Aqueous Electrolyte-Gated ZnO Transistors for Environmental and Biological Sensing

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Abstract

Electrolyte-gated transistors (EGTs) based on ZnO thin films, obtained by solution processing of suspensions of nanoparticles, have a low turn-on voltage (<0.5 V), a high on/off ratio and transconductance exceeding 0.2 mS. Importantly, the ZnO surface can be functionalized with a large variety of molecular recognition elements, making these devices ideal transducers in physiological and environmental monitoring. We present simple glucose-sensing and ion-selective EGTs, demonstrating the versatility of such devices in biosensing.

The development of simple yet reliable sensors for the identifcation of biomolecules, pathogens, ions and pollutants has become a primary research challenge due to the expected widespread application and integration of sensors in our society and environment.[1–3] One illustrative example is the glucose sensor which, despite being commercially available for the past 25 years, is still attracting considerable research efforts because of the demand for low-cost and reliable methods for the self-monitoring of blood glucose.[4–6] While the commonly applied transduction mechanisms are mostly electrochemical or optical,[7,8] the application of field-effect transistors (FETs) to biosensing has gained increasing attention due to the intrinsic signal amplification of such devices.[9,10] From the perspective of their low-cost and simple manufacturing process, the organic thin-film transistors represent the most promising candidates for such applications, thanks also to the unique possibility of tuning the properties of the organic semiconductor through rational chemical design.[11–13] A limited number of examples exist of conjugated molecular materials that are stable in an aqueous environment.[14,15] Metal oxides represent a possible alternative as the semiconductor in biosensing applications. They have high carrier mobilities,[16] easiness of surface functionalization,[17,18] and can be processed by simple solution methods, leading to inexpensive devices, even on flexible substrates.[19,20] Unlike most organic semiconductors, metal oxide semiconductors are usually stable in air and in water, an essential prerequisite for sensor devices working in an aqueous or physiological environment. A type of transistor which is especially suited for biosensing is the electrolyte-gated transistor (EGT). The working principle of EGTs is analogous to that of traditional FETs, in which the gate insulator (usually a solid high-k dielectric) is replaced by a convenient electrolyte (solid, liquid or gel).[21,22] The variation of the conductivity of the channel with the gate voltage (V_G) is determined by the capaci-tance of the nanometrically thin electrical double

layer (EDL) that forms at the interface between the electrolyte and the semiconductor channel as a consequence of the ionic displacement. The capacitance of an EDL can be orders of magnitude larger compared to that of traditional insulators, and for this reason EGTs usually show high transconductance (g_m) at very low voltages.[21] A few recently reported examples of EGTs employing semiconducting metal oxides thin films suggest that such devices can have performances superior to the associated FET, and show how they could even be used in the development of biosorbable, implantable devices.[23,24] A unique feature of metal oxides is that it is possible to obtain stable nanoparticle (NP) dispersions from them, which can be casted forming nanostructured thin films with enhanced surface area and tunable properties. Taking advantage of the unique properties of metal oxides and EGTs, in this paper we present aqueous EGTs employing solution processed ZnO NPs as the semiconducting material. The high surface area of the nano- structured channel further enhances the EDL capacitance and allows the saturation of the drain current (I_g) at V_g as low as 1.1 V. What makes EGTs ideal candidates for sensing applica tions is that the drain current is influenced by any physical or chemical modification of the EDL. As a proof of principle, we demonstrate the potential of these devices by presenting ion-selective EGTs, realized through the integration of an ion-selective membrane (ISM) into the device architecture, as well as simple enzymatic glucose sensors, obtained by the covalent binding of the enzyme to the ZnO surface. The EGTs were prepared on glass slides with pre-patterned indium tin oxide (ITO) source–drain electrodes, with a channel width (W) and length (L) of 2 mm and 20 mm, respectively ($\frac{W}{L} = 100$), Fig. 1a). The ITO/glass substrates were cleaned by chemical and plasma methods. Commercially available ZnO NPs in suspension in ethanol (5 wt%) were filtered through a 0.22 mm PTFE membrane and spin-coated onto the substrates. The layers were subsequently annealed at 450 C for 30 minutes in order to remove the stabilizing ligands (Fig. S1†). The final thickness of the layers was about 60 nm. In spite of the high annealing temperature, the ZnO surface shows a high porosity (Fig. 1b), with the grain size resembling the average particle size of the suspension (<35 nm). The grazing incident X-ray diffraction (GIXRD) pattern confirms a high degree of crystal linity of the nanostructured film. Moreover, the crystal size estimated from signal broadening on the (101) direction is 35 nm, which is consistent with morphological measurements and manufacturer's datasheet. Glass wells, used to confine the electrolyte, were integrated onto the transistor array using a thin layer of polydimethylsiloxane (PDMS). An Ag/AgCl pellet elec trode or a platinum wire immersed in the electrolyte were used as transistor gate electrodes.

