

**Ultra-sensitive triethylamine sensor based on oxygen vacancy
enriched ZnO/SnO₂ micro-camellia**

Yong-Hui Zhang,^{*,a} Chao-Nan Wang,^a Fei-Long Gong,^a Jun-Li Chen,^a Ke-Feng Xie,^b

Hao-Li Zhang,^{*c} and Shao-Ming Fang^{*,a}

^a College of Materials and Chemical Engineering, Collaborative Innovation Center of
Environmental Pollution Control and Ecological Restoration, Zhengzhou University
of Light Industry, Zhengzhou 450002, P. R. China

*Email: yonghui.zhang@zzuli.edu.cn; mingfang@zzuli.edu.cn

^b School of Chemical and Biological Engineering, Lanzhou Jiaotong University,
Lanzhou, Gansu 730070, P. R. China

^c State Key Laboratory of Applied Organic Chemistry (SKLAOC); Key Laboratory of
Special Function Materials and Structure Design (MOE); College of Chemistry and
Chemical Engineering, Lanzhou University, Lanzhou, 730000, P. R. China

*Email: haoli.zhang@lzu.edu.cn

Sensor fabrication and response measurement

The gas sensor was fabricated as follows: the as-prepared pure ZnO and ZnO/SnO₂ composite materials were ground uniformly, then mixed with terpinol formed into a paste. Then the paste was coated onto the surface of the Al₂O₃ tube with four Pt wires. The A Ni-Cr alloy wire was inserted into the tube as a heater to control the operating temperature of the sensor by adjusting the voltage. Before the gas sensing measurement, the sensor was aged at 300 °C for 10 day to improve the stability. The gas sensing properties were measured by a computer controlled WS-30 A static gas sensing test system.

The sensors were put into a glass chamber (18 L) at the beginning. During the test, the relative humidity (RH) of the test chamber was 20±5 %. The working temperature of the gas sensor was controlled by adjusting the heating voltage (V heating) of the Ni-Cr alloy resistor. During the test, the analytical reagent solution is injected into the static test system and evaporated with an evaporator. Two fans are installed in the glass chamber to make the gas rapidly and evenly dispersed. For the target gases obtained from liquid, the concentration of target gas was calculated by the

following formula:
$$V_1 = \frac{C * V_2 * M}{22.4 * \rho * d * 1000}$$
 V₁(μL) is the volume of the liquid, C (ppm) is the concentration of the target gas, ρ (g/mL) is the density of the liquid, d is the purity of the liquid, V₂ (L) is the volume of the glass chamber, and M (g/mol) is the molecular weight of the liquid. The concentration of the gas can be transferred to the volume of the target reagent, and the required test dose can be obtained with a microsyringe. After injecting the target gas, remove the glass cover of the test chamber when the sensor resistance reaches the equilibrium value. The analysis system automatically acquires the resistance and response values of the sensor. During the test, a reference resistor (R load) was added to the sensor circuit, and the working voltage is 5V. The sensor response in air or target gas can be measured by monitoring the voltage across the reference resistor.

For n-type semiconductor, sensitivity (response) is defined as the ratio of resistance in the air (R_a) to the resistance in gas (R_g). If the gas is reduced gas, $S=R_a/R_g$. If the gas is oxidized, then $S=R_g/R_a$. The response and recovery time are respectively defined as the time required for the resistance to reach the total resistance change of 90% after injecting the target gas and the time required for the resistance to decrease to the total resistance change of 10% after removing the target gas.

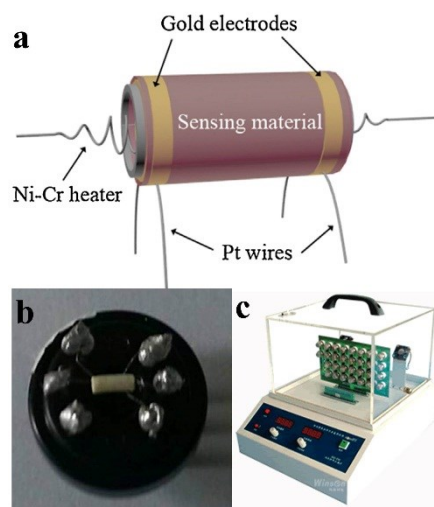


Fig. S1 (a) The structural illustration, (b) photo of an ZnO sensor and (c) measurement setup.

