

Supporting Information

Confined NiO in DNA like helical SnO₂ nanocoils and its excellent hydrogen sensing performance

Qingmin Hu^{a, b}, Cuixia Wu^c, Zhe Dong^a, Gaixia Zhang^b, Zhiheng Ma^a, Xiaohong Wang^a,
Shuhui Sun^{b, *}, Jiaqiang Xu^{a, *}

Experimental Method

Prior to fabrication of NiSnNCs, Al₂O₃ and SnO₂ were deposited on the CNCs, respectively. 50 ALD Al₂O₃ were deposited with Al(CH₃)₃ and H₂O as precursors.

The sensing performance for NiSnNCs samples were carried out with home-made tester. The operating temperature for the self-heated MEMS is controlled by heating voltage. The sensing performance for NiSnNCs samples was performed with a stationary state gas distribution method. The temperature and humidity of the test chamber is measured by a temperature sensor and a humidity sensor, respectively.

In this measurement, the sensing performance test was tested with the relative humidity of 50% RH at room temperature with a humidifier (Bear, JSQ-A50U1) and dehumidifier (Sen Electric, CH928B) to control ambient humidity.

For the stationary state gas distribution method, the desired gas concentration was obtained by changing the injection volume as calculated as follow:

$$C = C_s * V_x / V$$

Equation S1

The V_x is the injection volume (mL), V is the test chamber volume (200 mL), C_s is the gas concentration of standard gases (ppm).

The response of a sensor is usually defined as the change R_a/R_g in this work, where R_a is the resistance in air and R_g is the resistance in analyte gas.

UV-vis diffuse reflectance spectroscopy of the NiSnNCs samples were carried out on a Perek TU-1950. The bandgap energies of the NiSnNCs samples was calculated with:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad \text{Equation S2}$$

where α , ν , E_g , and A are the absorption coefficient, light frequency, bandgap, and a constant, respectively. n depends on the characteristics of the transition in a semiconductor: direct transition ($n=1$) or indirect transition ($n = 4$). The bandgap energy of the NiSnNCs samples in this work is calculated with $n = 4$.

Experimental section for EXAFS data collection and fitting

All the XAFS data were collected at room temperature at BL11B beamline of Shanghai Synchrotron Radiation Facility (SSRF). Monochromatized X-ray beam was provided by a double-crystal Si(111) monochromator, with an energy resolution $\Delta E/E \sim 1.4 \times 10^{-4}$. The rejection of higher harmonics was achieved by a pair of Cr-coated mirrors at 4 mrad. The spot size at the sample was $\sim 200 \mu\text{m} \times 250 \mu\text{m}$ ($H \times V$). The photon energies were calibrated to the first inflection point of the K edge from Ni foil at 8333 eV. The spectra were recorded in transmission mode. The acquired EXAFS data were normalized using the ATHENA module implemented in the IFEFFIT software packages. The k^3 -weighted $\chi(k)$ data of Fe K-edge were Fourier transformed to real (R) space using a hanning window ($dk=1.0 \text{ \AA}^{-1}$) to separate the EXAFS contributions from different coordination shells. The ARTEMIS code was used to obtain the quantitative structural parameters by least-squares fitting. For the in-situ XANES, H_2 (5%) and air were flown into the reactor with a 10 mL/min and 50 mL/min.

DFT calculation

The relative energy of target gas adsorbed on the SnO₂ (111) is defined as:

$$\Delta E_{\text{ads}} = E_{\text{adsorbate+surface}} - (E_{\text{adsorbate}} + E_{\text{surface}}),$$

Where $E_{\text{adsorbate+surface}}$ is the total energy of the adsorbed gas molecular and SnO₂ system, E_{surface} is the energy of the SnO₂ (111) surface with/without oxygen vacancy, and $E_{\text{adsorbate}}$ is the energy of the gas molecular.