The performance of the transistors was evaluated in aqueous electrolyte (KCl 0.1 M) using a porous Ag/AgCl pellet as the gate electrode (Fig. 2). The output characteristics at five different gate voltages are reported in Fig. 2a. The device shows a high modulation of the current, both in the linear and saturation regimes, with large saturation currents of >75 mA at very low driving voltages (V_g = 1.1 V, V_d > 0.5 V). A turn on voltage (V_{on}) of only 0.4 V is observed from the transfer curve measured at V_d = 0.4 V (Fig. 2b), with a corresponding threshold voltage of V_{th} = 0.57 V and a current on/off ratio of about 10^3. The high current modulation at very low voltages is the hallmark of EGTs, and can be quantified by the device transconductance $g_m = \frac{\partial I_d}{\partial V_g}$. The maximum g_m = 215 mS was obtained for V_g = 0.88 V (Fig. 2b), giving a normalized transconductance per channel width of $\frac{g_m}{W}$ = 107 mS mm^{-1}, which compares favorably to the values reported for atomically flat, single crystal ZnO EGTs (~800 mS mm^{-1}).[25] It is important to point out that the device performances are limited by the absence of insulation between the ZnO-NP films and the electrolyte

in the area surrounding the channel. Moreover, nanostructured films, when compared to poly-/mono-crystalline layers, will suffer from reduced charge mobility due to the intrinsically high defect concentrations. In spite of these limitations, the ZnO-NP EGT performs favorably and exhibits a saturation electron mobility of 0.81 $cm^2\ V^{-1}\ s^{-1}$ (calculated using the EDL capacitance C_{dl} = 8.04 mF cm^{-2}, ESI†), in agreement with values obtained using compact ZnO thin flms gated through ion-gel dielectrics.[26] The capacitance of the EDL for the nanostructured ZnO almost doubles that of a flat ZnO layer (C_{dl} = 4.14 mF cm^{-2}), confirming the enhancement effect of the increased surface area (ESI, Fig. S2†).

The remarkable device performance in water-based electro-lytes makes the ZnO NP-based EGTs attractive elements for sensors working in an aqueous environment. Since the working principle of these devices is based on the displacement of cations in the proximity of the metal oxide surface, their use as ion sensors is the most obvious direct application. Ion-selective EGTs were prepared by integrating a polymer ISM doped with a potassium ionophore, using an architecture recently described for electrochemical transistors based on both semiconducting and conducting polymers.[27,28] The device structure (Fig. 3a) consists of a reference electrolyte (KCl 10^{-2} M) in contact with the ZnO channel, separated from the analyte by the ISM. The ISM consists of a polyvinylchloride matrix containing a plasti- cizer, an anionic exchanger and the potassium ionophore III. As previously detailed, the solution containing the ISM components was drop-casted onto a glass substrate and, after drying, the obtained membrane was transferred onto the EGT array.[28] Changes in the K^+ concentration (c_{K^+}) in the sample shift the potential at the electrolyte/membrane interfaces and the resulting electric field drops onto the channel modulating its conductivity.[29] Stock solutions with increasing K^+ concentrations were exchanged in the upper chamber while monitoring the consequent variation of the current I_d. Fig. 3b shows the response of the transistor, $\frac{\Delta I}{I_0}$ (with ΔI being the difference between I_d at a given concentration and I_0, the current at infinite dilution), for c_{K^+} spanning 7 orders of magnitude. The response of the device was measured 60 s after injection with the saline solution, but we observed that at least 90% of the current response was reached in less than 20 s (Fig. S2†). The IS-EGTs are capable of sensing K^+ with a detection limit of c_{K^+} 4.7×10^{-4} M and with a thirty-fold increase in the current for the concentration range $10^{-4} \leq c_{K^+} \leq 10^{-1}$ M. The detection limit was estimated as the cross point between the slope of the dataset and a line corresponding to the noise level of the device (I_d at a low K^+ concentration). It is important to emphasize again that the ZnO film exposed to the electrolyte is not restricted solely to the channel area, leading to a detection limit which is somewhat higher compared to what is expected by using this particular ISM formulation.

Through the precise patterning of the channel together with insulation of the ITO contacts and interconnects, we expect the device to show a sensitivity and detection limit in agreement with similar ion-sensing structures.[28] A key advantage of metal oxides over conducting polymers or molecular semiconductors is that it is possible to tune their properties as well as introduce tailored functionalities by direct surface modifications.[30] As in most metal oxides, the surface of ZnO is rich in –OH groups, which can be readily functionalized by electrostatic or covalent bonding of virtually any type of molecule.[31] For these reasons, ZnO has been widely used as an electroactive substrate in the preparation of amperometric enzymatic sensors.[32] As a proof of principle, we prepared simple glucose-sensing EGTs by covalent binding of the enzyme glucose oxidase (GOD) onto the ZnO NPs' surface. GOD was grafted onto the metal oxide by using (3-gly- cidyloxypro-

pyl)-trimethoxysilane (GOPS) as the covalent linker. The methoxysilane functionality of the GOPS binds onto the ZnO surface, while the epoxide group allows the formation of a secondary amine bond with the enzyme (Fig. 4a).33,34 A 10 wt% GOPS solution in isopropanol (iPrOH) was deposited by spin coating onto the ZnO channel and annealed at 100 ºC for 10 minutes. The layer was subsequently rinsed with 0.1 M KCl in water to remove the excess of unbound GOPS. Afterwards, an aqueous GOD solution was added onto the transistor and was allowed to dry at RT overnight. Before the device characterization was carried out, the functionalized ZnO films were rinsed gently with 0.1 M KCl in water to remove any excess of unattached GOD. For the sensor characterization, a Pt wire was used as the gate electrode in order to avoid the necessity of adding a redox mediator.[4] We observed an increased V_{th} of 0.83 V and a reduction of the on/off ratio to about 2 orders of magnitude (Fig. 4b), in accordance with the increased electrode work function of Pt.[35] In this case, the achievement of the current saturation (and thus higher on/off ratio) is limited by the electrochemical window of water. The current response $\Delta I/I_0$ of the sensor was measured 60 s after the injection with stock 0.1 M KCl aqueous solutions with increasing D-glucose concentrations [Glc], and is reported in Fig. 4c.