Computation method and model:

In this work DFT was employed to investigate the interaction of TEA molecule with pristine/Vo ZnO surface. The DFT calculations were performed using Dmol³ code. Where a generalized-gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) was used to describe the exchange-correlation function. Additionally

DFT (DSPP) with some degree relativistic corrections was used to replace the electrons of core and nuclei and only considering the valence electrons. The ZnO surface was constructed by cleaving the ZnO bulk in (001) direction. Each calculated system consisted of a $16.25 \times 16.25 \times 28.42$ Å ZnO super cell (200 atoms) with an aniline molecule adsorbed in the center region (Fig. 11). For the Ov-ZnO, only one O was missing in the ZnO super cell for reducing complexity (Figure 11b). The vacuum distance to separate the adjacent ZnO layers was kept as 20 Å. The k -point was set to $3 \times 3 \times 1$ for all systems, and the convergence tolerance was set as 1.0×10^{-5} Hartree in energy and the 0.002 Hartree/Å in force. The adsorption energy of aniline molecule on ZnO was calculated as:

$$E_{\text{ad}} = E_{(\text{aniline}+\text{ZnO})} - E_{(\text{ZnO})} - E_{(\text{aniline})}$$

Where $E_{(\text{aniline}+\text{ZnO})}$, $E_{(\text{ZnO})}$ and $E_{(\text{aniline})}$ are the total energies of the relaxed aniline on ZnO system, ZnO and the aniline molecule, respectively.

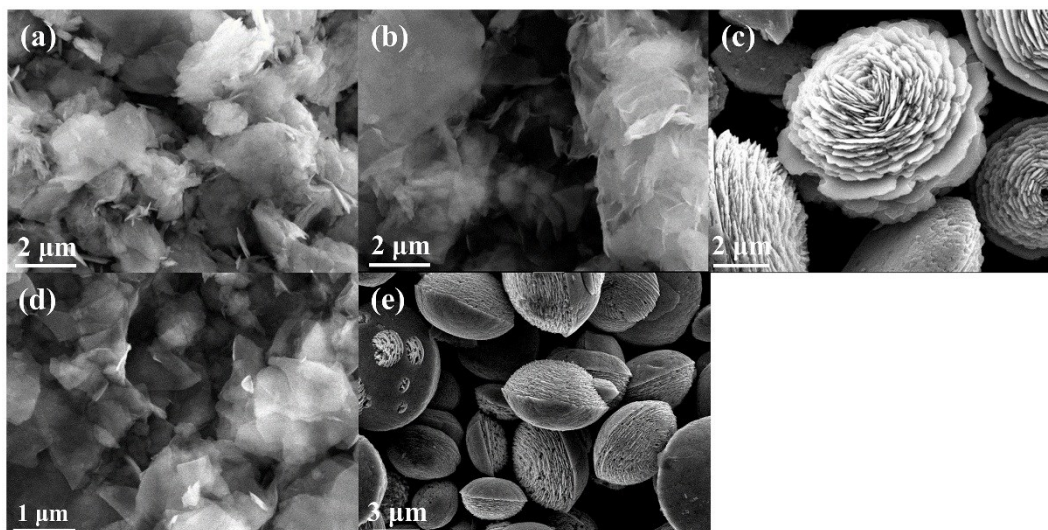


Fig. S2 High-magnification FESEM images of pure ZnO synthesized under different alcohol-water ratios (1:3, 3:5, 3:1, 5:3, 7:1)

