Supporting Information

Boosting Performance of NO₂ Gas Sensor based on n-n Type Mesoporous ZnO@In₂O₃ Heterojunction Nanowires: In-situ Conducting Probe Atomic Force Microscopic Elucidation of Room Temperature, Localized Electron Transfer

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1. Characterization Techniques:

The XRD patterns were acquired using Power X-ray diffractometer (Rigaku ULTIMA IV, Japan) using Cu Kα radiation of wavelength 1.5418 Å at a scanning rate of 0.02°/ sec in the 2θ range of 20– 80°. Micro Raman spectra (WITec, 300 Alpha, Germany) of heterojunction ZnO@In₂O₃ nanowires were obtained using He-Cd laser (λ = 532 nm) as an excitation light source with 1800g/mm gratings. The structure and morphology of the ZnO@In₂O₃ heterojunction nanowires were examined using High-Resolution Transmission Electron Microscopy (JEOL JEM-2010, Japan) and Scanning Electron Microscopy (ZEISS EVO 18, USA), with in-built Energy-Dispersive X-Ray Spectrometer (Oxford Instruments, INCA, UK). CaRIne crystallography 3.1 was used to simulate the lattice atoms present in each plane and calculated the ratio of Zn²⁺ and O²⁻ ions present in the ZnO planes and as well as In³⁺ and O²⁻ present in the In₂O₃ planes. UV-DRS absorption spectra were acquired using JASCO UV (V-750) spectrophotometer. The spreading resistance imaging and scanning kelvin probe microscopy analysis of the prepared materials was performed on multimode scanning probe microscope (NTMDT, NTEGRA-AURA, Russia) under ambient conditions (24°C). Photoluminescence (PL) characterization was carried out using spectrofluorophotometer (RF-5301PC, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Phoibos 100 MCD energy analyzer using monochromatized Al Kα excitation to analyze the elemental and chemical states of the materials. AFORS-HET software v2.5 was used to simulate the energy band bending diagram of ZnO@In₂O₃ heterojunction nanowires.
Brunauer-Emmett-Teller (BET) specific surface area analysis of samples was estimated by nitrogen adsorption-desorption isotherm (BELSORP-MAX, Microtrac BEL Corp, Japan).

2. Evaluation of gas sensor sensing properties:

The sensor device was fabricated as inter-digitated array (IDA) electrode made of Au (∼150 nm) with an inter-finger gap of 16 µm using planar DC magnetron sputtering on alumina substrates. Thin films of porous ZnO nanowires and porous ZnO@In$_2$O$_3$ heterojunction nanowires (1mg/mL) were dispersed in ethanol and drop-casted on IDA transducer electrodes at 55°C. The gas sensing properties of the materials were analyzed using a custom-built gas sensor test station consisting of a stainless steel double-walled test chamber equipped with temperature-controlled hot stage, sensor holder, mass flow controllers (MFC, Alicat, USA), digital multimeter (Agilent 34401A, USA) connected with a data acquisition system interfaced with Labview software. During measurements, NO$_2$ gas was mixed with dry nitrogen to achieve the desired concentrations and the flow rate was maintained as 300sccm using mass flow controllers (Alicat, U.S.A.). A temperature controller (Eurotherm, 2420, U.K.) was used to maintain the working temperature of the sensor mounted inside the sensing chamber. Constant gas pressure was maintained in the sensing chamber (710 Torr) throughout the testing which was measured using Baratron 722B Absolute Capacitance Manometer (MKS Instruments, Singapore).

3. Optical Band gap calculation of ZnO@In$_2$O$_3$ heterojunction nanowires using UV–visible diffuses reflectance spectroscopy (DRS):

Solid state UV–visible diffuses reflectance spectra (DRS) of ZnO nanowires and core-shell heterojunction ZnO@In$_2$O$_3$ nanowires shown in Figure S1. ZnO nanowires exhibits UV absorption peak centered at 365nm, which corresponds to the ground excitonic peak of Zn-O. Also core-shell ZnO@In$_2$O$_3$ nanowires exhibits the same with an additional broad peak near the region of 450nm. The crystalline purity of the sample has been confirmed by observing absence of additional peaks in the spectrum.
The band gap energy of the samples is measured by the extrapolation of the linear portion of the graph between the modified Kubelka-Munk function \( [F(R)^*h\nu]^2 \) versus photon energy \( (h\nu) \) shown in the inset Figure S1(b).

\[ F_{KM} = \frac{(1 - R)^2}{2R} \]  

(S1)

The band gaps of the pristine ZnO nanowires and heterojunction ZnO@In\(_2\)O\(_3\) nanowires were calculated to be 3.3 and 3.27 eV respectively. The considerable change observed in the band gaps is due to the interfacial electron transfer between ZnO nanowires and In\(_2\)O\(_3\) nanocluster as shell layer.