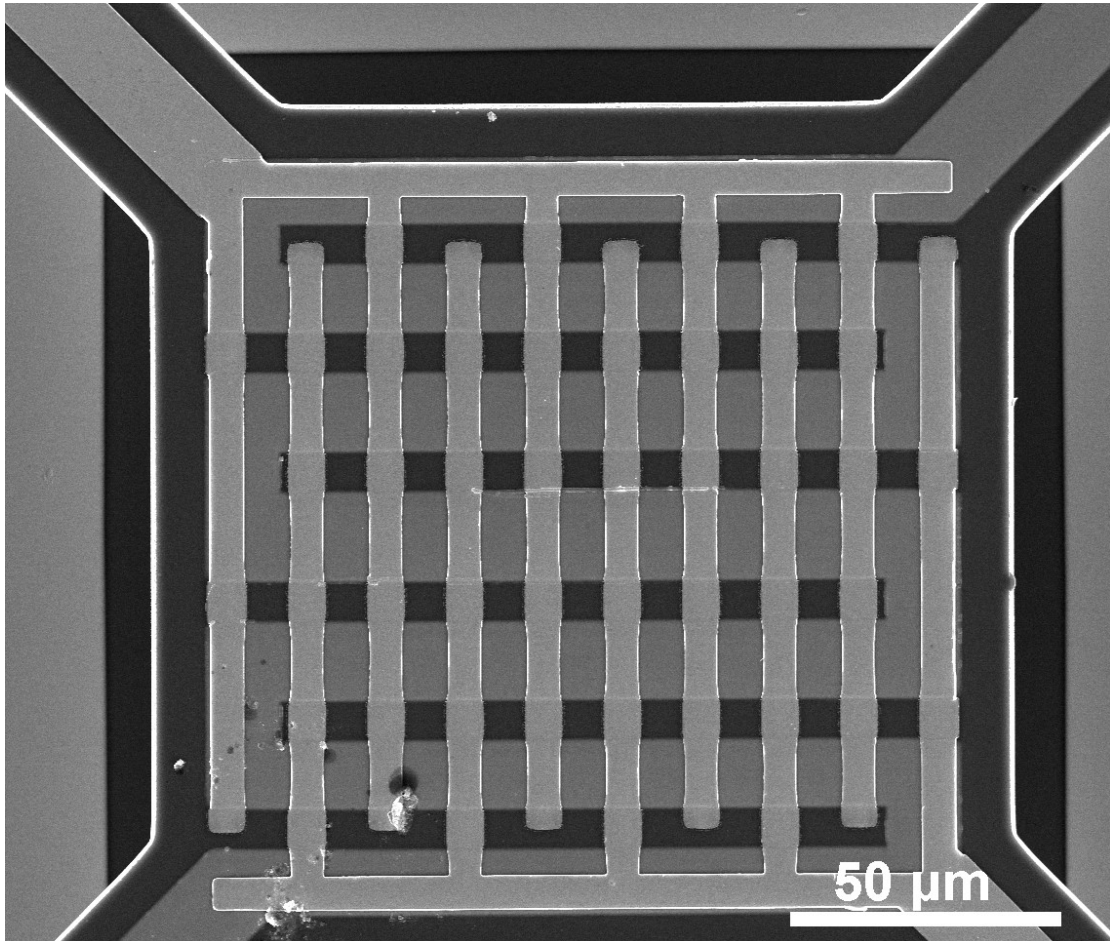


Figure S1. The SEM image for ALD SnO₂ film.

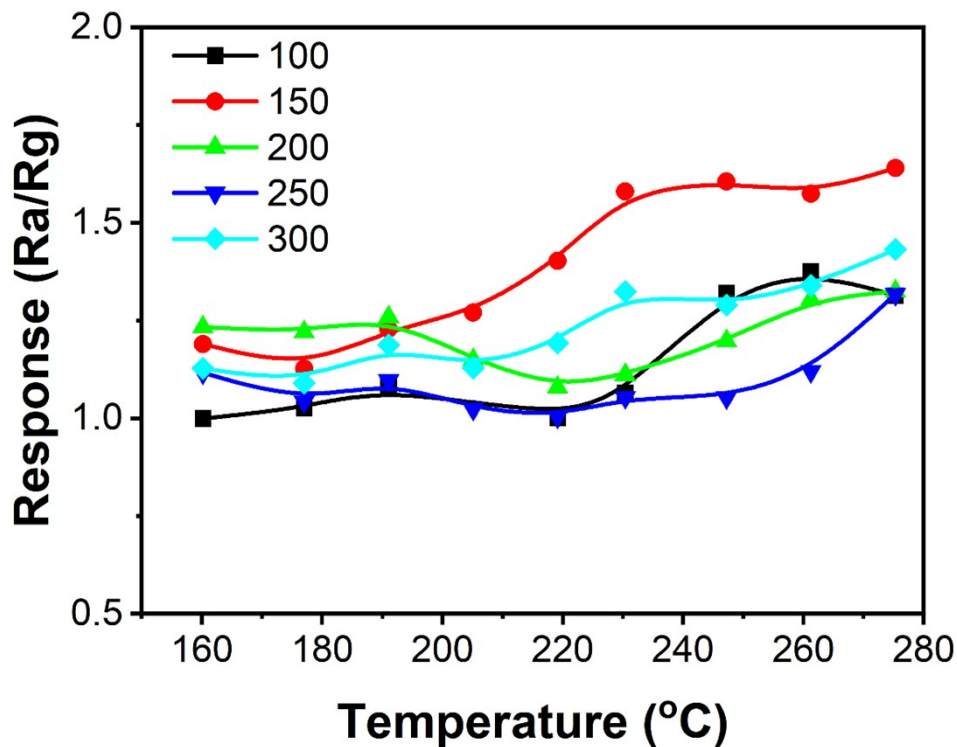


Figure S2. Sensing performance of SnO₂ based MEMS sensors with different ALD cycle numbers of 100, 150, 200, 250, and 300 for H₂ (30 ppm)

