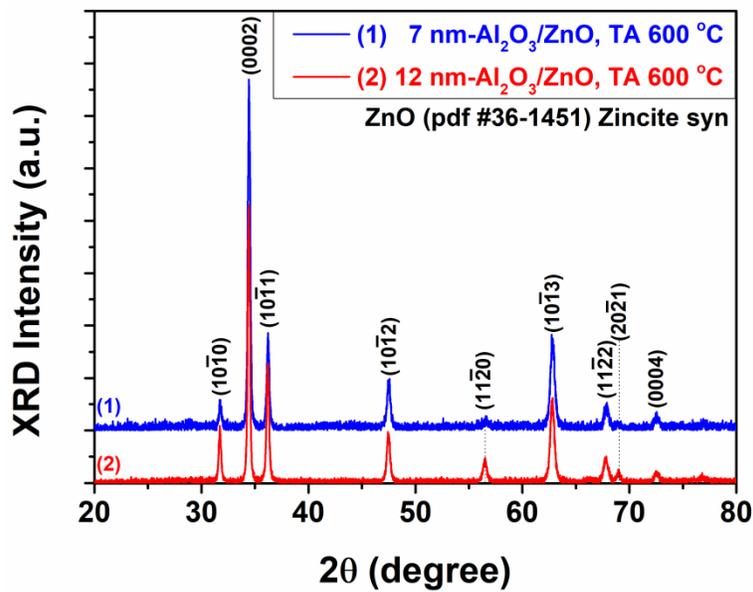


Figure S2. X-ray diffraction (XRD) patterns of the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures thermally annealed at 600 °C for 30 min with different thicknesses of the Al_2O_3 overlayer: 7 nm – curve 1 and 12 nm – curve 2.

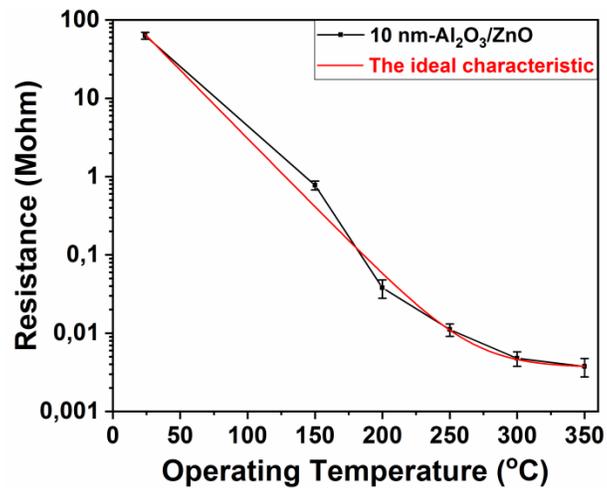


Figure S3. Electrical resistance as a function of the operating temperature.

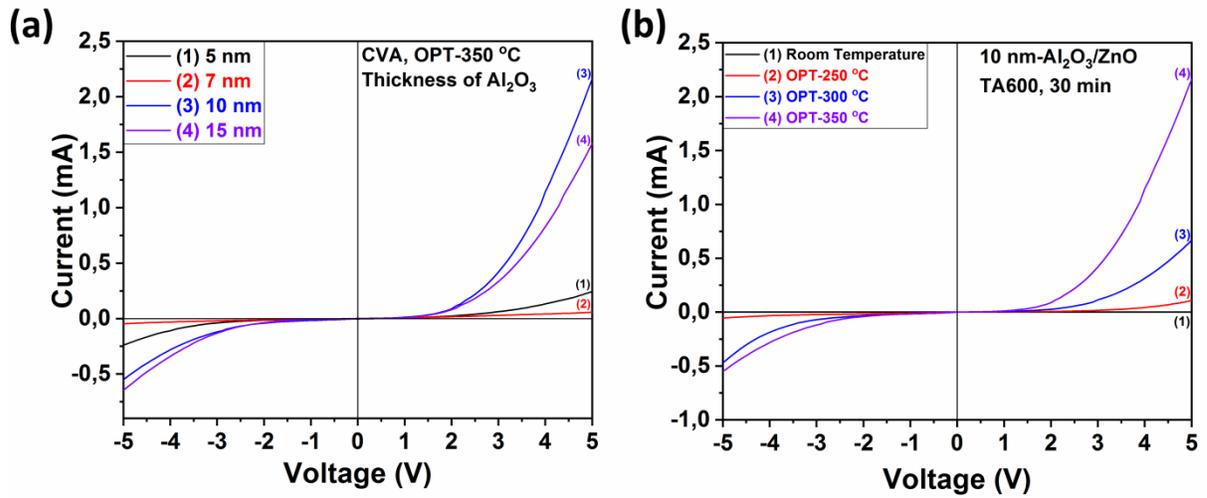


Figure S4. (a) Current-voltage characteristics of the Al₂O₃/ZnO heterostructures with different thicknesses of the Al₂O₃ overlayer. (b) The current-voltage characteristics of the Al₂O₃/ZnO heterostructures with an Al₂O₃ thickness of 10 nm is shown at different operating temperatures.

