Supporting information for

Design of highly sensitive volatile organic compounds sensors by controlling NiO loading to ZnO nanowire networks

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Experimental

ZnO Nanowires were grown on the alumina substrates (size: 1.5 ×1.5 mm^2) with two Au electrodes (on its top surface) by thermal evaporation using a mixture of ZnO powders (99.9%, Aldrich), graphite powders (<20 micron, Aldrich) and Sn powders (99.8%, Acros). The source (ZnO: graphite: Sn = 1 : 1 : 0.01 by weight%) was loaded in the Al_2O_3 boat and was located in the center of the quartz tube (diameter: 2.5 cm). The alumina substrates were placed 5 cm downstream from the source. After evacuating the quartz tube to ~ 9 x 10^{-2} torr using a rotary pump, the furnace temperature was increased to 900°C. The ZnO nanowires were formed by a reaction between the source and Ar-O_2 mixture gas (Ar: 100 sccm, O_2: 1 sccm). The NiO-decorated ZnO nanowires were prepared using the following procedures. The as-grown ZnO nanowires on the patterned Al_2O_3 substrates and $NiCl_2$ powders (99.99%, Aldrich) were placed in the left and right part of Al_2O_3 boat (length 4 cm), respectively. After evacuating the quartz tube to ~ 9 x 10^{-2} torr using a rotary pump, the furnace temperature was increased to 500 °C. The lenticular/angular configuration of nano-scale NiO islands could be coated on the surface of the ZnO nanowires by a reaction between the source and Ar gas (Ar: 200 sccm). The Ni-doped ZnO nanowires were prepared using 2 zone quartz tube reactor. $NiCl_2$ (99.99%, Aldrich) powders were located at the 1st zone (temperature: 600 °C). The mixture between ZnO powders (99.9%, Aldrich), graphite powders (< 20 micron, Aldrich) and Sn powders (99.8%, Acros) were located at the 2nd zone (temperature: 900 °C). An alumina substrate was located on the top of the mixture. The distance between $NiCl_2$ and the mixture 10 cm. Argon gas was flowed while increasing or decreasing the temperature of the reactor. The Ni-doped ZnO nanowires were formed by a reaction between the sources and Ar-O_2 mixture gas (Ar: 100 sccm, O_2:1 sccm).

For X-ray analysis, ZnO, NiO-decorated ZnO and Ni-doped ZnO nanowires were grown on a large area of Si substrates using the same thermal evaporation procedure.

Characterization:

The structural properties were examined by X-ray diffraction (XRD, Rigaku D/MAX-2500 V/PC), scanning electron microscopy (SEM, Hitachi S-4700), field-emission transmission electron microscopy (FE TEM, FEI TECNAI G2, 200 kV and JEOL JEM 3010, 300 kV) and Energy dispersive X-ray spectroscopy (EDS). The PL measurements were carried out at room temperature using a He-Cd laser (λ =325 nm) as the excitation source. The chemical states of the films were determined by X-ray photoelectron spectroscopy (ULVAC-PHI, PHI 5000 VersaProbe) with an Al Ka radiation (1486.6 eV) source. The binding energies were corrected for specimen charging by referencing the C 1s peak to 284.6 eV.

SEM and TEM analyses of pristine ZnO NWs:

The ZnO NWs were synthesized on an alumina substrate with two gold electrodes (Fig. S1a) The diameter was 50-80 nm, the length was approximately tens of micrometers (Fig. S1b). The selected area electron diffraction (SAED) pattern confirmed that the highly crystalline ZnO NWs were grown in the [01$\bar{1}$0] direction (Fig. S1c). A lattice-resolved image of a single NW showed that highly crystalline (01$\bar{1}$0) fringes were separated by 2.81 Å (Fig. S1d).

