

Supporting Information

Title: Core-Shell Electrospun Polycrystalline ZnO Nanofibres for Ultra-Sensitive NO₂ Gas Sensing

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Figure S-1 shows the electron micrograph of the ZnO fibres after calcination at 500°C in air. The inset is the distribution of the width of the fibres. Which show that the mean diameter of the fibres is about 50nm.

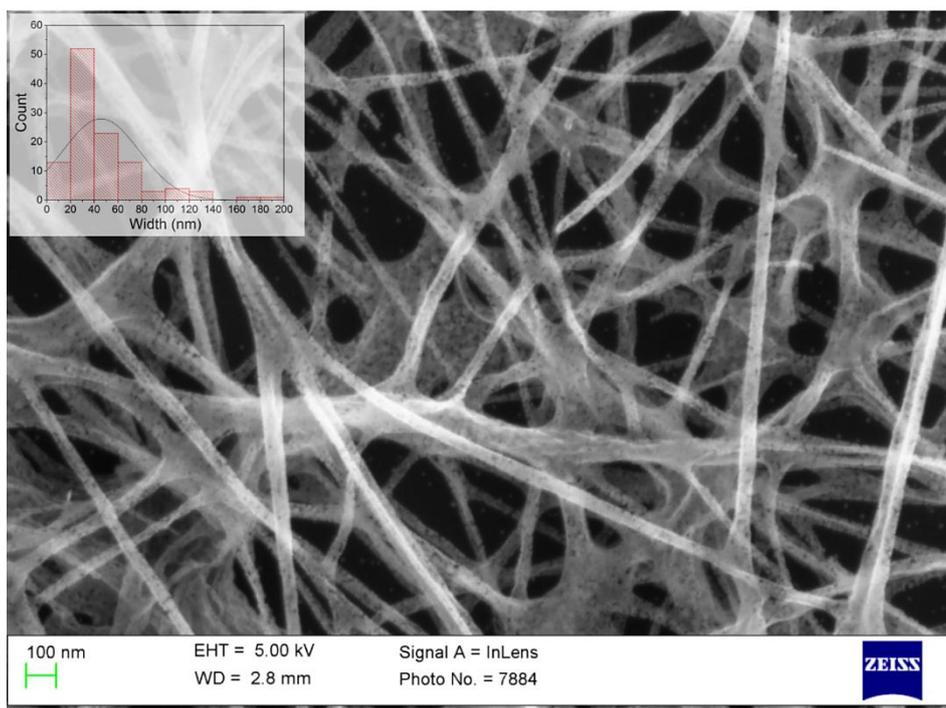


Figure S-1: SEM of calcined nanofibres.

Figure below is the photograph of the coaxial needle used for the core-shell electrospinning, presented in this paper. Inner needle is gauge 22, whereas the outer needle is gauge 18. Inlet to the outer needle is from the side as shown in the figure below.

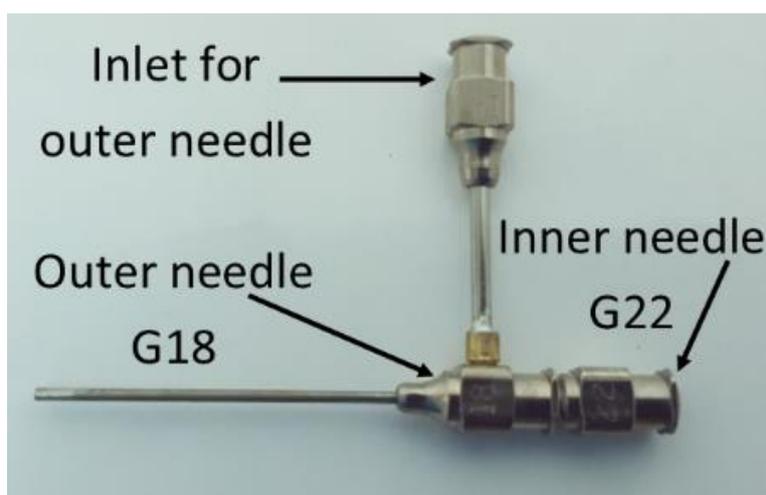


Figure S-2: Photograph of a coaxial needle used in this experiment.