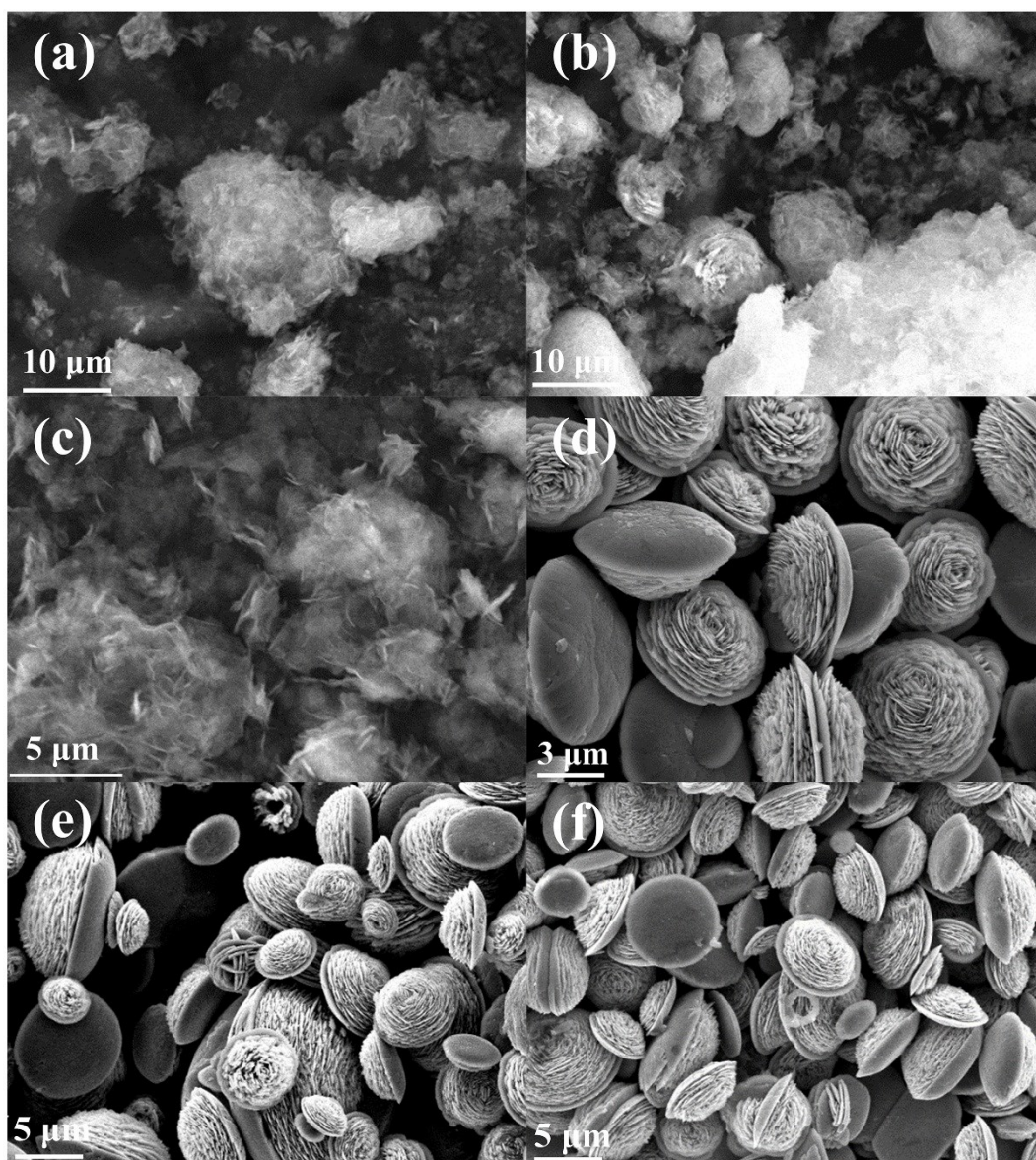


Fig. S3 High-magnification FESEM images of pure ZnO with different amounts of urea.