The operation of the device as a glucose sensor confirms that the biological activity of the enzyme is preserved after its covalent bonding onto the ZnO NPs. The functionalized EGT is capable of sensing Glc in the concentration range of $10^{-4} \leq [\text{Glc}] \leq 10^{-1}$ M, with the highest sensitivity (slope of the response curve) above 10 M, which matches the physiological concentration of glucose in humans (1–20 mM).[4] The corre- sponding detection limit, calculated as in the case of the ion- selective transistor, is 7×10^{-4} M. As a final test, we evaluated the overall stability of the EGT by continuously cycling it between $V_g = 0$ V and $V_g = 0.9$ V (maximum of trans-conductance) at $V_d = 0.4$ V. The on/off ratio readily reaches and stabilizes at 60% of its maximum value for at least 2.5 h (ESI, Fig. S4†), indicating a remarkable lifetime of the aqueous electrolyte-gated ZnO transistor.

Conclusions

In summary, we have presented electrolyte-gated transistors (EGTs) prepared by a simple solution processing of commercial ZnO NP suspension. The device can work in an aqueous envi- ronment at biases as low as 1 V, and shows electron mobility of 0.81 cm^2 V s^{-1}. Of great importance is the versatility of such devices for the realization of a variety of biosensors. Ion-selective membranes can be integrated with the electrolyte-gated transistors leading to sensitive ion sensors capable of determining K^+ concentration over a wide range of concentrations. In addition to this, ZnO is an extraordinary platform for further chemical modifications, since virtually any type of chemical transducer (electrochemical and even optical) can be bonded onto its surface leading to a variety of different functionalities. Through the use of an alkoxysilane functional group, we covalently attached glucose oxidase to the surface of the transistor channel, resulting in a simple sensor for the physiological monitoring of glucose. These results clearly show the potential of metal oxide electrolyte-gated transistors in environmental and biomedical applications, and pave the way for a new generation of low-cost, disposable and even flexible biosensors.

Acknowledgements

This work has been supported by the European Union (HYSENS, Grant STRP 263091), the Spanish Ministry of Economy and Competitiveness (MINECO) (MAT2011-24594), and the Gen- eralitat Valenciana (Prometeo/2012/053). E. B. acknowledges MINECO for an FPI grant. The authors thank Jorge Ferrando and Alejandra Soriano for technical assistance in the charac- terization of the transistors and XRD measurements.