Figure S-3 is the high resolution TEM of a ZnO fibres of region indicated by a black box in figure 2e of the paper. Crystallographic planes can be seen for almost all the grains, which clearly shows that the nanofibre consists of polycrystalline nanograins and the PVA shell is completely decomposed during calcination.

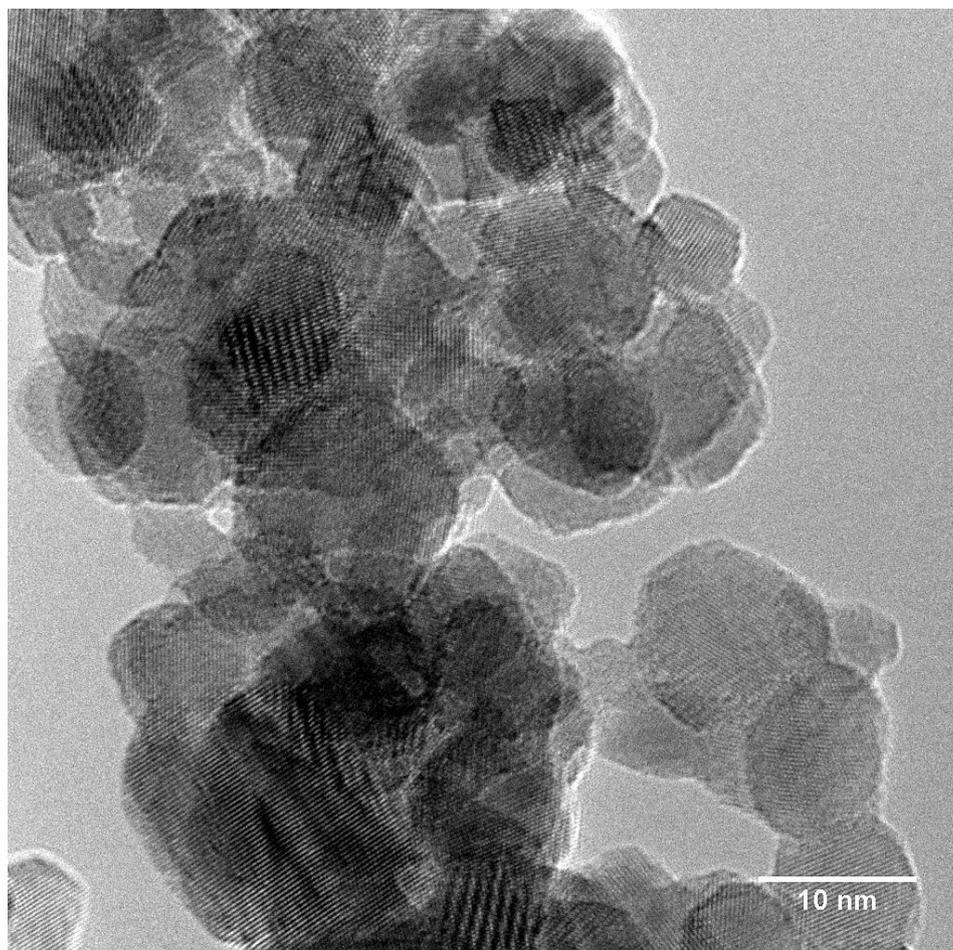


Figure S-3: High resolution TEM image of boxed region in Figure 2e.

Figure S-4 is the NO₂ gas sensing measurements performed using a device similar to the one discussed in the paper but with a lower density of ZnO fibres. Due to fewer fibres, this device has higher resistance and the signal to noise ratio is lower. However, sensitivity, which is depends on the material property and the interaction between the gas molecules and the sensor is very similar to the results presented in Figure 3f.