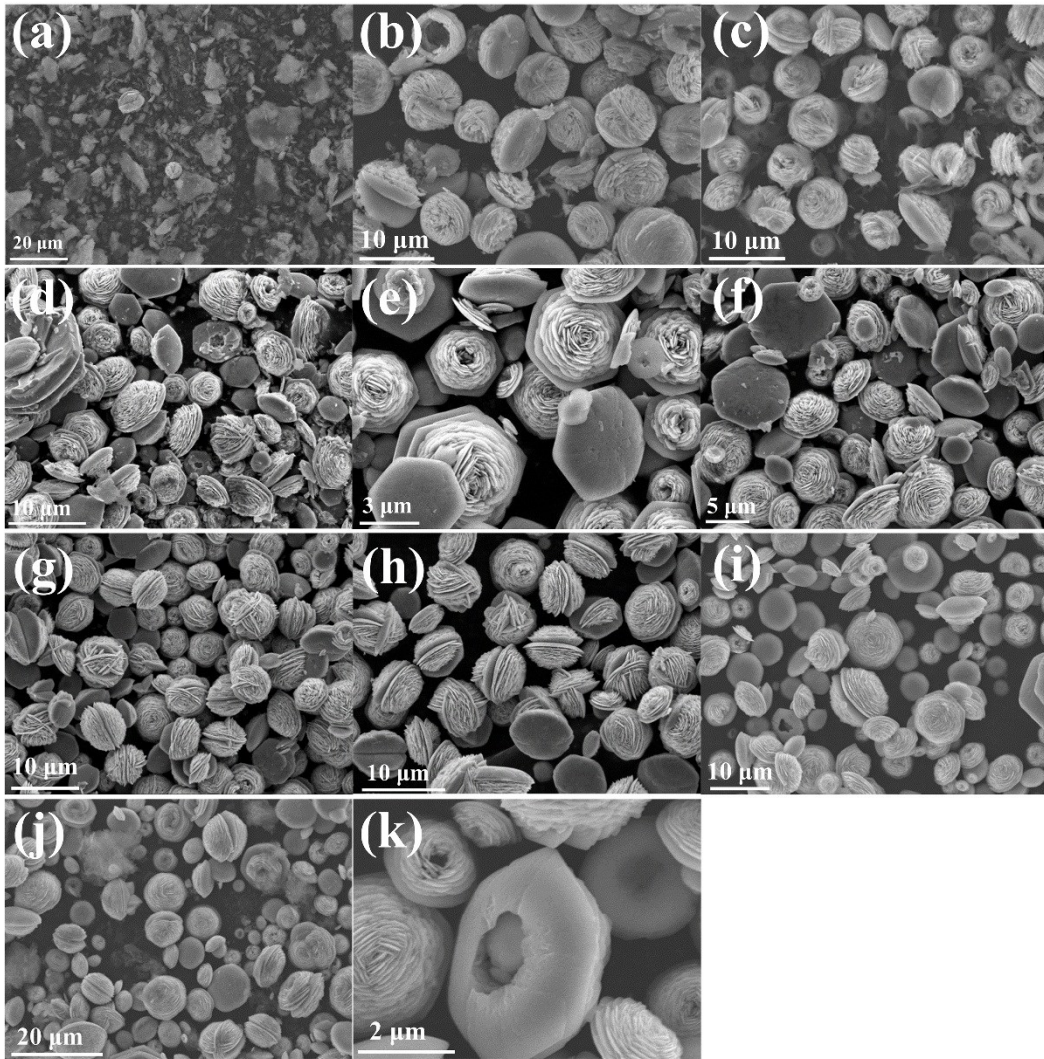


Fig. S4 High-magnification FESEM images of pure ZnO with different reaction time

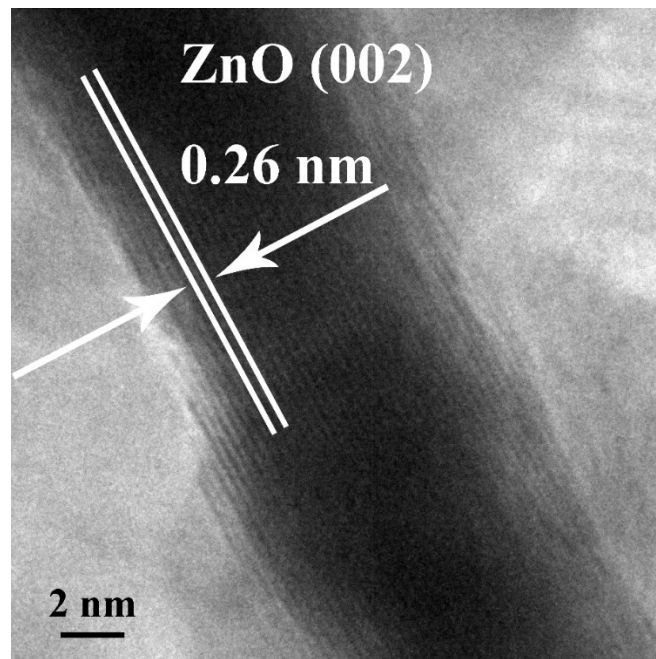


Fig. S5 HRTEM image of ZnO.