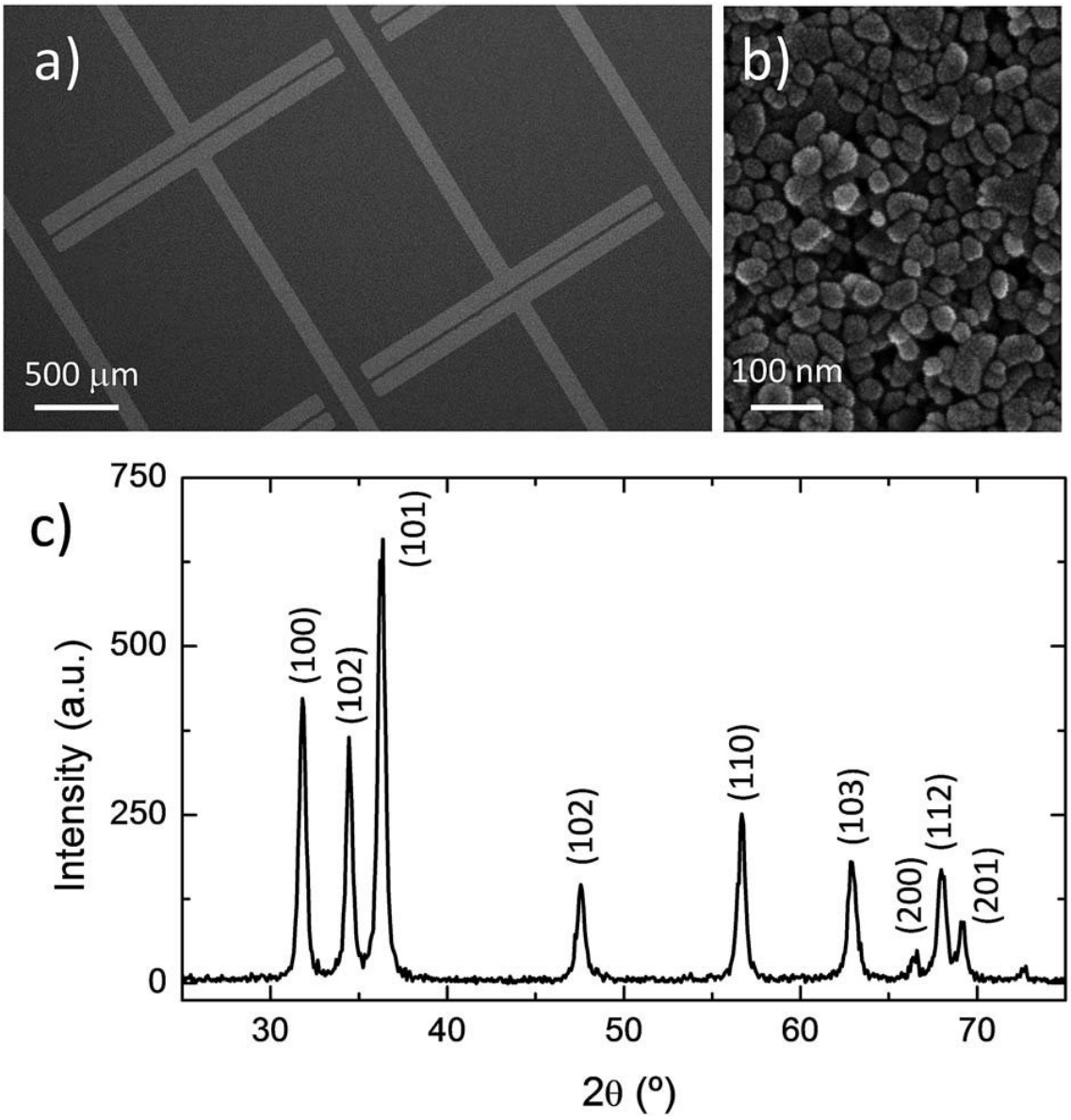

Fig. 1 SEM images of (a) the transistor array radiation with visible ITO source–drain electrodes and (b) the detailed ZnO nanostructured surface. (c) The GIXRD pattern with Cu Ka_1 (l ¼ 1.54056 A˚) of the thin films.

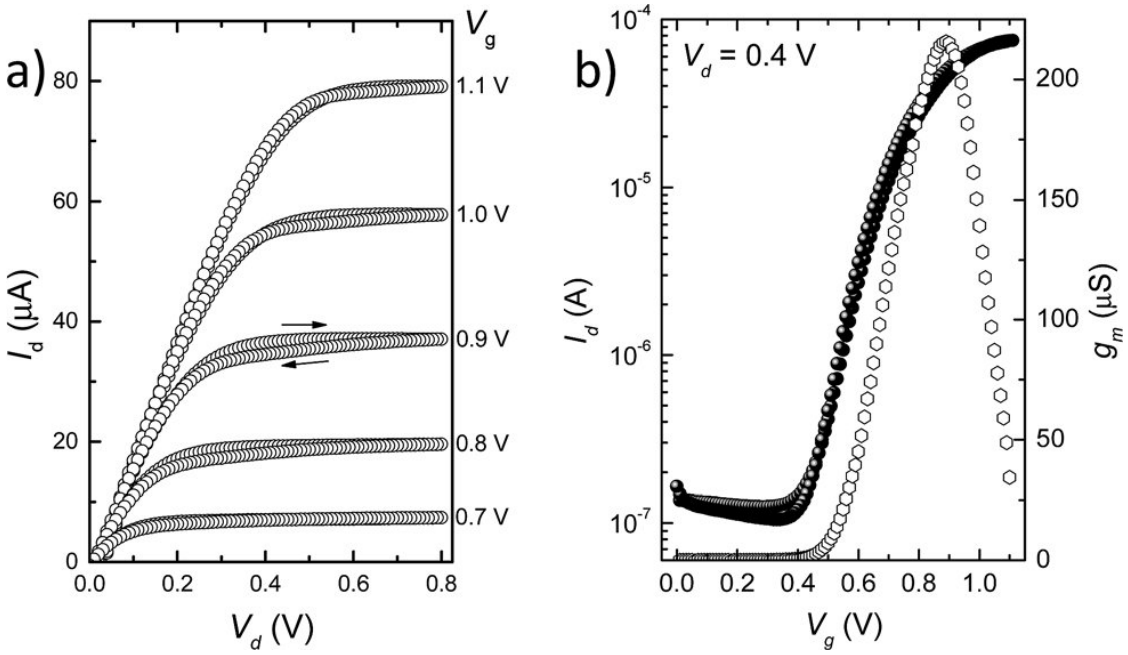

Fig. 2 (a) The output characteristics of the EGTs in aqueous electrolyte with V_g varying from 0.7 V to 1.1 V with a step of 0.1 V. (b) The transfer curve for V_d = 0.4 V (full circles) with the associated trans-conductance (empty hexagons).

