Supplementary Information

Transmission electron microscopy (TEM) images of the nanorods obtained from different concentrations of 0.01, 0.04, and 0.05 M are shown in Fig. S2. A high-resolution TEM image (Fig. S2-d) shows that the nanorod was grown along the [0001] direction as determined by the interplanar spacing of 0.25 nm corresponding to the (0002) plane of hexagonal ZnO.

Fig. S1 Photograph of a sensor device.

Fig. S2 TEM image of the nanorods in the ZnO-UL structures grown in (a) 0.01 M, (b) 0.04 M, and (c) 0.05 M solutions. (d) A high-resolution image for growth with 0.04 M solution.

Fig. S3 XRD pattern of the hollow ZnO-UL structures grown for (a) 0.01 M, (b) 0.04 M, and (c) 0.05 M solutions.

The sensing responses of the urchin structures having short ZnO nanorods and long nanorods are compared. The simplest case is that the former has one short nanorod-to-nanorod current path [characterized by the resistance \( r_s(2) \)] and the latter has two current paths in parallel, one short nanorod and one long nanorod [characterized by the resistance \( r_s(2) \) and \( r_s(1) \), respectively], as illustrated in Fig. S4.

Fig. S4 The schematic urchin structure sensors having different nanorod lengths, and thus different number of parallel current paths.

The resistance of each path in air is given by

\[
\begin{align*}
    r_s(1) &= 2r_s^{uv}(1) + r_s'(1) \\
    r_s(2) &= 2r_s^{uv}(2) + r_s'(2)
\end{align*}
\]  

(e1)

and the resistances upon exposure to NO gas are given by

\[
\begin{align*}
    r_s(1) &= 2r_s^{uv}(1) + r_s'(1) \\
    r_s(2) &= 2r_s^{uv}(2) + r_s'(2)
\end{align*}
\]  

(e2)

Here we can assume that the nanorod diameters are all the same, and then the resistances at the nanorod-nanorod contacts due to energy barrier are also to be same for all the lengths of nanorods, or \( r_s'(1) = r_s'(2) = r_s' \) and \( r_s'(1) = r_s'(2) = r_s' \). Also note that \( r_s(1) > r_s(2) \) due to the length difference in nanorods, and then we can put \( r_s^{uv}(1) = \alpha r_s^{uv}(2) \) with the ratio of nanorod lengths \( \alpha > 1 \). Accordingly \( r_s(1) = \alpha r_s(2) \).
Now the responses of the sensors \( S_1 \) for Sensor 1 and \( S_2 \) for Sensor 2 due to gas adsorption on the surface of the nanorods can be described by

\[
S_1 = \frac{R_f - R_o}{R_o} = \frac{r_a(2)}{r_a(2)} - 1 \tag{e3}
\]

\[
S_2 = \frac{R_f - R_o}{R_o} = \frac{G_s - G_o}{G_o} = 1 + \frac{1}{r_a(1) + r_a(2)} - 1 \tag{e4}
\]

\[
= \frac{r_a(1)r_a(2)(r_a(1) + r_a(2))}{r_a(1)r_a(2)(r_a(1) + r_a(2))} - 1
\]

Then

\[
S_2 - S_1 = \frac{r_a(1)r_a(2)(r_a(1) + r_a(2))}{r_a(1)r_a(2)(r_a(1) + r_a(2))} - 1 = S_1 \left[ r_a(1)r_a(2) - r_a(1)r_a(2) \right] \tag{e5}
\]

with

\[
S_o = \frac{r_a(2)}{r_a(1)r_a(2)(r_a(1) + r_a(2))} \tag{e6}
\]

Now insert the Eqs. (e1) and (e2) to Eq. (e5) to obtain

\[
S_2 - S_1 = 2S_o \left[ \left( r_a''(1) - r_a''(2) \right) - \frac{1}{r_a(1)r_a(2)} \left( r_a''(1) - r_a''(2) \right) \right] + \left( \frac{G_s - G_o}{G_o} \right) \left( r_a''(1) - r_a''(2) \right) - \frac{1}{r_a(1)r_a(2)} \left( r_a''(1) - r_a''(2) \right) \tag{e7}
\]

Since \( S_2 > S_1 \) from the experimental results (for example, the response of ZnO-UL-4 is larger than that of ZnO-UL-1), the term

\[
f = \frac{r_a''(2)}{r_a''(2)} - \frac{r_a''(1)}{r_a''(2)} \tag{e8}
\]

\[
f = \left( \frac{r_a''(2)}{r_a''(2)} \right) - \left( \frac{r_a''(1)}{r_a''(2)} \right) - 1
\]

\[
= \frac{\Delta r_a''(2)}{r_a''(2)} - \frac{\Delta r_a''(1)}{r_a''(2)} > 0 \tag{e9}
\]

One finally obtains that the general inequality condition