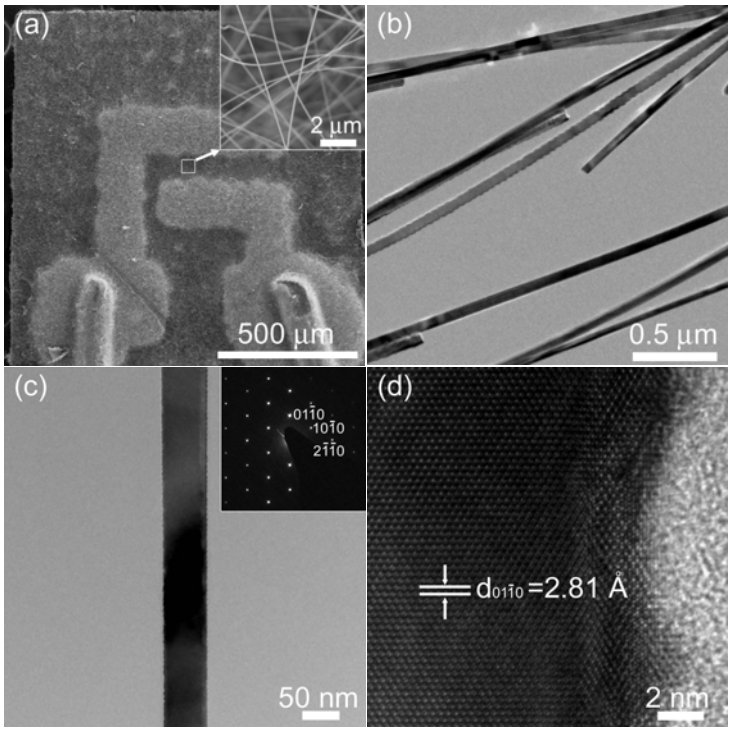

Fig. S1 Morphologies and crystal structures of the pristine ZnO NWs: (a) SEM images of ZnO NWs grown on an alumina substrate with two gold electrodes; (b) TEM images of ZnO NWs; (c) and (d) TEM images and electron diffraction pattern of ZnO NW.

SEM and TEM analyses of Ni-doped ZnO NWs:

The Ni-doped ZnO NWs were fabricated on an alumina substrate with two gold electrodes (Fig. S2a) The diameter was 50-80 nm, and the length was approximately tens of micrometers (Fig. S2b). The selected area electron diffraction (SAED) pattern confirmed that highly crystalline Ni-doped ZnO NWs were grown in the [01$\bar{1}$0] direction (Fig. S2d). A lattice-resolved image of a single NW showed that highly crystalline (01$\bar{1}$0) fringes were separated by 2.8 Å (Fig. S2e). High-angle annular dark field (HAADF) scanning TEM (STEM) and EDS-line scanning of Zn, Ni, and O (Fig. S2f) indicated that Ni was doped uniformly in the ZnO NW.