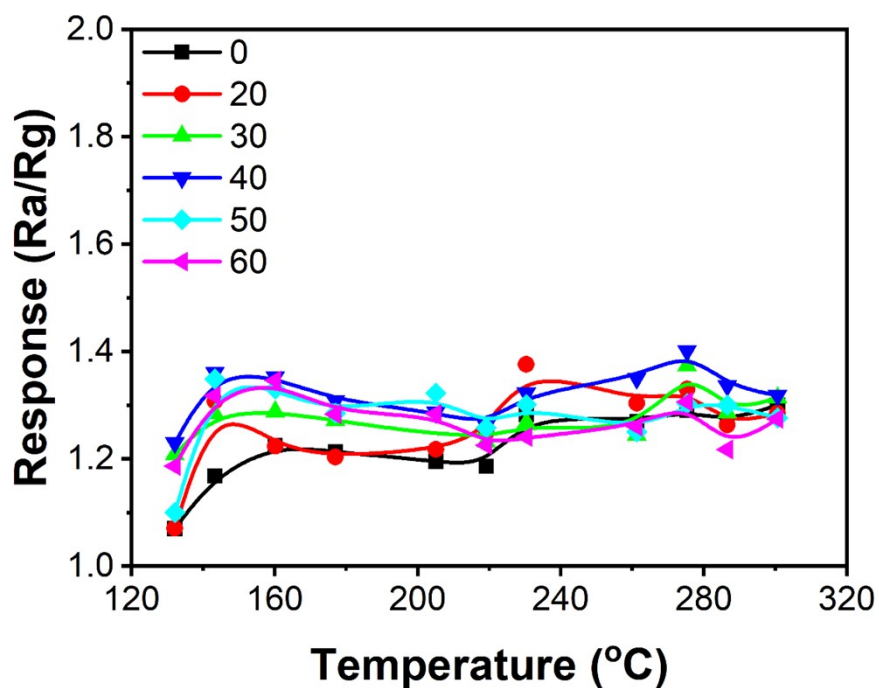


Figure S3. Sensing performance of NiO-SnO₂ based MEMS sensors with different cycle numbers of 0, 20, 30, 40, 50 and 60 ALD NiO for H₂ (10 ppm)