4. Morphological analysis of mesoporous ZnO nanowires:

TEM analysis was carried out for ZnO nanowires to infer about the structure and morphological characteristics. Fig. S2(a) shows the TEM images of bare ZnO nanowires, where the uniform distribution of nanowires having length and width of 15 ± 0.5 \( \mu \)m and 150 ± 0.5 nm respectively were observed. Each nanowire extends to several micrometers with high aspect ratio as suited for electronics and sensing applications. Fig. S2 (c) showing HR-TEM image of ZnO...
nanowires clearly shows the d-spacing value of 0.25 nm between the adjacent lattice planes corresponding to (100) plane lattice distance of hexagonal-wurtzite structured ZnO, indicating the growth direction along c-axis [0001]. Fig. S2(b) showing the SAED pattern of ZnO nanowires clearly implies the growth direction of ZnO in c-axis with single crystalline nature. The SAED pattern were indexed and matching with the standard JCPDS data card no.65-3411.

**Figure S2.** (a) TEM and (c) HRTEM image of ZnO nanowires and (c) corresponding SAED pattern of ZnO nanowires.

**Figure S3.** Typical nitrogen adsorption–desorption isotherm plots of bare ZnO, porous ZnO and porous ZnO@In$_2$O$_3$ nanowires.
Table S1. BET parameters of bare ZnO, porous ZnO and porous ZnO@In$_2$O$_3$ nanowires:

| Sample                                | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Pore size (nm) | Pore Specific Surface Area (m$^2$/g) |
|---------------------------------------|------------------------|------------------------|----------------|-------------------------------------|
| Bare ZnO nanowires                    | 1.8816                 | 2.5628                 | 3.0200         | 3.6655                              |
| Porous ZnO nanowires                  | 6.2636                 | 8.2457                 | 3.5133         | 10.5092                             |
| Porous ZnO@In$_2$O$_3$ heterojunction nanowires | 10.2961                | 15.2394                | 4.8705         | 12.5193                             |

5. SKPM tip calibration:

Figures S4. SKPM measurements on standard Au film for calibration of Au coated Si tip
(a) topographic image of Au thin films (b-c) surface potential difference of Au thinfilms (d) CPD plot.
The work function calibration of the tip using the known value of Au film based on the above equation (5) is given below,

\[ 4.9 \text{ eV} - 1.096 \times 1.60 \times 10^{-19} \times 6.24 \times 10^{18} \text{eV} = \Phi_{\text{tip}} \]

\[ \Phi_{\text{tip}} = 4.86805 \text{ eV} \]

Table: S2 NO\textsubscript{2} Gas sensing parameter of bare and heterojunction ZnO@In\textsubscript{2}O\textsubscript{3} nanowires:

| Conc. of NO\textsubscript{2} (ppm) | ZnO nanowires | Heterojunction ZnO@In\textsubscript{2}O\textsubscript{3} nanowires |
|----------------------------------|----------------|-------------------------------------------------|
|                                 | Response [(Rg− Ra)/Ra] S (%) | Response time (s) | Recovery time (s) | Response [(Rg− Ra)/Ra] S (%) | Response time (s) | Recovery time (s) |
| 0.5                             | 30.79          | 39      | 76      | 274.1          | 4       | 76       |
| 1                               | 121.97         | 26      | 114     | 722.9          | 6       | 97       |
| 1.5                             | 186.49         | 26      | 196     | 799.8          | 10      | 116      |
| 2                               | 290.55         | 29      | 166     | 908.7          | 11      | 128      |
| 2.5                             | 391.10         | 35      | 239     | 1074.2         | 12      | 175      |
| 3                               | 498.35         | 36      | 256     | 1419.9         | 13      | 189      |

6. NO\textsubscript{2} Adsorption/Desorption Kinetics of heterojunction ZnO@In\textsubscript{2}O\textsubscript{3} nanowires:

The chemical adsorption kinetics of NO\textsubscript{2} gas on the surface of ZnO nanowires and P ZnO@In\textsubscript{2}O\textsubscript{3} heterojunction nanowires was further elucidated using Elovich model. The general form of Elovich plot can be expressed as,

\[ q = \frac{1}{\alpha} \ln(\alpha \alpha') + \frac{1}{\alpha} \ln(t) \quad (S2) \]