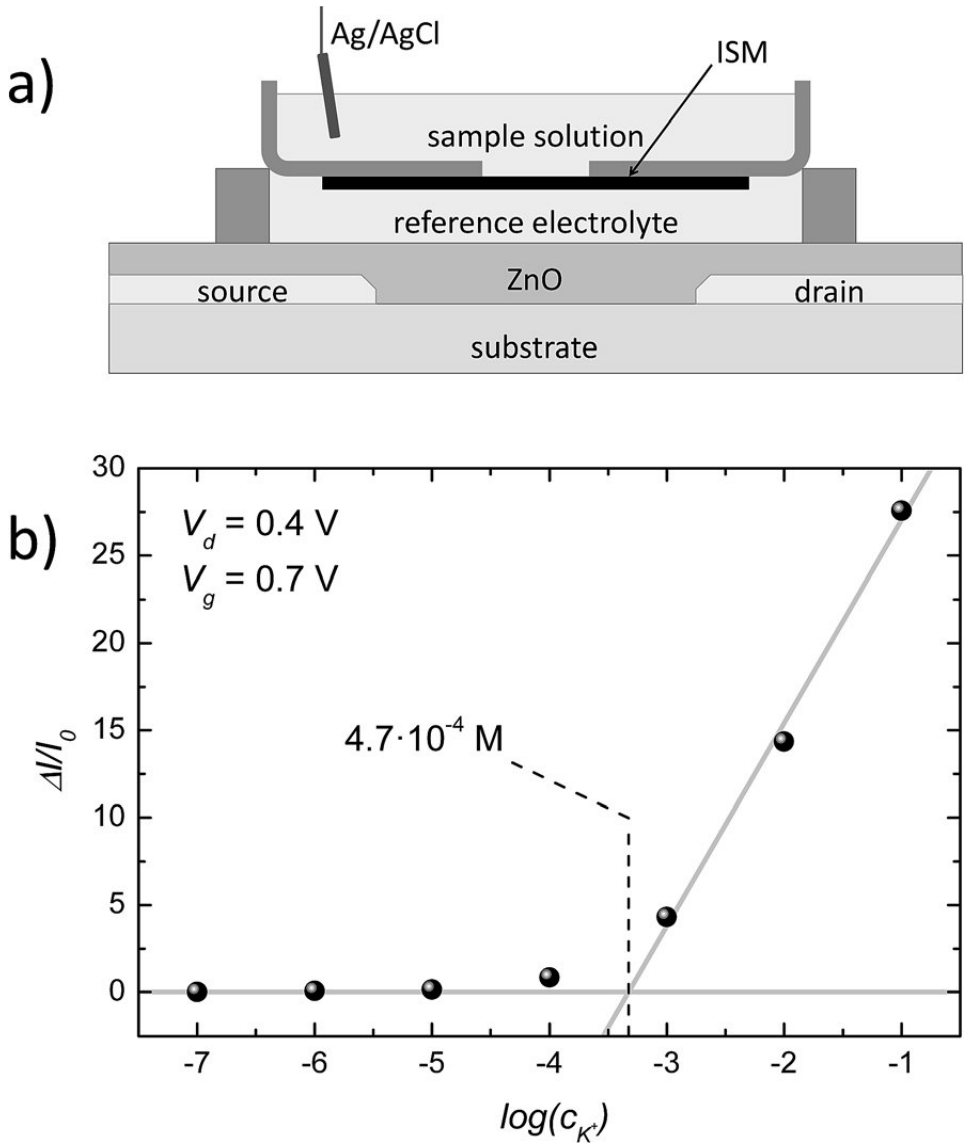

Fig. 3 (a) A schematic of the device architecture used in the prepa-ration of the ion-selective EGTs. (b) The device response as a function of the $c_{K}+$ expressed in decades of molar concentration.

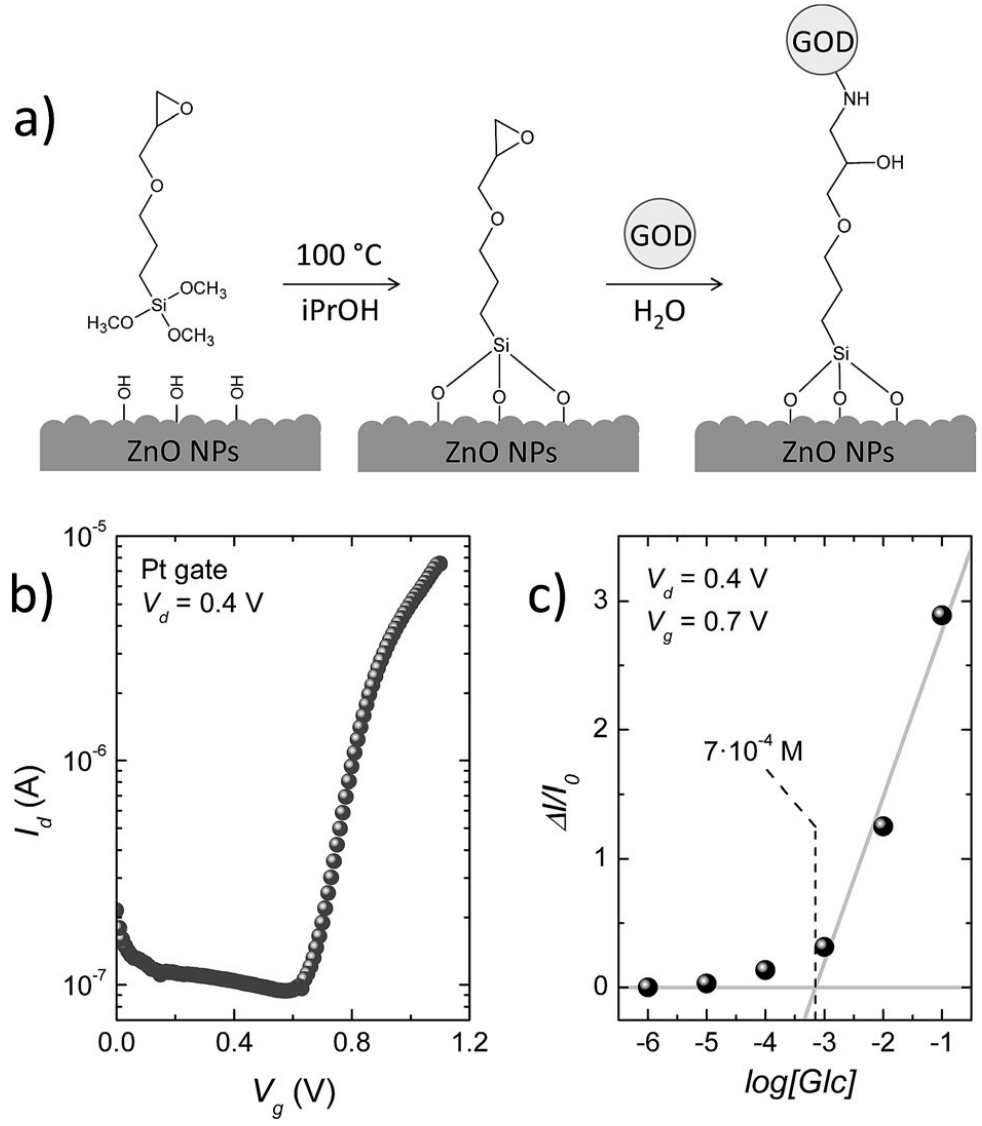

Fig. 4 (a) The reaction scheme for the functionalization of the ZnO NPs' surface with the enzyme GOD. (b) The transfer curve of the GOD-functionalized EGTs employing a Pt gate electrode. (c) The device response to increasing glucose concentration, expressed in decades of molar concentration.

