Supporting Information

Room-Temperature Photodetectors and VOCs sensors based on Graphene Oxide – ZnO Nano-Heterojunctions

Eleonora Pargoletti,^{1,2} Umme H. Hossain,³ Iolanda Di Bernardo,⁴ Hongjun Chen,⁴ Thanh Tran-Phu,⁴ Josh Lipton-Duffin,⁵ Giuseppe Cappelletti,^{1,2*} and Antonio Tricoli^{4*}

¹ Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133, Milano, Italy

² Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121, Firenze, Italy

³ Department of Electronic Materials Engineering, Research School of Physics and Engineering, The Australian National University, Canberra ACT 2601, Australia

⁴ Nanotechnology Research Laboratory, College of Engineering and Computer Science, The Australian National University, Canberra ACT 2601, Australia

⁵ Institute for Future Environments (IFE), Central Analytical Research Facility (CARF), Queensland University of Technology (QUT), Brisbane, Australia

e-mails: giuseppe.cappelletti@unimi.it; antonio.tricoli@anu.edu.au

Figure S1. (a) XRD patterns $(2\theta = 10-80^\circ)$ of graphite, graphene oxide (GO), pure ZnO and hybrid ZnO/GO nanocomposites (100% intensity reflection planes have been assigned to the main phase of each compound). (b) FTIR of all the investigated samples and (c, d) fitted Raman spectra of graphite and graphene oxide (the deconvolution in eight and five modes by using the Lorentzian function has been reported, respectively).

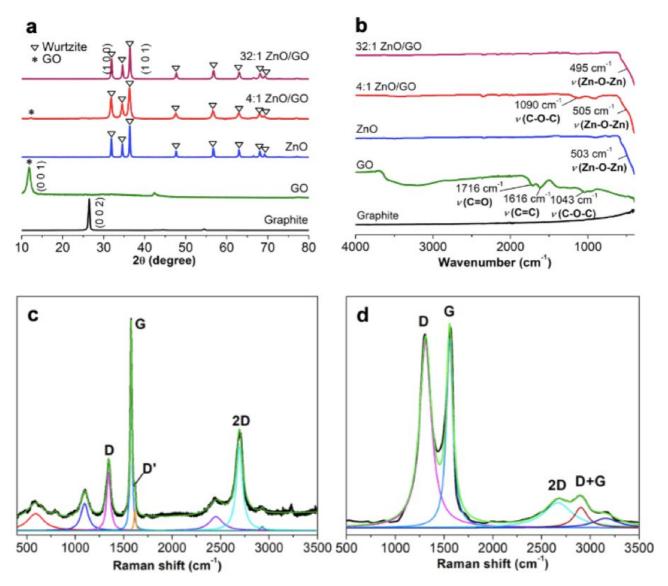


Figure S2. XPS surveys of (a) graphite, GO and (b) ZnO/based samples (inset: Zn/C atomic ratio from XPS surveys).

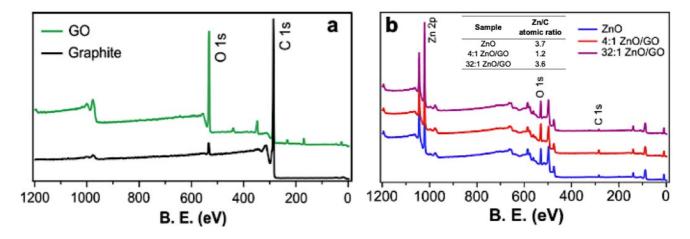


Figure S3. (a) UV-Vis spectra of both pure and GO-hybrid ZnO films on glass substrate. Band gap values determined by (b) Tauc plot ($n = \frac{1}{2}$, direct allowed band gap) and (c) Kubelka-Munk elaboration.

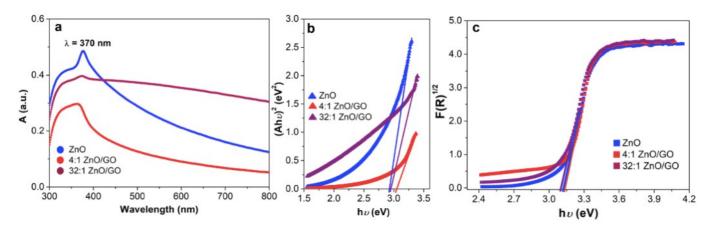


Figure S4. Pure ZnO sensor response when exposed to 8 ppm of ethanol, in simulated air ($20\% O_2 - 80\% N_2$), at RT and under UV light

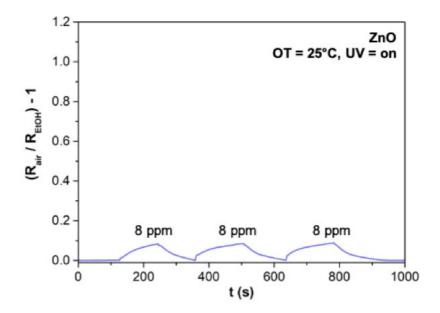


Figure S5. (a) Pure ZnO and (b–d) hybrid 32:1 ZnO/GO sensors response when exposed to different ethanol concentrations (1 ppm to 10 ppb) in simulated air ($20\% O_2 - 80\% N_2$). OT = Operating Temperature.