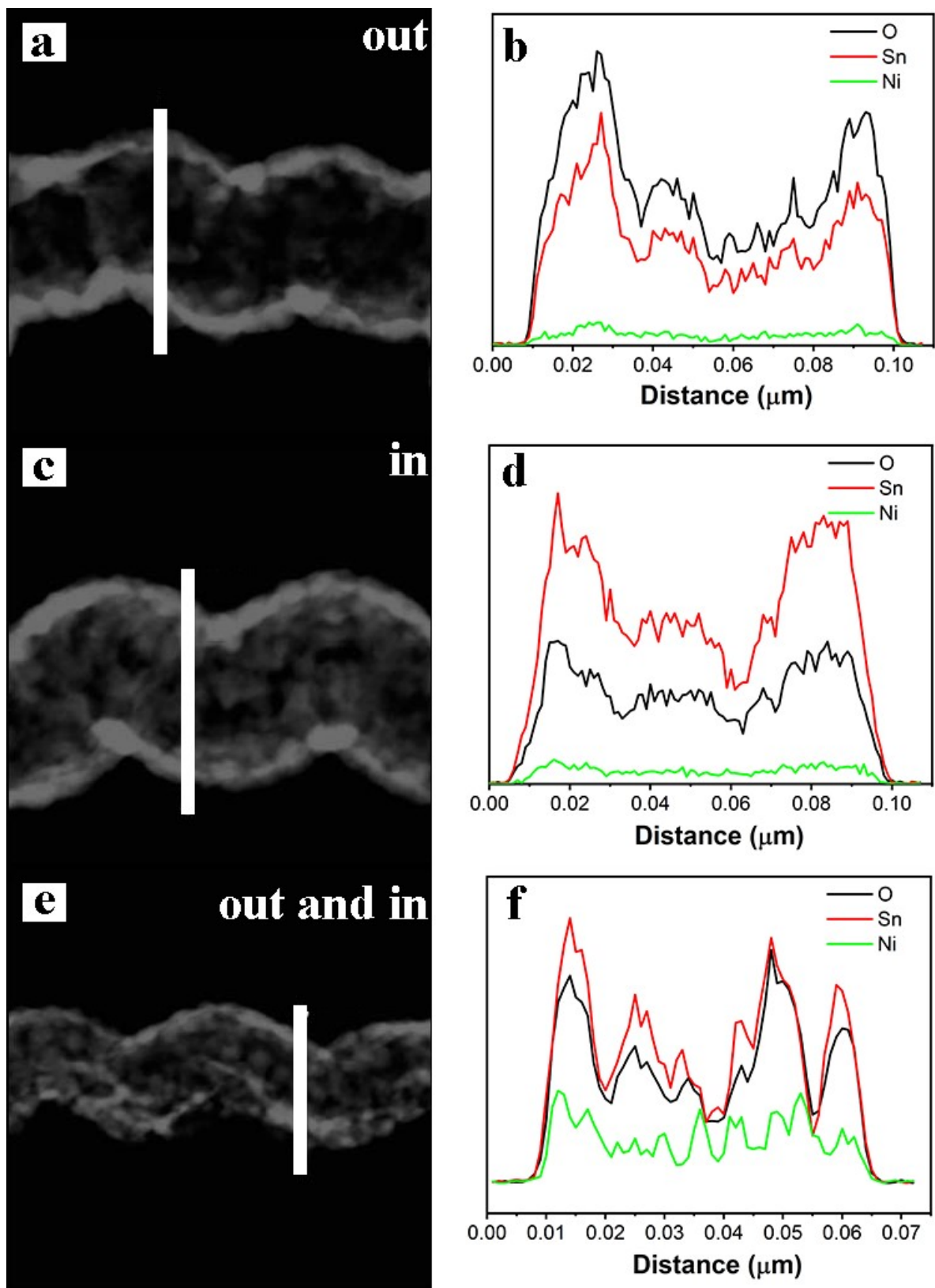


Figure S4. The EDS line-scanning spectra for different NiSnNCs samples are shown in d, e and f.

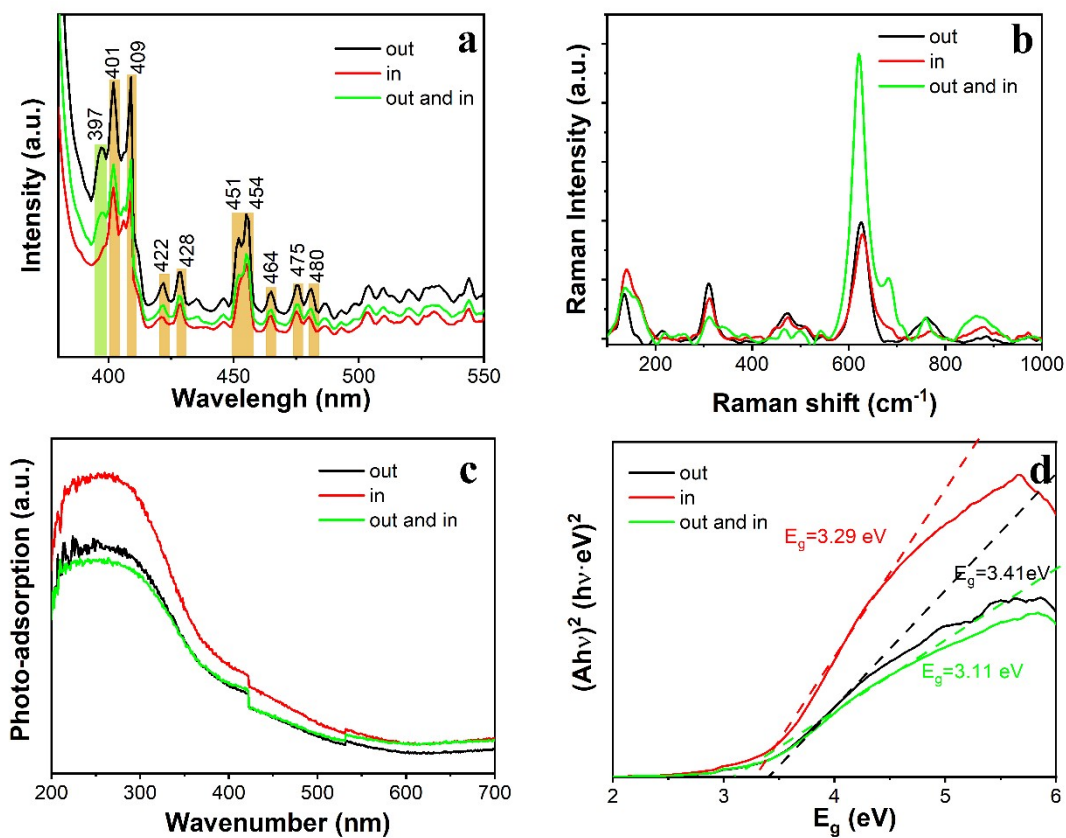


Figure S5. PL(a), Raman (b) and UV-vis (c, the d is for bandgap) spectra for the NiSnNCs samples.