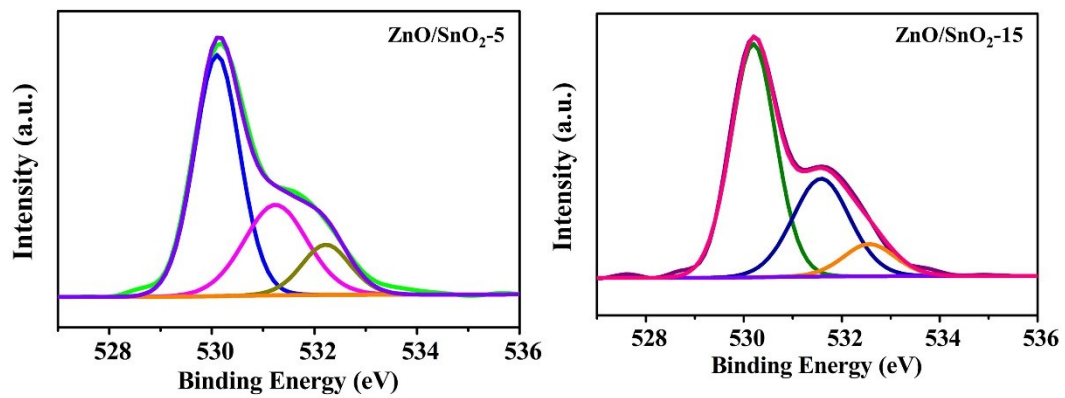


Fig. S6 The O 1s spectra of (a) ZnO/SnO₂-5 and (b) ZnO/SnO₂-15.

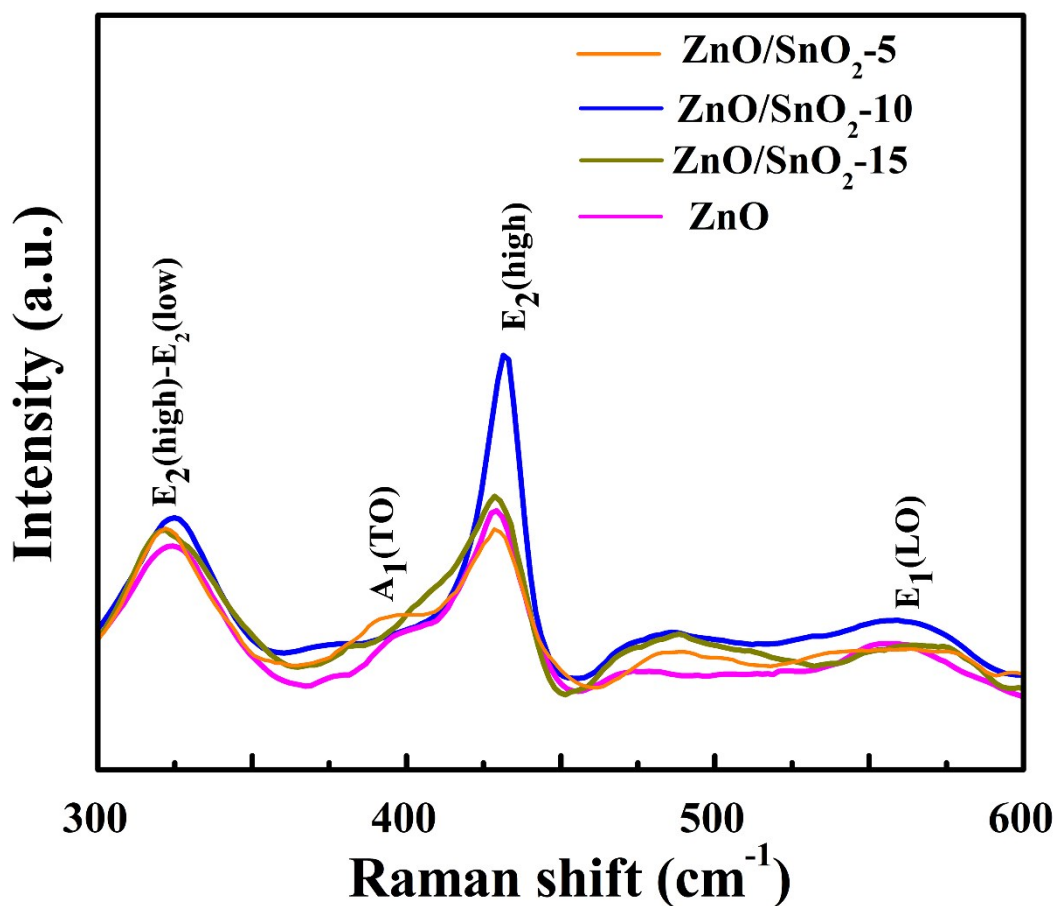


Fig. S7 The Raman atlas of ZnO, ZnO/SnO₂-5, ZnO/SnO₂-10 and ZnO/SnO₂-15.