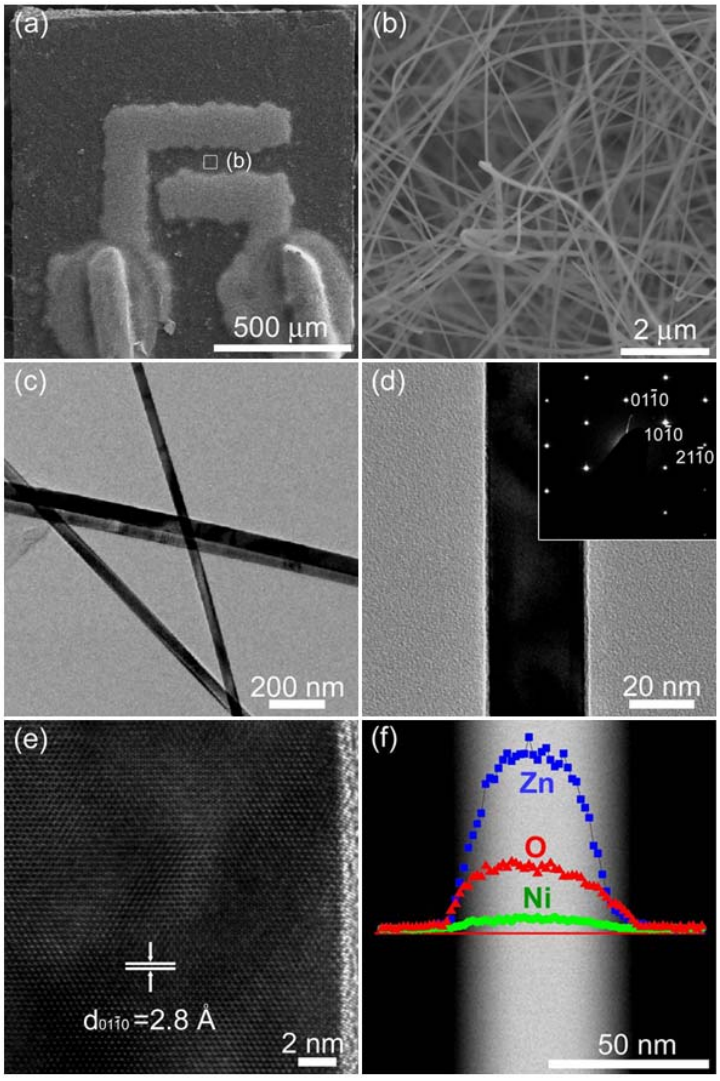

Fig. S2 Morphologies and crystal structures of the Ni-doped ZnO NWs: (a), (b) SEM images of Ni-doped ZnO NWs on the alumina substrate with two gold electrodes; (c) and (d) TEM images of Ni-doped ZnO NWs; (e) a lattice image of Ni-doped ZnO NW; (f) high-angle annular dark field (HAADF) scanning TEM (STEM) image and EDS line scanning of Zn, Ni, and O.

Photoluminescence:

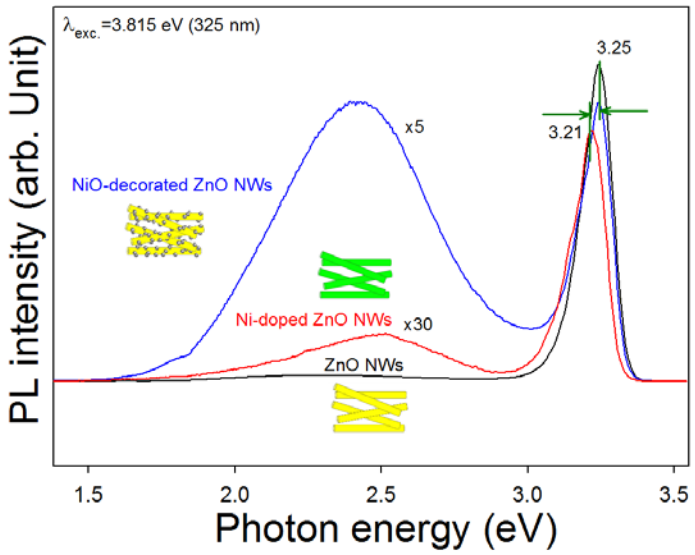

Fig. S3 Room-temperature PL spectrum of the ZnO NWs, NiO-decorated ZnO NWs, and Ni-doped ZnO NWs. (excitation wavelength: 325 nm (3.815 eV))

X-ray diffraction analysis:

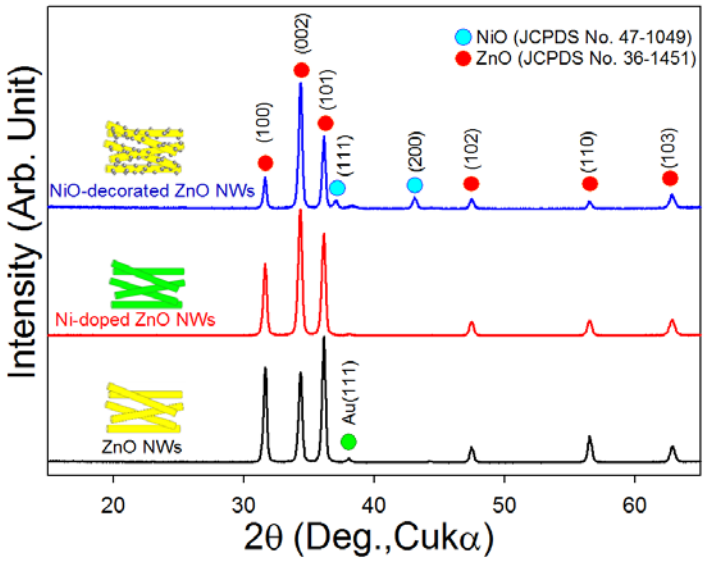

Fig. S4 X-ray diffraction patterns of pristine ZnO NWs, Ni-doped ZnO NWs, and NiO-decorated ZnO NWs.