References

1 A. Milenković, C. Otto and E. Jovanov, *Comput. Commun.*, 2006, 29, 2521–2533.
2 A. Pantelopoulos and N. G. Bourbakis, *IEEE Trans. Syst. Man Cybern. C Appl. Rev.*, 2010, 40, 1–12.
3 V. Velusamy, K. Arshak, O. Korostynska, K. Oliwa and C. Adley, *Biotechnol. Adv.*, 2010, 28, 232–254.
4 A. Heller and B. Feldman, *Chem. Rev.*, 2008, 108, 2482–2505.
5 E. H. Yoo and S. Y. Lee, *Sensors*, 2010, 10, 4558–4576.
6 Y. Wang and M. Hu, in *Detection Challenges in Clinical Diagnostics*, The Royal Society of Chemistry, 2013, pp. 65–88, DOI: 10.1039/9781849737302-00065.
7 S. Scarano, M. Mascini, A. P. F. Turner and M. Minunni, *Biosens. Bioelectron.*, 2010, 25, 957–966.
8 N. J. Ronkainen, H. B. Halsall and W. R. Heineman, *Chem. Soc. Rev.*, 2010, 39, 1747–1763.
9 P. Bergveld, *Sens. Actuators, B*, 2003, 88, 1–20.
10 K. I. Chen, B. R. Li and Y. T. Chen, *Nano Today*, 2011, 6, 131–154.
11 M. E. Roberts, A. N. Sokolov and Z. Bao, *J. Mater. Chem.*, 2009, 19, 3351–3363.
12 P. Lin and F. Yan, *Adv. Mater.*, 2012, 24, 34–51.
13 L. Torsi, M. Magliulo, K. Manoli and G. Palazzo, *Chem. Soc.Rev.*, 2013, 42, 8612–8628.
14 O. Knopfmacher, M. L. Hammock, A. L. Appleton, G. Schwartz, J. Mei, T. Lei, J. Pei and Z. Bao, *Nat. Commun.*, 2014, 5, 2595.
15 D. Khodagholy, J. Rivnay, M. Sessolo, M. Gurfinkel, P. Leleux, L. H. Jimison, E. Stavrinidou, T. Herve, S. Sanaur, R. M. Owens and G. G. Malliaras, *Nat. Commun.*, 2013, 4, 2133.
16 M.-G. Kim, H. S. Kim, Y.-G. Ha, J. He, M. G. Kanatzidis, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2010, 132, 10352–10364.
17 D. Weber, S. Botnara¸s, D. V. Pham, J. Steiger and L. De Cola, *J. Mater. Chem. C*, 2013, 1, 3098.
18 M. M. Rahman, A. J. Ahammad, J. H. Jin, S. J. Ahn and J. J. Lee, *Sensors*, 2010, 10, 4855–4886.
19 S. R. Thomas, P. Pattanasattayavong and T. D. Anthopoulos, *Chem. Soc. Rev.*, 2013, 42, 6910–6923.
20 Y. Sun and J. A. Rogers, *Adv. Mater.*, 2007, 19, 1897–1916.
21 S. H. Kim, K. Hong, W. Xie, K. H. Lee, S. Zhang, T. P. Lodge and C. D. Frisbie, *Adv. Mater.*, 2013, 25, 1822–1846.
22 T. Fujimoto and K. Awaga, *Phys. Chem. Chem. Phys.*, 2013, 15, 8983–9006.
23 A. Al Naim and M. Grell, *Appl. Phys. Lett.*, 2012, 101, 141603.
24 L. Torsi, M. Singh, G. Palazzo, G. Romanazzi, G. P. Suranna, N. Ditaranto, C. Di Franco, M. V. Santacroce, M. Y. Mulla, M. Magliulo and K. Manoli, *Faraday Discuss.*, 2014, DOI: 10.1039/c4fd00081a.
25 H. Yuan, H. Shimotani, A. Tsukazaki, A. Ohtomo, M. Kawasaki and Y. Iwasa, *Adv. Funct. Mater.*, 2009, 19, 1046–1053.
26 K. Hong, S. H. Kim, K. H. Lee and C. D. Frisbie, *Adv. Mater.*, 2013, 25, 3413–3418.
27 K. Schmoltner, J. Ko%er, A. Klug and E. J. W. List-Kratochvil, *Adv. Mater.*, 2013, 25, 6895–6899.

28 M. Sessolo, J. Rivnay, E. Bandiello, G. G. Malliaras and H. J. Bolink, *Adv. Mater.*, 2014, 26, 4803–4807.
29 E. Bakker, P. Bühlmann and E. Pretsch, *Chem. Rev.*, 1997, 97, 3083–3132.
30 M. A. Neouze and U. Schubert, *Monatshefte fur Chemie*, 2008, 139, 183–195.
31 Y. Zhang, T. R. Nayak, H. Hong and W. Cai, *Curr. Mol. Med.*, 2013, 13, 1633–1645.
32 Shi, W. Gu, B. Li, N. Chen, K. Zhao and Y. Xian, *Microchim. Acta*, 2014, 181, 1–22.
33 X. Strakosas, M. Sessolo, A. Hama, J. Rivnay, E. Stavrinidou, G. G. Malliaras and R. M. Owens, *J. Mater. Chem. B*, 2014, 2, 2537–2545.
34 D. Jung, C. Streb and M. Hartmann, *Int. J. Mol. Sci.*, 2010, 11,762–778.
35 L. Kergoat, L. Herlogsson, B. Piro, M. C. Pham, G. Horowitz, X. Crispin and M. Berggren, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, 109, 8394–8399.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Electrolyte-gated nanostructured ZnO transistors for environmental and biological sensing