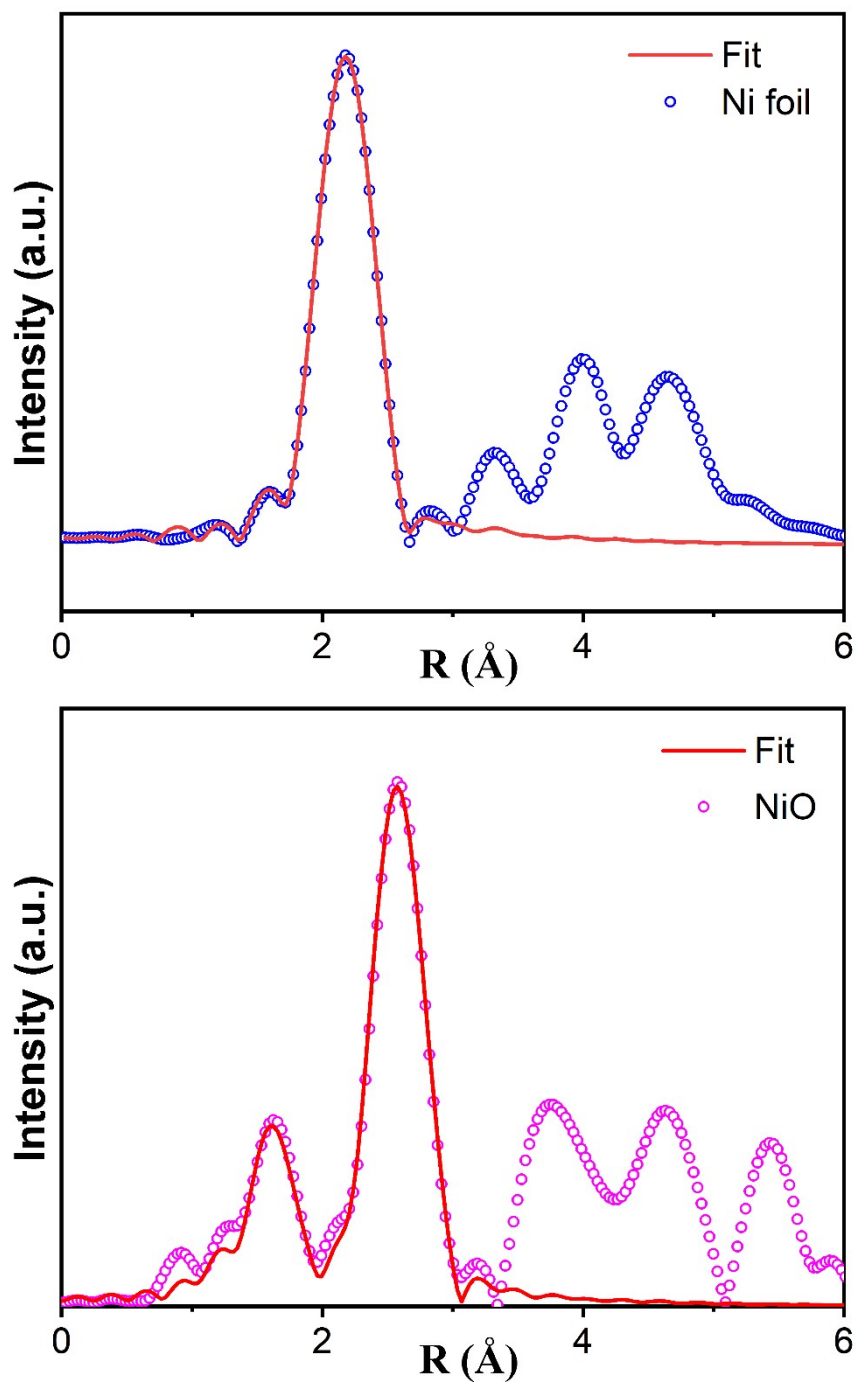


Figure S6. FT-EXAFS spectra for Ni foils and NiO (Open circles indicate experimental data, and lines indicate fitted results).

Table S1. EXAFS fitting parameters at the Ni K-edge for various samples ($S_0^2=0.747$)

	shell	CN	R(Å)	σ^2	ΔE_0	C3	R factor
Ni foil	Ni-Ni	12.0	2.48±0.01	0.0058	5.0±0.4		0.0016
NiO	Ni-O	6.3±1.3	2.14±0.03	0.0061	-2.5±2.8	0.0008	0.0084
	Ni-Ni	12.6±2.5	2.94±0.01	0.0061	-8.6±1.2		
O-NiSnNCs	Ni-O	5.4±0.8	2.15±0.01	0.0054	2.5±2.6	0.0012	0.0070
	Ni-Ni	11.1±1.8	2.94±0.01	0.0082	-9.7±1.4		
I-NiSnNCs	Ni-O	5.3±1.1	2.15±0.01	0.0052	2.9±3.3	0.0010	0.0096
	Ni-Ni	9.7±1.9	2.94±0.01	0.0080	-9.5±1.8		
B-NiSnNCs	Ni-O	5.5±1.3	2.18±0.03	0.0048	-4.9±3.5	0.0015	0.0072
	Ni-Ni	12.3±2.4	2.94±0.01	0.0082	-8.9±1.7		

^aN: coordination numbers; ^bR: bond distance; ^c σ^2 : Debye-Waller factors; ^d ΔE_0 : the inner potential correction. R factor: goodness of fit. S_0^2 was set to 0.747, according to the experimental EXAFS fit of Ni foil reference by fixing CN as the known crystallographic value; δ : percentage.