Where, \( q \) is the amount of gas adsorbed during time and \( t \), \( \alpha \), and \( \alpha' \) are constants. The change in the conductance (\( C_{tg}−C_0 \)) is proportional to the amount of adsorbed NO\textsubscript{2} molecules (\( q \)). The constant \( \alpha' \) is the initial adsorption rate and \( \alpha \) is the measure of potential barrier for successive adsorption of gas molecules, that is, depleted layer formed by previously adsorbed gas molecules.
that act as a barrier for the next incoming gas molecules. The values of these constants can be obtained from the slope and the intercept by plotting \((C_{tg} - C_0)\) versus \(\ln(t)\). \(C_0\) and \(C_{tg}\) are conductance of ZnO nanowires and mesoporous heterojunction ZnO@In₂O₃ nanowires at \(t=0\) and \(t=g\) upon exposing to NO₂ gas environment, respectively.

**Figure S5** (a-b) Elovich plot for NO₂ adsorption on ZnO nanowires and mesoporous heterojunction ZnO@In₂O₃ nanowires surfaces (c-d) Relationship between initial adsorption rate \((\alpha')\), barrier potential \((\alpha)\) and NO₂ concentration of ZnO nanowires and heterojunction ZnO@In₂O₃ nanowires.
Table: S3 Values of constants $\alpha'$ and $\alpha$ from Elovich plot:

| Conc. of NO$_2$ | Initial Adsorption rate ($\alpha'$) $(10^{-9})\Omega^{-1}s^{-1}$ | Surface Potential barrier ($\alpha$) M\Omega |
|-----------------|-------------------------------------------------|---------------------------------|
|                 | ZnO Nanowires | ZnO@In$_2$O$_3$ Nanowires | ZnO Nanowires | ZnO@In$_2$O$_3$ Nanowires |
| 0.5             | 0.93         | 10.71                      | 4.00         | 19.92                      |
| 1               | 3.92         | 8.70                       | 2.53         | 20.40                      |
| 1.5             | 4.24         | 7.15                       | 3.46         | 19.79                      |
| 2               | 3.15         | 6.66                       | 1.97         | 20.64                      |
| 2.5             | 3.88         | 8.90                       | 4.66         | 19.83                      |
| 3               | 4.02         | 8.11                       | 1.05         | 19.44                      |

Table: S4 Calculated parameters from the KPFM analysis:

| Sample                  | Work Function $(\phi_0)$ eV | Band Bending $(\Phi_B)$ eV | Carrier Density $(n_s)$ $10^{19}$ cm$^{-2}$ | Depletion Width (nm) |
|-------------------------|-----------------------------|----------------------------|-----------------------------------------------|----------------------|
| ZnO nanowires in Air    | 4.83                        | 1.927                      | 1.29                                          | 2.96                 |
| ZnO nanowires in NO$_2$ | 4.93                        | 1.959                      | 1.02                                          | 3.34                 |
| ZnO@In$_2$O$_3$ nanowires in Air | 4.97                      | 2.049                      | 1.18                                          | 3.19                 |
| ZnO@In$_2$O$_3$ nanowires in NO$_2$ | 5.01                      | 2.086                      | 0.87                                          | 3.78                 |
7. Cross selectivity of the gases:

Figure S6 Cross selectivity studies of ZnO nanowires and core-shell heterojunction ZnO@In$_2$O$_3$ nanowires.

To observe the cross interference selectivity properties of the mesoporous heterojunction ZnO@In$_2$O$_3$ nanowires towards NO$_2$ gas, their responses were analyzed towards exposure to several interfering gases, such as NH$_3$, H$_2$S, ethanol, acetone and SO$_2$ by keeping constant 2 ppm gas concentration (Figure S7). The heterojunction material was observed to be greatly selective towards NO$_2$ rather than other reducing and volatile organic gases due to the presence of In$_2$O$_3$ nanocluster effectively forming heterojunction onto the surfaces of ZnO Nanowires which could enhances the physisorption process. The charge accumulated at the junction interface of In$_2$O$_3$ nanocluster favors the strong adsorption of the oxidizing gas (NO$_2$) than other reducing and volatile organic gases.
Figure S7 (a-b) Relative humidity studies of mesoporous ZnO@In$_2$O$_3$ heterojunction nanowires

![Graph showing relative humidity studies](image)

Scheme S1 Schematic energy band structure of ZnO@In$_2$O$_3$ heterojunction nanowire before contact.

![Diagram showing energy band structure](image)