X-ray photoelectron spectroscopy:

The survey-scanned and fine-scanned XPS spectra of the ZnO, Ni-doped ZnO, and NiO-decorated ZnO NWs were measured. Figure 4Sb shows the Ni *2p* spectra of the Ni-doped ZnO and NiO-decorated ZnO NWs. The Ni $2p_{3/2}$ and Ni $2p_{1/2}$ spectra of the Ni-doped ZnO NWs have five peaks from 854.7 to 879.1eV. The red line (854.7 eV) and green line (856.2 eV) were assigned to the Ni^{2+} and Ni^{3+} bonding structures, respectively, which is consistent with the studies of NiO (K. S. Kim and N. Winograd, *Surface. Sci.*, 1974, **43**, 625).

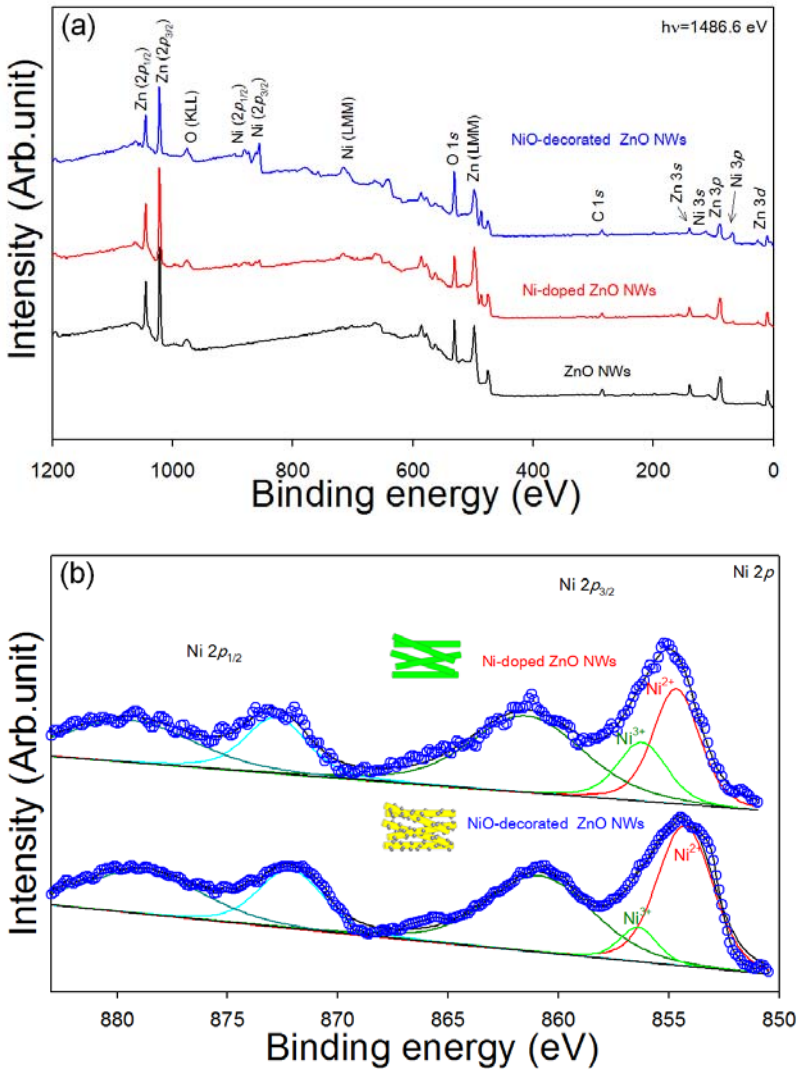

Fig. S5 X-ray photoelectron spectroscopy results: (a) full range spectra and (b) Ni $2p_{1/2}$ and Ni $2p_{3/2}$.