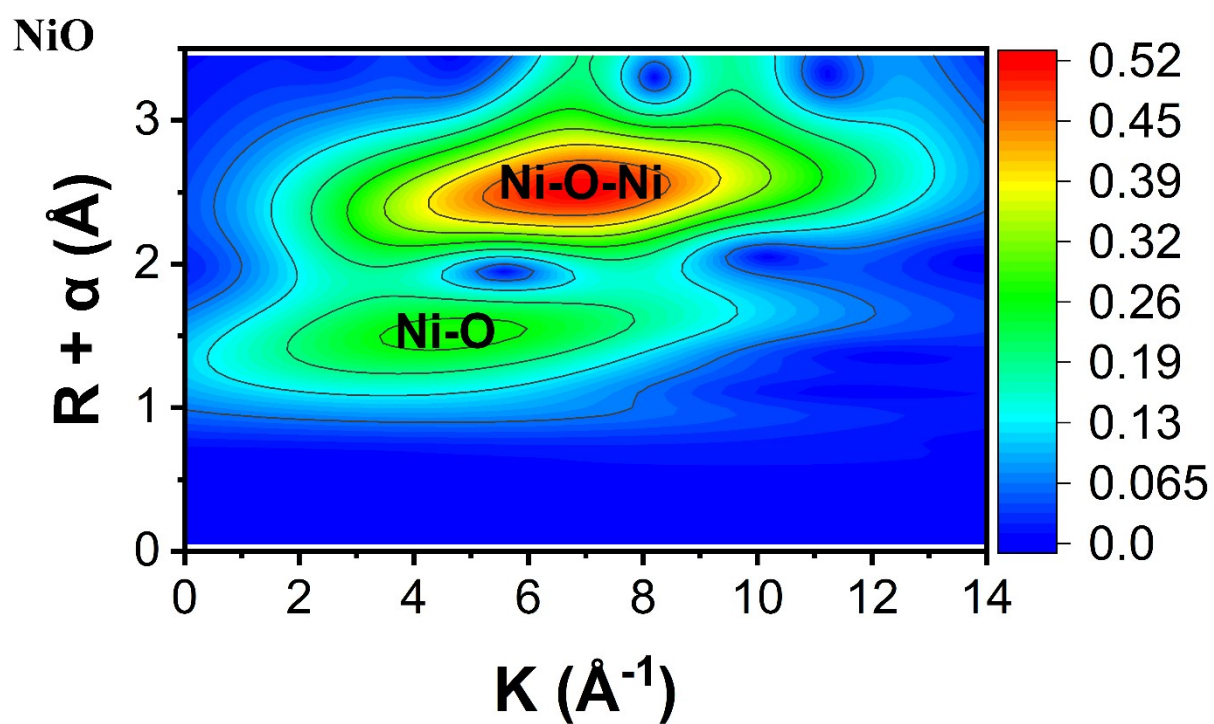
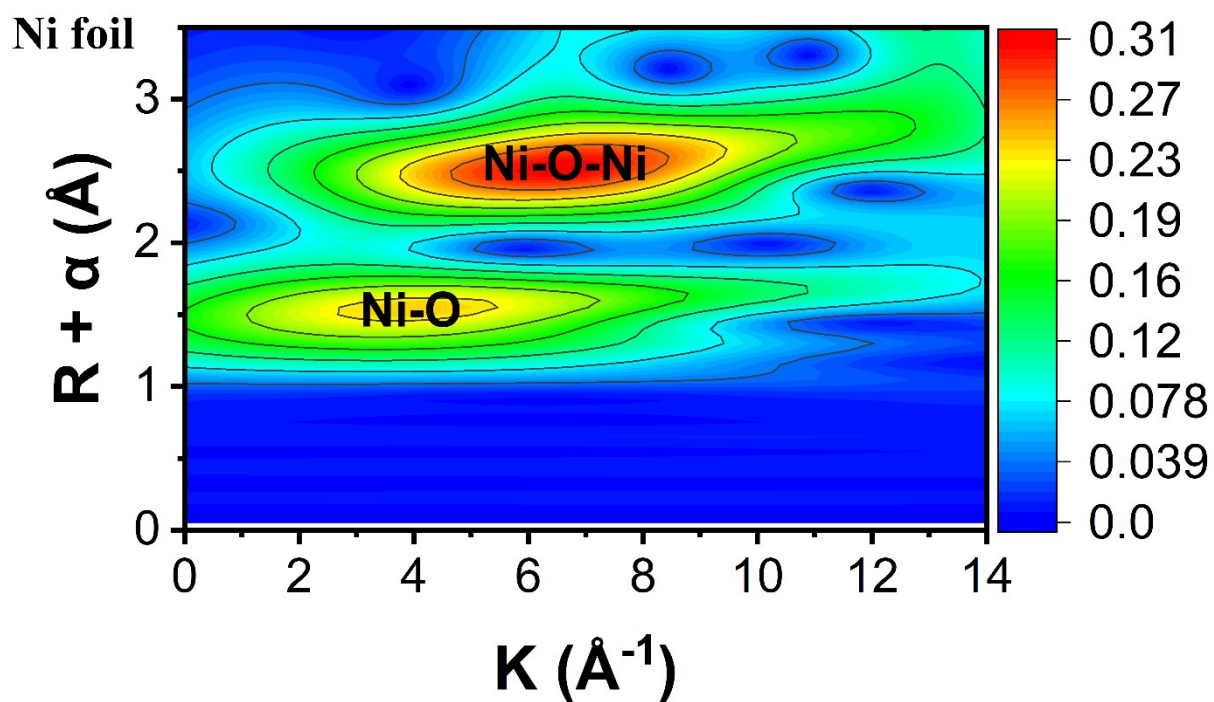


