Electronic Supplementary Information (ESI)

Pd-loaded In₂O₃ nanowire-like network synthesized by CNTs templates for enhancing NO₂ sensing performance

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Figure S1. Pd3d XPS spectra of Pd-In₂O₃ nanowire-like network.

The high-resolution scan of the Pd3d was shown in Fig. S1. The peaks located at 341.6 and 337.2 eV are assigned to $Pd3d_{3/2}$, $Pd3d_{5/2}$ of PdO_x/Pd , respectively, and a small peak with a binding energy of 336.4 eV corresponds to $Pd3d_{5/2}$ of PdO, proving that partial palladium has been oxidized at 550 °C. Moreover, the peak at 343.7 eV is assigned to $Pd3d_{3/2}$ of residual $PdCl_2$, which was from the process of activation. The signal is weak because of low Pd content.



Figure S2. TEM images of porous unloaded- In_2O_3 : (a) low magnification, and (b) high magnification for the observation of size and structure.

Figure S2 shows the sample obtained by electroless using CNTs as templates and followed by calcination in the absence of activation by $PdCl_2$. As can been seen, lots of single crystals were stacked together and the morphology of unloaded- In_2O_3 duplicated that of CNT, forming a porous structure. It is noteworthy that the morphology and grain size (about 20 nm) of porous unloaded In_2O_3 is basically the same as that of porous Pd- In_2O_3 shown in Figure 5a.



Figure S3. TEM Images of precursor (In/CNTs) obtained by sensitization and electroless plating, but without activation by PdCl₂: (a) TEM image, and (b) HRTEM image of an individual In/CNT.

Figure S3 shows the images of In/CNTs obtained by sensitization and electroless plating, but without activation by PdCl₂. Due to the lack of the activation of Pd, indium (In) deposition on the surface of CNTs (In/CNTs) exhibited inhomogeneity and aggregation, and large amounts of amorphous In reduced by NaBH₄ was scattered around the CNTs. After oxidization and calcination, porous unloaded-In₂O₃ was obtained due to the crystallization of In loaded on the surface of CNTs.



Figure S4. Gas response of three In_2O_3 -based sensors exposed to NO_2 at concentrations ranging from 1 to 20 ppm at optimum operating time (110 °C).

Figure S4 shows the correlation of gas response with NO₂ concentration. Porous unloaded- In_2O_3 and porous Pd- In_2O_3 sensors have the similar response at various concentrations. In addition, the response of Pd- In_2O_3 nanowire-like network sensor is much higher than that of the other two sensors. And Pd- In_2O_3 network also has a faster rising tendency with the increasing of NO₂ concentration.



Figure S5 5-point BET surface area plots of three sensors. (W is the quantity of adsorbed NO₂. P and Po are the equilibrium and the saturation pressure of the adsorbate, respectively.)

Figure S5 shows the 5-point BET surface area plots of three sensors, by which the BET surface areas were calculated. The results indicate that nanowire-like network sensor presents much higher surface to volume ratio than that of the other two sensors. This is a major reason why nanowire-like network sensor possesses very high response.



Figure S6 Typical dynamic response curves of the porous Pd-In2O3 sensor exposed to 5 ppm NO2 at different temperatures.

Figure S6 revealed the response curves of porous $Pd-In_2O_3$. It has the same trend of variability as that of $Pd-In_2O_3$ NW-like network. The changing process can be divided into three steps: 1) the amplitude of fluctuation drastically decreased until it was lower than that of "pulse signal". 2) The "cyclical fluctuations" disappeared firstly. 3) Both of "pulse signal" and "cyclical fluctuations" were missing.



Figure S7. Dynamic response curves of the original Pd-In₂O₃ nanowire-like network sensor prepared 3 month ago for stability testing.

Figure S7 shows the dynamic response curves of the original $Pd-In_2O_3$ nanowire-like network sensor prepared 3 months ago. After storing in a small centrifugal tube for 3 months, this sample shows the unchangeable gas sensing property, such as response, response/recovery time, and almost the same change of two novel characteristics. This demonstrates that the as-obtained Pd- In_2O_3 nanowire-like network sensor has excellent stability.



Figure S8. Dependence of the sensor recovery rates on operating temperature of porous unloaded-In₂O₃ and porous Pd- In₂O₃.

Because of the similar specific surface area of porous unloaded- In_2O_3 and porous Pd- In_2O_3 , the reciprocal of recovery time was utilized to represent the recovery rate per unit area. As shown in Figure S8, the recovery rate of unloaded In_2O_3 presents much sensitive to temperature. When temperature exceeds 195 °C, the recovery rate of porous unloaded- In_2O_3 is faster than that of porous Pd- In_2O_3 . This proved that Pd-loaded In_2O_3 and unloaded- In_2O_3 had their own gas sensing mechanisms.