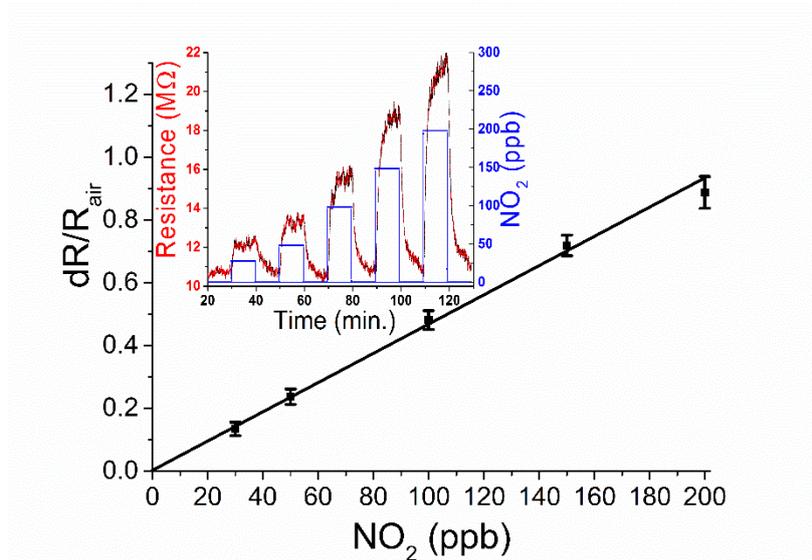


Figure S-4: Sensitivity of the ZnO nanofibre device containing fewer fibres than the results presented in Figure 3f.

Additional measurements:

NO₂ gas sensing measurements have also been performed at the higher concentration (ppm) of NO₂ gas at different temperature, UV and humidity conditions, as shown in the Figure S-5. At higher concentration, the device start to saturate and the sensitivity is reduced as compared to the low (parts per billion) concentration regime.