Figure S7. WT-EXAFS spectra for Ni foil and NiO.

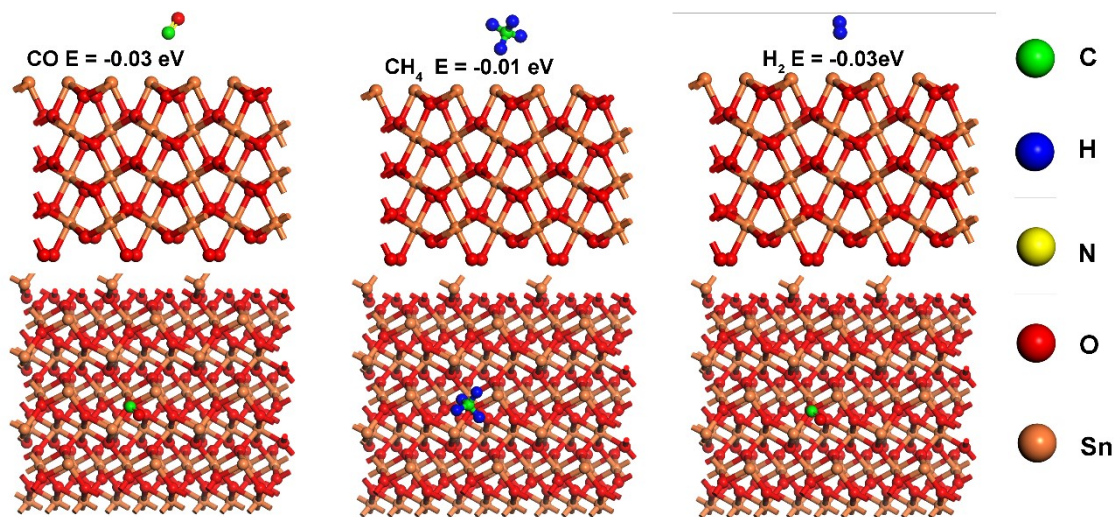


Figure S8. DFT calculation for adsorption energy of different gas molecular on SnO₂ (111).

The sensing performance is attributed to the related reactions as follow: for adsorption of O₂