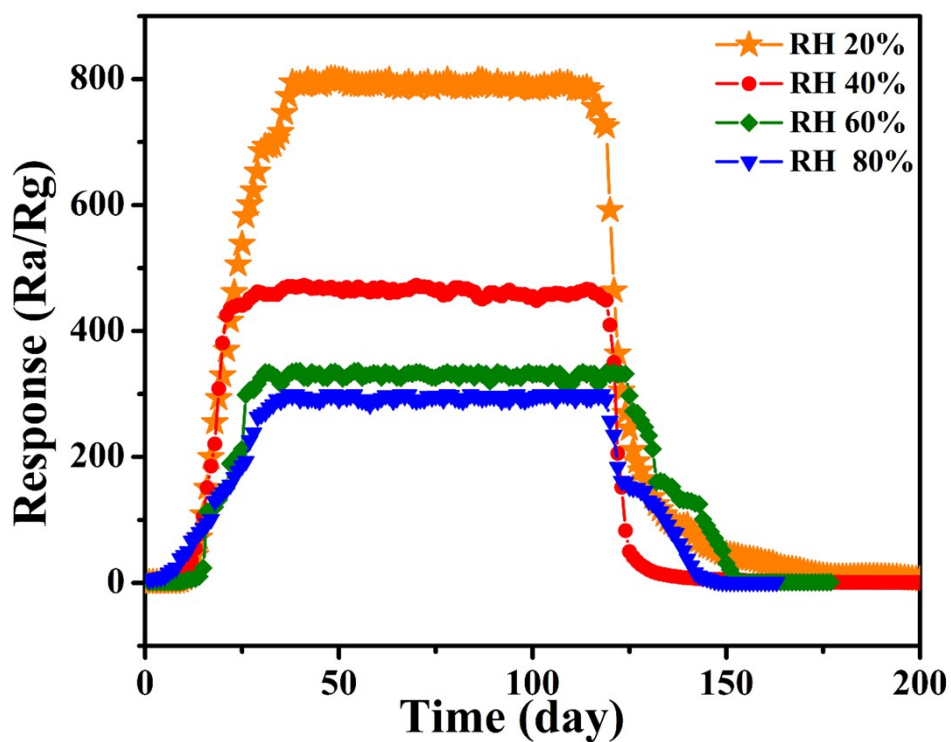


Fig. S8 Responses of ZnO/SnO₂-10 gas sensors under different humidity.

Table S1 The grain parameters of ZnO, ZnO/SnO₂-5, ZnO/SnO₂-10 and ZnO/SnO₂-15.

| Materials | 2 θ (°) | d(001)(Å) | FWHM (°) | G (nm) |
|--------------------------|----------------|-----------|----------|--------|
| ZnO | 34.285 | 2.6134 | 0.111 | 86.587 |
| ZnO/SnO ₂ -5 | 34.397 | 2.6051 | 0.113 | 85.168 |
| ZnO/SnO ₂ -10 | 34.449 | 2.6012 | 0.116 | 83.017 |
| ZnO/SnO ₂ -15 | 34.387 | 2.6058 | 0.122 | 78.876 |

Table S2 The X-ray diffraction data results of ZnO, ZnO/SnO₂-5, ZnO/SnO₂-10 and ZnO/SnO₂-15.

| material | (hkl) | I/I ₀ | TC [%] |
|--------------------------|-------|------------------|--------|
| ZnO | (100) | 20.30 | 29.09 |
| | (002) | 30.23 | 43.32 |
| | (101) | 19.25 | 27.59 |
| ZnO/SnO ₂ -5 | (100) | 47.86 | 32.61 |
| | (002) | 57.5 | 39.18 |
| | (101) | 41.41 | 28.21 |
| ZnO/SnO ₂ -10 | (100) | 23 | 34.37 |
| | (002) | 23.05 | 34.43 |
| | (101) | 20.88 | 31.20 |
| ZnO/SnO ₂ -15 | (100) | 24.09 | 31.21 |
| | (002) | 28.5 | 36.92 |
| | (101) | 24.6 | 31.87 |

Table S3 oxygen species content of ZnO, ZnO/SnO₂-5, ZnO/SnO₂-10 and ZnO/SnO₂-15.

| Sample | O _L | O _V | O _C |
|--------------------------|----------------|----------------|----------------|
| ZnO | 63.69% | 27.39% | 8.92% |
| ZnO/SnO ₂ -5 | 57.47% | 29.89% | 12.64% |
| ZnO/SnO ₂ -10 | 47.85% | 39.71% | 12.44% |
| ZnO/SnO ₂ -15 | 59.17% | 31.36% | 9.47% |