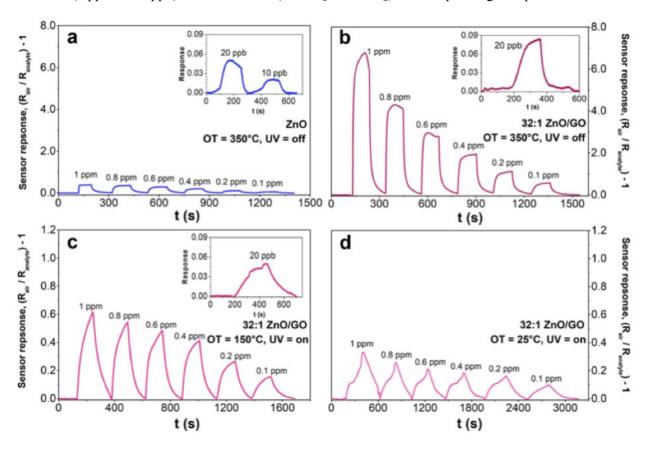
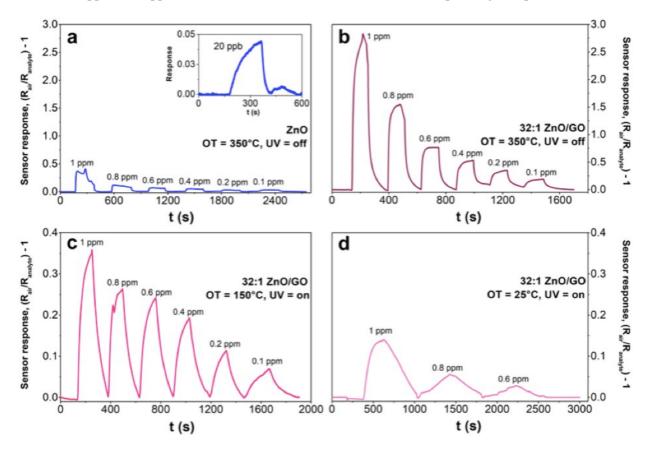
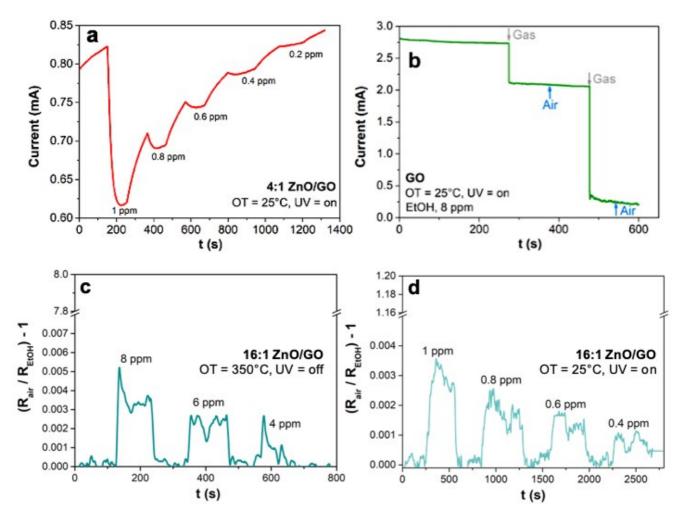


Figure S6. (a) Pure ZnO and (b–d) hybrid 32:1 ZnO/GO sensors response when exposed to different ethylbenzene concentrations (1 ppm to 20 ppb) in simulated air ($20\% O_2 - 80\% N_2$). OT = Operating Temperature.



For all the three detected species (namely ethanol, acetone and ethylbenzene), a distinction between high and low operating temperatures in terms of selectivity can be made. Particularly, ZnO reaches very low 10-20 ppb-concentrations whereas 32:1 ZnO-GO achieves 20 ppb level towards ethanol and acetone, and only 100 ppb of ethylbenzene (Figures 4, S5 and S6). Furthermore, the signal intensities obtained with the hybrid sample are always definitely higher with respect to pure ZnO. As concern RT sensing, only with 32:1 ZnO/GO a signal was recorded (Figures 4, S5 and S6). In this case, instead, slightly greater target analytes concentrations were detected, namely 100 ppb of ethanol and acetone and 600 ppb of ethylbenzene. Besides, as for chemical sensing, photodetectors measurements (see Table 2) reveal a very similar sensitivity trend. Specifically, for photocurrent, responsivity and detectivity values, the trend is always 32:1 ZnO/GO > ZnO > 4:1 ZnO/GO, thus corroborating the higher performance of the 32:1 ZnO/GO hybrid material.

Figure S7. (a) Hybrid 4:1 ZnO/GO, (b) pure GO, (c,d) hybrid 16:1 ZnO/GO sensors responses when exposed to different ethanol concentrations, in simulated air (20% $O_2 - 80\% N_2$) at (a,b,d) room temperature (under UV light) and (c) 350°C.



As stated in the Results and Discussion section, a range between 4:1 and 32:1 ZnO-GO ratio has been evaluated. Particularly, in the range between 4:1 and 32:1 ZnO/GO, two other ratios were investigated, namely 8:1 and 16:1 (Figures S7c and d). Hence, in order to have an overview on the compounds performances and to identify the optimal ZnO-GO ratio, ethanol was adopted as the reference target gas, due to the higher responses obtained towards this species. Notably, as reported in Figures S7c and d, 16:1 ZnO/GO powder does not show a good signal both at 350°C and RT (under UV light). Therefore, since ratios lower than 32:1 do not have very promising features, 32:1 ZnO/GO hybrid can be considered the optimum combination of GO and ZnO due to the enhanced sensing performances, even with respect to pristine ZnO.

Figure S8. Example of 32:1 ZnO/GO response to oxidizing species such as NO₂, at RT by exploiting the UV light. Tests were conducted in simulated air $(20\% O_2 - 80\% N_2)$.