Selectivity analysis:

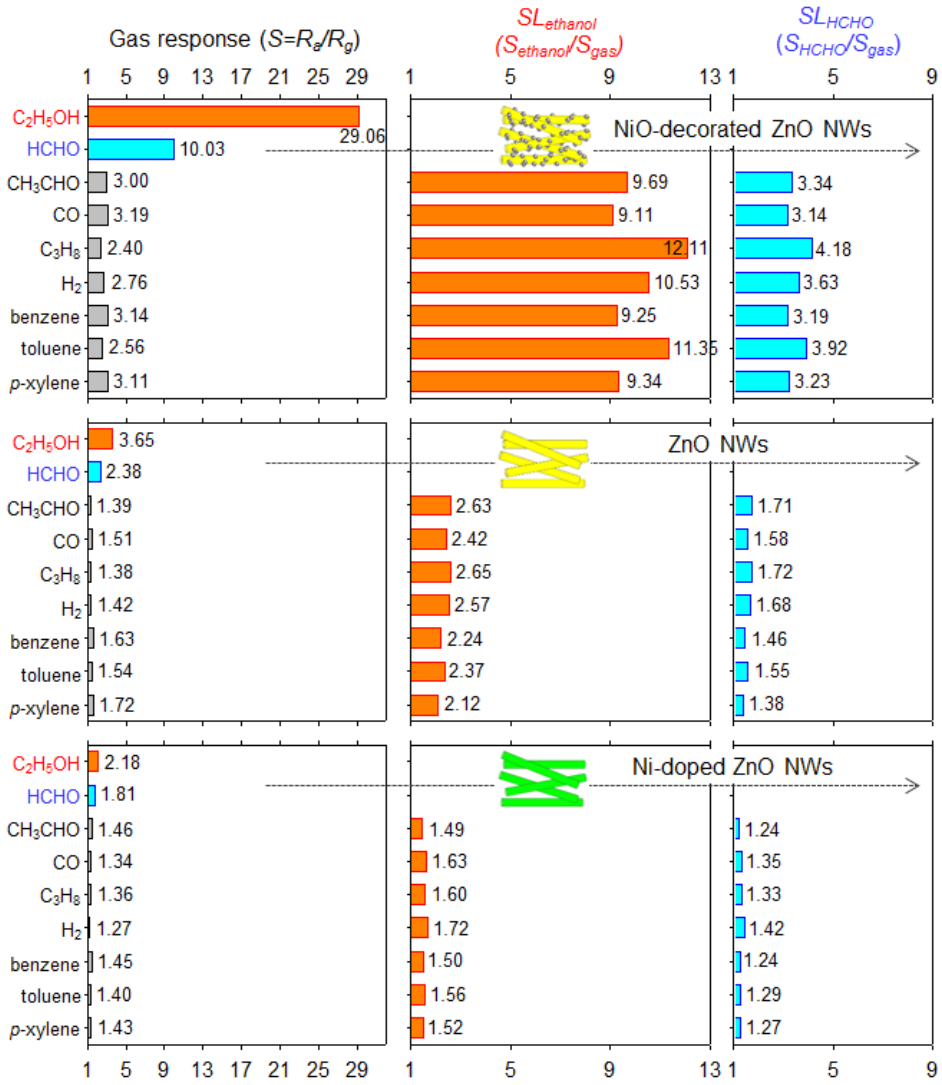

Fig. S6 The responses of the NiO-decorated ZnO, pristine ZnO, and Ni-doped ZnO NW network sensors to 5 ppm C_2H_5OH, HCHO, CH_3CHO, CO, C_3H_8, H_2, benzene, toluene, and *p*-xylene at 450 °C. The selectivity to 5 ppm C_2H_5OH (or HCHO) was defined as the ratio between the gas responses to 5 ppm C_2H_5OH (or HCHO) and those to other interfering gases ($SL_{ethanol}=S_{ethanol}/S_{gas}$, $SL_{HCHO}=S_{HCHO}/S_{gas}$).