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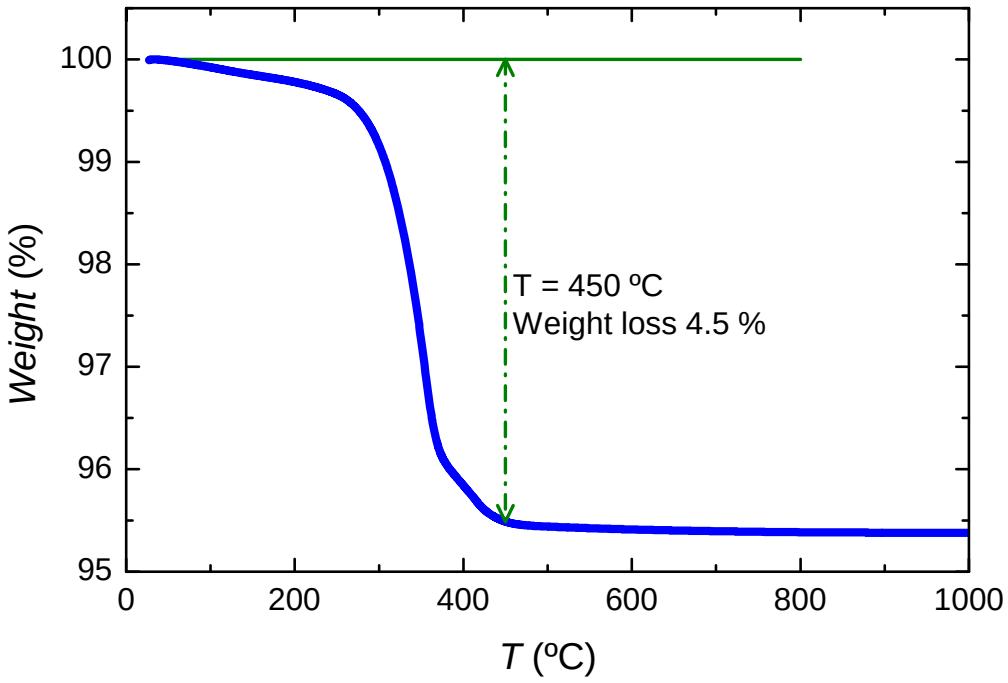

Figure S1. Thermogravimetric analysis of a dry sample of the ZnO nanoparticles used as the semiconducting channel (dispersions were obtained from Sigma Aldrich) in electrolyte-gated transistors. At the annealing temperature used for device preparation (450 ºC), the weight loss is

about 4.5 % and no substantial mass change is observed when further increasing the temperature to 1000 ºC.

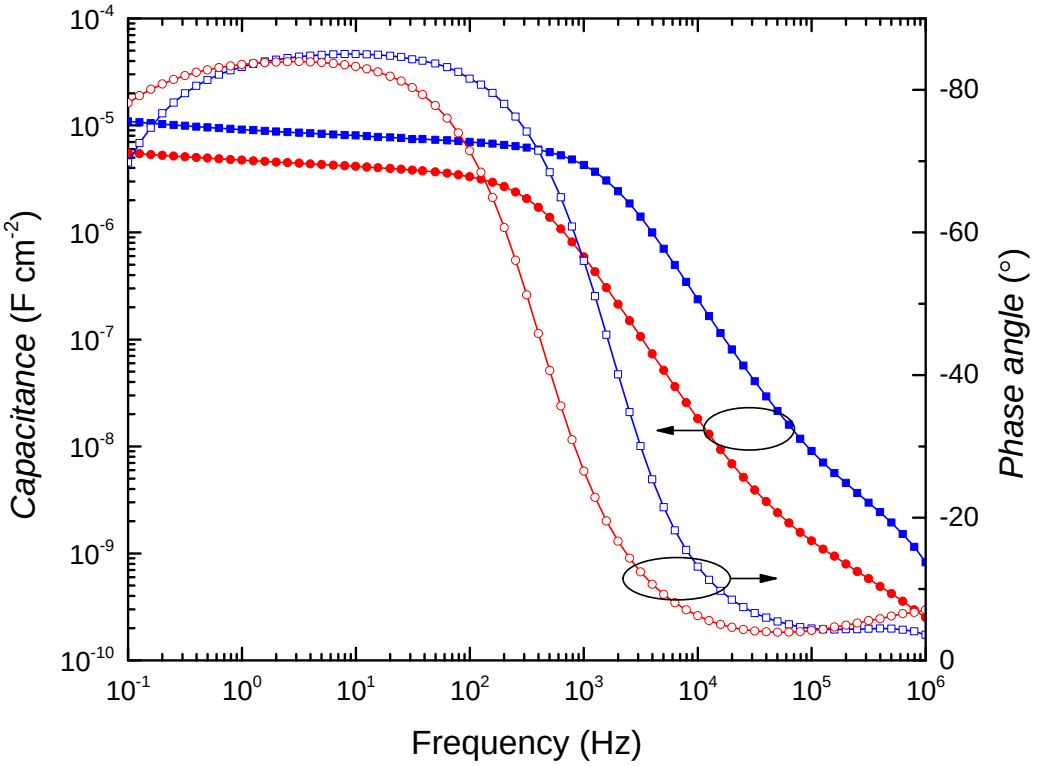

Figure S2. Capacitance (*full squares*) and phase angle (*open squares*) of a nanostructured ZnO films deposited onto an ITO electrode and measured in the three electrode configuration. The specific capacitance was extracted at the minimum of the phase angle (capacitive regime, -85.1º at 10 Hz) and scaled to the electrode area (4.46 mm^2). The capacitance and the phase angle for a flat ZnO layer, deposited by a sol-gel method, are also reported (*full and open circles*). At 10 Hz, the capacitance of the nanostructured ZnO is ~1.9× that of the flat film, confirming the increment of the surface area.