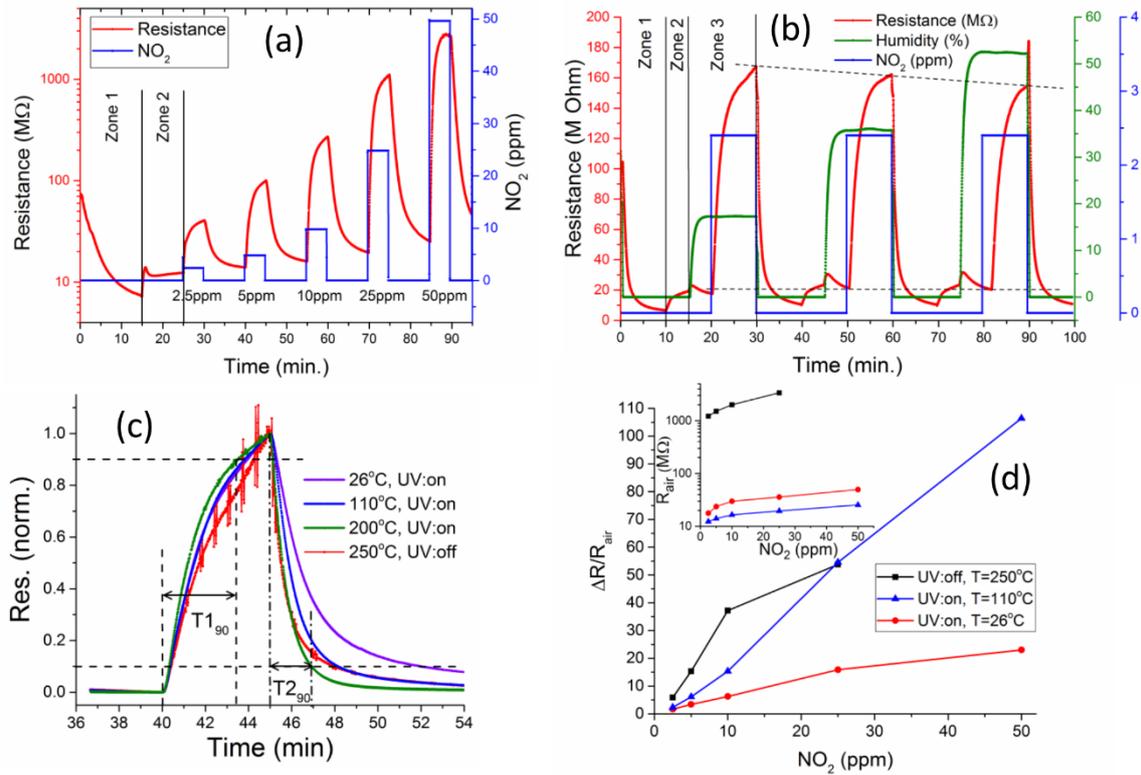


Figure S-5: Gas sensing measurements at higher concentration of NO₂ gas. Measurements presented in (a), (b), (c) and (d) are discussed below.

Figure S-5a shows the change in resistance of the ZnO gas sensor as the NO₂ gas concentration is increased from 2.5ppm to 50ppm. During zone 1, the chamber is evacuated for 15 minutes and temperature is ramped from room temperature to 110°C, which provides the initial condition to start the gas testing process. During zone 2, a dry air in introduced to the chamber so that the pressure is increased to the atm pressure but the humidity remains to zero. Measurements shown in S-5a were effectively performed at zero humidity. After zone 2, NO₂ gas was injected to the chamber for 5 minutes and then turned off for 10 minutes, NO₂ gas concentration was gradually increased and the response of the ZnO devices was continuously measured. The blue curve in Figure S-5d summarise the measurements presented in the figure S-5a. The inset of Figure S-5d shows the R_{air} values, which is the resistance of the ZnO nanofibre devices just before the NO₂ gas is introduced to the chamber. The non-linearity of the R_{air} curve shows that at high concentration of gas, the device recovery time is much longer than 10 minutes. Similar behaviour is observed for measurements performed at 250C, with the UV off and at the room temperature with the UV on. Although, the response of the device is higher in the absence of UV light but at higher temperature (250°C), the resistance of the device is very high. Therefore, these devices completely pinch of at high concentration of NO₂ gas. At room temperature but in the presence of UV light, the sensitivity is reduced. To understand the role of UV light and the temperature during gas detection, normalized gas detection curves are drawn for different

measurement conditions in the presence of 2.5ppm gas as shown in S-5c. Where T_{190} is the time signal takes to reach to the 90% of the maximum change and T_{290} is the time signal takes to recover back to the 10% of the starting value. It shows that the device gas detection response is much faster when UV is on, where as the recovery is much faster at higher temperature. i.e. the presence of UV promote the electron transfer from ZnO to NO_2 molecules. Photo induced electrons facilitate the faster response time and the high temperature helps in desorption of NO_2 gas molecules and promotes the faster recovery of the sensor. Therefore, using a combination of UV light and heating is the best strategy for effective NO_2 gas sensors.

Figure S-5b shows an NO_2 gas detection in the presence of humidity. Zone 1 and zone 2 are the same as explained in the previous paragraph. In Zone 3 first humidity is introduced to the chamber as indicated by the green curve. When humidity is reached to an equilibrium condition, the NO_2 gas is introduced to the chamber. Measurements are performed at about 18%, 35% and 54% humidity. After every humidity test, zone 1, 2 and 3 conditions are repeated. These measurements show that there is only a slight decrease in the sensitivity of the NO_2 gas in the presence of humidity. It demonstrates that these devices can be used in ambient conditions for detecting NO_2 gas.

Figure S-6 below shows a comparison been the ZnO device response to ammonia (NH_3), which is a reducing gas and NO_2 , which is a oxidising gas, at 5ppm, 10ppm and 25ppm gas concentrations. There are two key observations, firstly, the change in resistance is very small when ZnO sensor is exposed to NH_3 as compare to NO_2 (note the resistance shown in a log scale). In a linear scale NH_3 response is not appreciable. Secondly, the resistance of the sensor drops after a few minutes exposure to the NH_3 gas, as indicated by black arrows. There is a small jump in the resistance when NH_3 gas is turned on, it can possible be due to a change in temperature, but an over all trends is a decrease in resistance. This trend is opposite to when sensor is exposed to the NO_2 gas. Adsorbed NO_2 molecule capture an electron from ZnO and increase the depletion region, resulting in an increase in resistance. Whereas, NH_3 molecule react with an adsorbe oxygen and release trapped electron to ZnO and decreases the depletion region, leading to a drop in resistance.