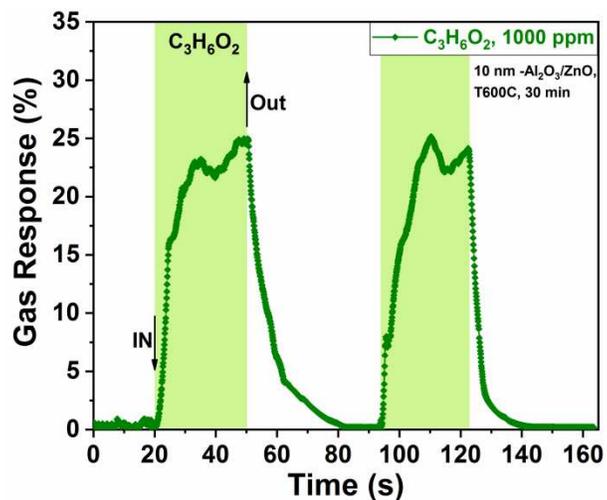


Figure S5. (a) Dynamic response to 1000 ppm of $\text{C}_3\text{H}_6\text{O}_2$ vapors for the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures thermally annealed at 600 °C for 30 min with an Al_2O_3 thickness of 10 nm.

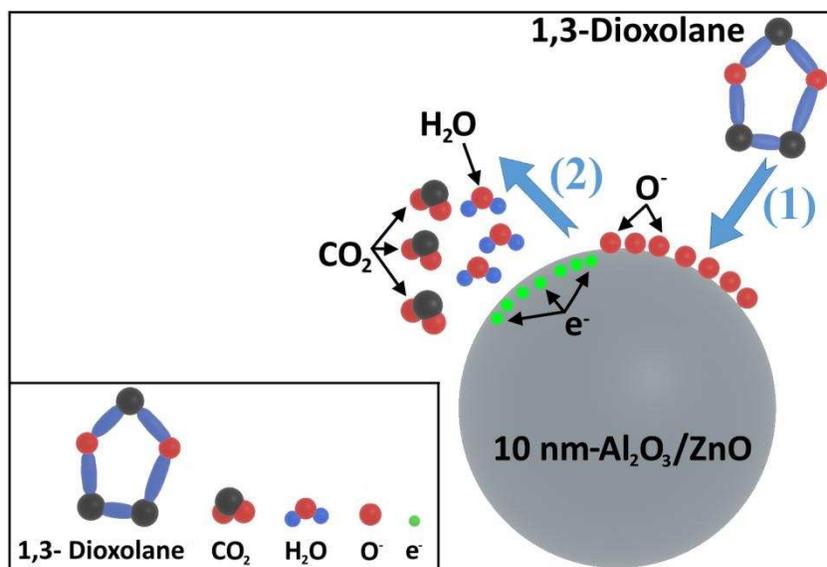


Figure S6. The interaction of the 1,3-Dioxolane molecule with oxygen ions on the surface of the Al₂O₃/ZnO heterostructure.

Table S1. Surface energies (γ_r) for the pristine α -Al₂O₃(0001) and ZnO(10 $\bar{1}$ 0) surfaces as well as surface free energy (σ_{int}) for the Al₂O₃/ZnO(10 $\bar{1}$ 0) interface. The average atomic charges (q) and work function (Φ) are also indicated for each surface.

Surface	α -Al ₂ O ₃ (0001)		ZnO(10 $\bar{1}$ 0)		Al ₂ O ₃ /ZnO(10 $\bar{1}$ 0)	
	layer		layer		layer	
$\gamma_r/\sigma_{\text{int}}$ (meV \AA^{-2})	110 ^a		84 ^b		99	
$q_{\text{Al/Zn}}$ (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
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 $\text{C}_3\text{H}_6\text{O}_2$, $\text{C}_4\text{H}_{10}\text{O}_2$, NO_2 , PF_5 and H_2O on the $\alpha\text{-Al}_2\text{O}_3(0001)$ and $\text{ZnO}(10\bar{1}0)$ surfaces as well as on the $\text{Al}_2\text{O}_3/\text{ZnO}(10\bar{1}0)$ interface. The adsorption site of the adsorbate is also indicated. A negative value of Δq denotes that the adsorbate gains electron charge.

Adsorbate	$\alpha\text{-Al}_2\text{O}_3(0001)$		$\text{ZnO}(10\bar{1}0)$		Site	$\text{Al}_2\text{O}_3/\text{ZnO}(10\bar{1}0)$	
	E_{ads} (eV)	Δq (e^-)	E_{ads} (eV)	Δq (e^-)		E_{ads} (eV)	Δq (e^-)
$\text{C}_3\text{H}_6\text{O}_2$	-1.593	0.019	-1.034	0.048	Al	-0.608	-0.018
					Zn	-1.401	0.065
$\text{C}_4\text{H}_{10}\text{O}_2$	-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

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- [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 -Al₂O₃, *ACS Omega*. 6 (2021) 29577–29587. <https://doi.org/10.1021/acsomega.1c03771>.
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