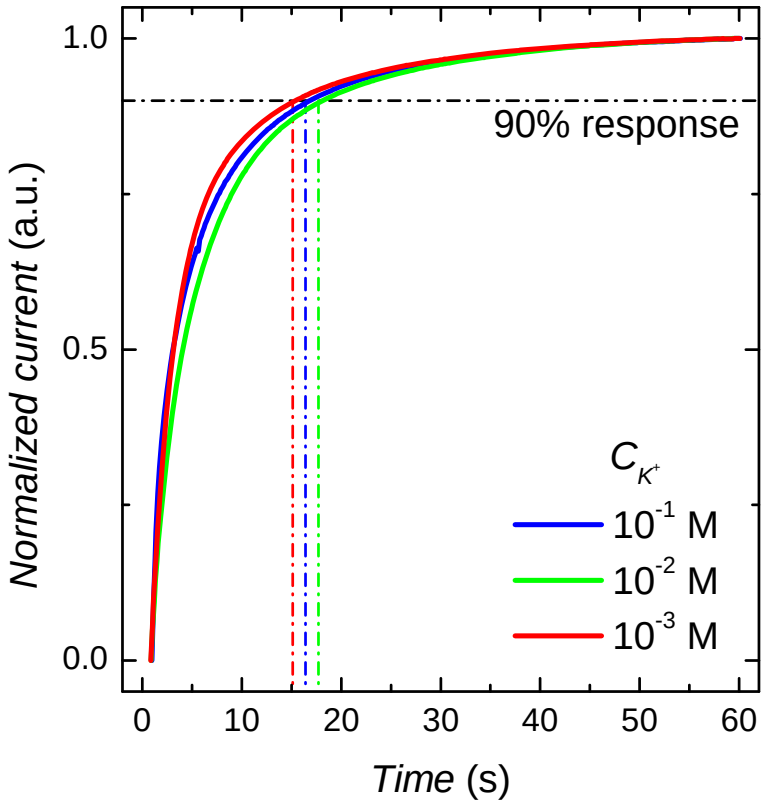

Figure S3. Normalized current response of the ion-selective electrolyte-gated transistor (IS-EGT) to different concentrations of potassium in water (C_{K+}). The time to reach 90% of the equilibrium current (t_{90}) is highlighted for the three different concentrations.

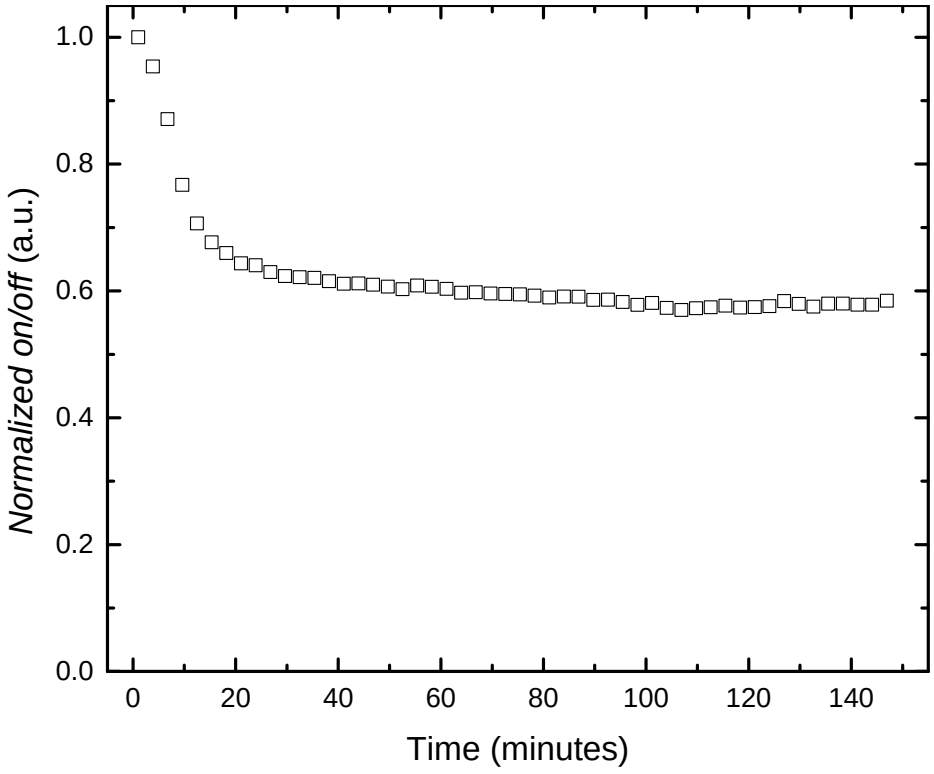

Figure S4. Normalized *on/off* ratio vs. time for the water-gated ZnO EGT. For this test, the transistor has been driven at V_d=0.4 V, while switching the gate bias between V_g=0 V (*off*) and V_g=0.9 V (*maximum transconductance*) with a period of 180 s. After 2.5 h, the *on/off* ratio is still at about 60% of its maximum value.