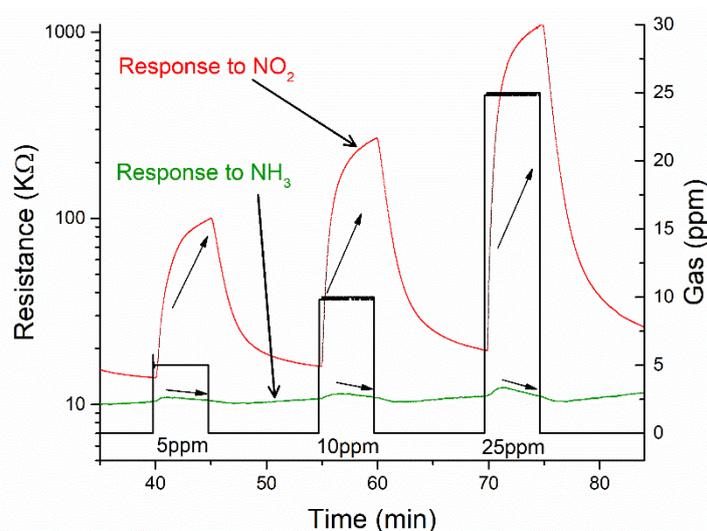


Figure S-6: Red (Green) curve is the response of the ZnO sensor to the NO_2 (NH_3) gas. Black curve shows the concentration of the gases- NH_3 and NO_2 . These two experiments are done seperately but drawn together for comparison.

Debye length:

Figure S-7 shows the Debye length (L_D) of ZnO as a function of charge carrier concentration at 100°C. Following relation has been used to perform this measurements: (p77, S. M. Sze Physics of Semiconductor Devices)

$$L_D = \sqrt{\frac{\epsilon_s k T}{q^2 n}}$$

Where, ϵ_s , k , T , q and n are the static dielectric constant of ZnO, Boltzmann constant, temperature, charge and the carrier concentration respectively. Values used for the calculation are: $\epsilon_s/\epsilon_o = 9$, $k = 1.38 \times 10^{-23} \text{ J/K}$, $T = 373 \text{ K}$, $q = 1.6 \times 10^{-19} \text{ C}$.

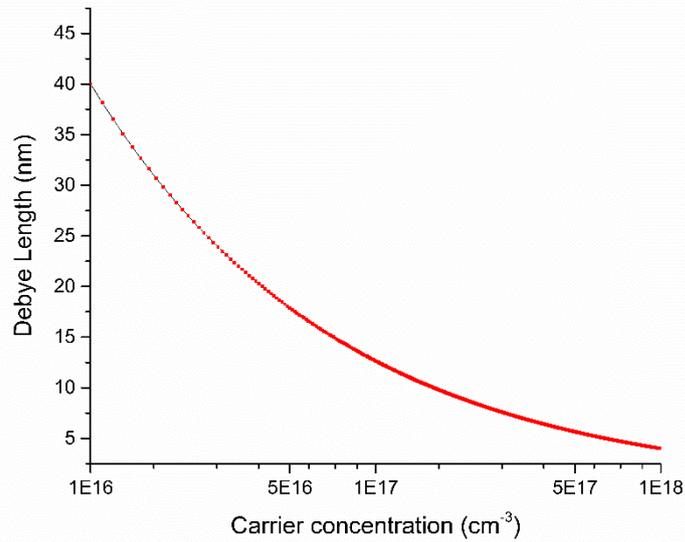


Figure S-7: Debye length of ZnO as a function of carrier concentration at 373 K.