Supporting Information

A. On the dynamic response of individual nanowires

Gas sensors are usually characterized using experimental set-ups similar to the depicted one in the sketch of Fig.A. These systems have customized chambers in which measurements are easily performed. Nevertheless, they exhibit slow dynamics which make very difficult to analyze the real time constants of metal oxides. This is the main reason that justifies slow responses towards gases such as those shown in Fig.5 of the manuscript for a SnO_2 nanowire. To accurately estimate the real time constants of sensors, smaller chambers with faster dynamics are required. Preliminary results demonstrate that gas responses with characteristics times in the range of a few seconds are achieved with nanowires if this experimental condition is fulfilled (Fig.B). However, the ultimate limits of nanowires, regarding to their dynamic behaviour, will be only determined if their responses are tested using complex experimental systems as those designed by Shimanoe [a].

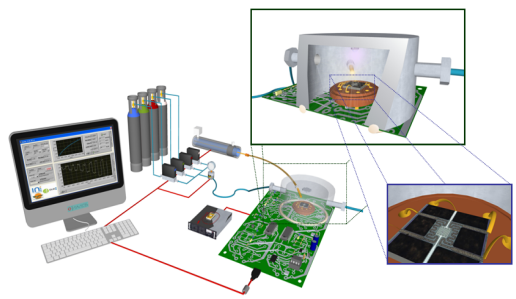

Figure A: Sketch of the typical experimental set-up required to operate gas sensors in research works. The chamber in which the sensor is placed is crucial to determine the dynamics of the whole system.

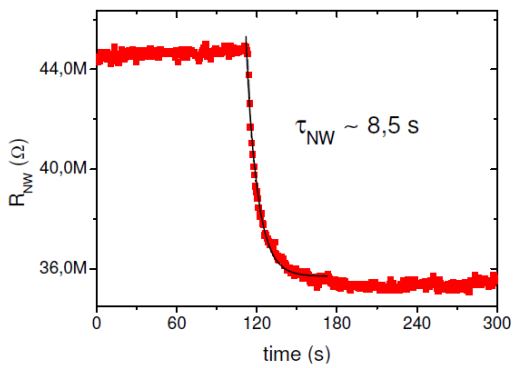

Figure B: Response of a SnO_2 nanowire ($T \approx 300°C$) to a suddent change from oxygen-rich atmosphere to N_2. Complete stabilization is reached in the second-range.

B. Interval between gas-surface collisions at the nanowires

The mean time interval t_c between two collision events (gas molecule-nanowire's surface) can be roughly estimated with the help of the classical kinetic theory of gases [b]. According to this theoretical description, collision rate *c.r.* (i.e. number of atomic/molecular collisions with a wall per unit area per unit time) can be expressed as,

$$\text{c.r.} = \frac{1}{t_c} = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{N_A m_g}{k_B T}} \frac{[g] p_{atm}}{m_g} \qquad \text{(a)}$$

where m_g is the molecular mass of the target gas, $[g] \cdot p_{atm}$ is the partial pressure of the target gas ($[g]$ target gas concentration is usually diluted in a reference gas at $p_{atm} = 1\ atm$), N_A is the Avogadro's number and k_B the Boltzmann's constant.

On the other hand, impact area S_{nw} can be easily estimated if the nanowire is described as an ideal cylinder with radius r_{nw} and length L_{nw}.

$$S_{nw} = 2\pi r_{nw} L_{nw} + 2\,\pi r_{nw}^2 . \qquad \text{(b)}$$

Combining (a) and (b), the mean interval t_c between two collisions corresponds to:

$$t_c = \sqrt{2\pi} \sqrt{\frac{k_B T}{N_A m_g}} \frac{m_g}{[g] p_{atm}} \left(2\pi r_{nw} L_{nw} + 2\,\pi r_{nw}^2\right) \qquad \text{(c)}$$

Fig.C shows the theoretical t_c values as function of the gas concentration for NO_2. Here, different working temperatures and nanowire's radi were considered. Even in the worse case (ultrathin nanowire of $r_{NW} = 2nm$ operated at $T = 600K$), t_c values are orders of magnitude shorter than the typical dynamic response of nanowire-based sensors (ranging from the second to minutes range – Fig.A). Similar conclusions can be drawn for other target gases.

These calculations demonstrate that the number of gas-surface interactions is high enough to initiate the transduction processes, in spite of the small dimensions of nanowires and the low gas concentrations used in the experiments.

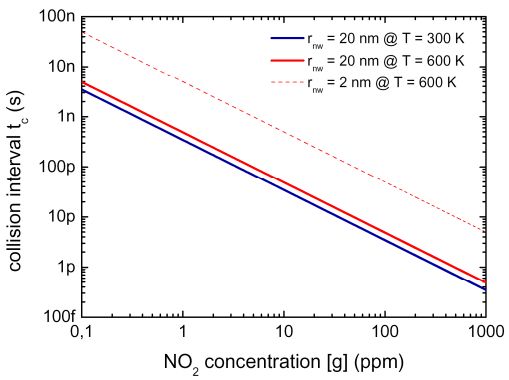

Figure C: Collision interval t_c as function of gas concentration (NO_2). Different nanowire's radii and working temperatures were considered. Nanowire's length was set to the typical length of the materials used in these devices $L_{nw} = 1\mu m$.

References

a. T. Kida, T. Kuroiwa, M. Yuasa, K. Shimanoe, N. Yamazoe, "Study on the response and recovery properties of semiconductor gas sensors using a high-speed gas-switching-system". Sens. Actuators B: Chem, 2008, 134, 928

b. L. C. Woods, "An Introduction to the Kinetic Theory of Gases and Magnetoplasmas", Oxford University Press (2003).