for adsorption of H₂



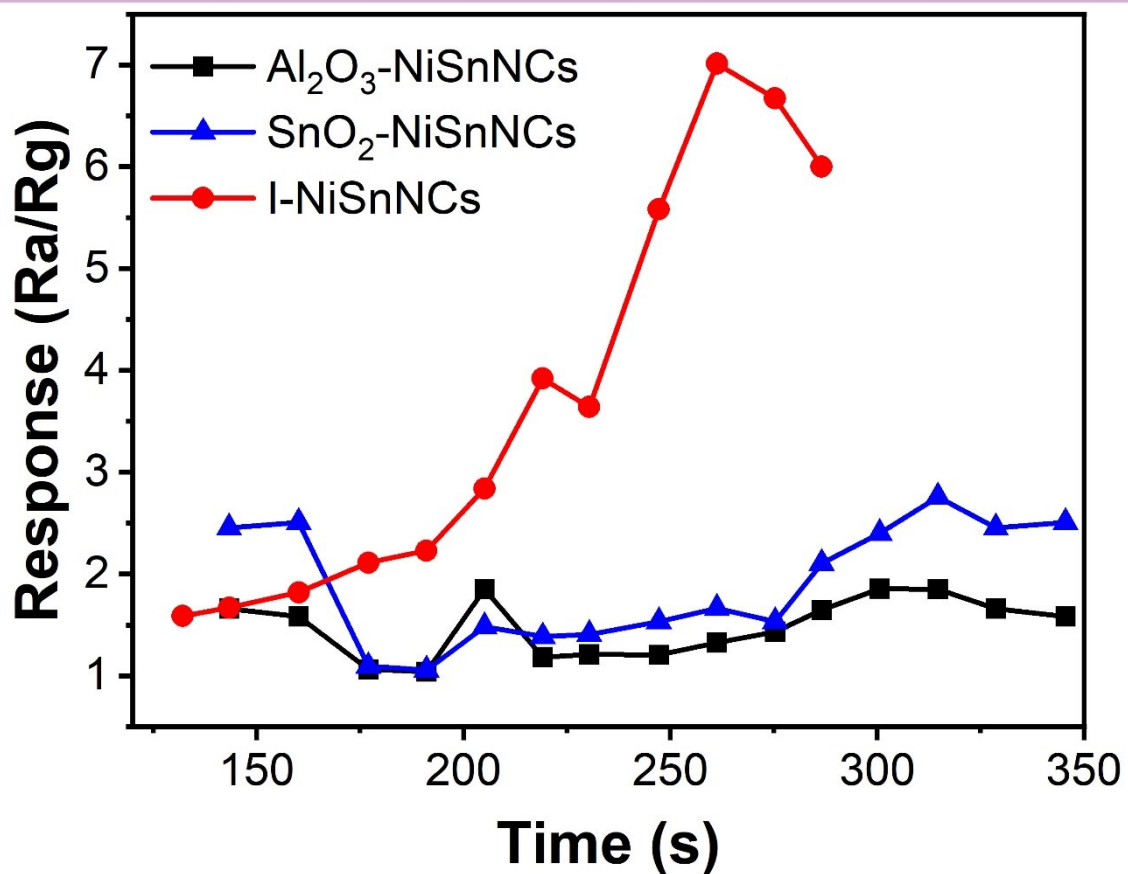
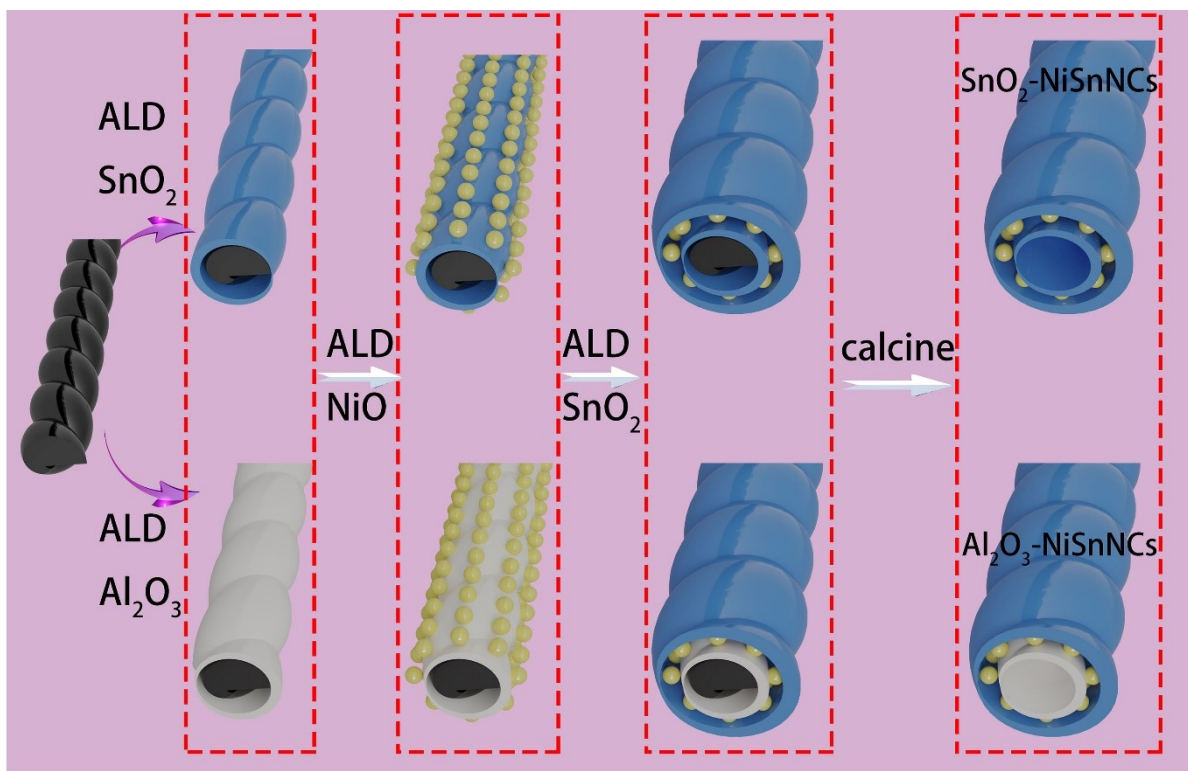


Figure S9. The schematic diagram for fabrication of $\text{Al}_2\text{O}_3\text{-NiSnNCs}$ and $\text{SnO}_2\text{-NiSnNCs}$, and the sensing performance to 500 ppm for $\text{Al}_2\text{O}_3\text{-NiSnNCs}$, $\text{SnO}_2\text{-NiSnNCs}$ and I-NiSnNCs.