

Self-Powered NO Gas Sensors Based on Ce-Doped ZnO Nanorod Piezoelectric Nanogenerators (PENGs)

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Keywords: Nitric oxide (NO) gas, hydrothermal method, piezoelectric nanogenerator (PENG), cerium dopant (Ce-doped), Zinc Oxide (ZnO)

1 Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor with excellent electrical, optical, and chemical stability, making it suitable for sensors and optoelectronic devices[1]. In gas sensing, its large surface area and high reactivity enable efficient gas adsorption and detection. Doping further enhances its performance, yet rare earth (RE) doping remains less explored. Cerium (Ce), with dual oxidation states ($\text{Ce}^{3+}/\text{Ce}^{4+}$), can improve ZnO's charge transfer, oxygen vacancy formation, and surface reactivity—key factors for gas sensing[2]. Nitric oxide (NO) is a toxic pollutant, requiring sensitive and reliable detection methods. This work investigates Ce-doped ZnO nanorods integrated into piezoelectric nanogenerators (PENGs) for self-powered NO gas sensing, aiming to enhance sensitivity and stability through the synergistic effects of Ce doping and piezoelectric modulation.

2 Experimental

A. Fabrication of Self-Powered Gas Sensors Based on PENGs With Ce-Doped 1-D ZnO NR Arrays.

As shown in Fig. 1, the device adopts a sandwich structure using ITO-PET as both top and bottom electrodes. A 100 nm Ag layer was deposited on the top ITO-PET by RF magnetron sputtering (50 W , $7.5 \times 10^{-3}\text{ Torr}$), while a ZnO seed layer was sputtered at 100 W and $1 \times 10^{-3}\text{ Torr}$. Ce-doped ZnO nanorods were grown hydrothermally on the bottom substrate using 50 mM zinc nitrate, 25 mM HMTA, and 0.75 mM cerium nitrate at 95°C for 3 h . After rinsing and drying at 60°C , the Ag-coated ITO/PET and Ce-doped ZnO NR array were assembled to form the PENG device.

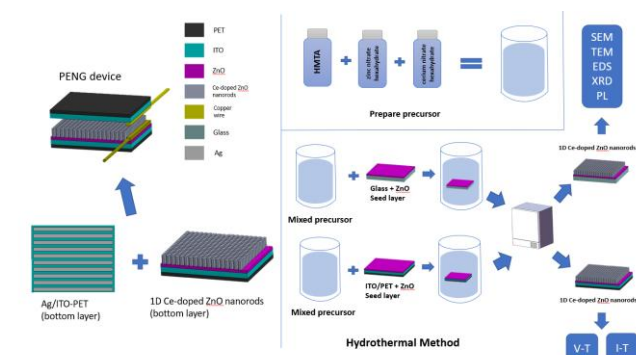


Fig.1: Schematic of the fabrication steps of PENGs with 1-D Ce doped ZnO NR arrays

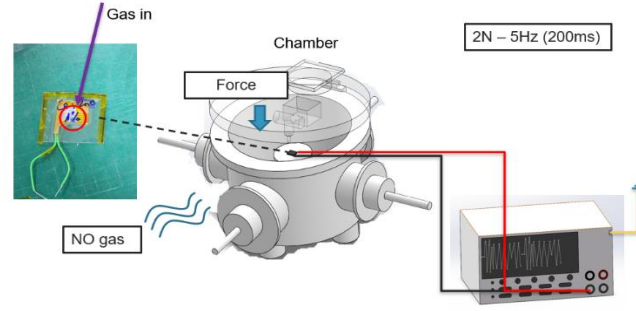


Fig.2: Electrical measurement with impact system for PENGs

B. Material Characterization and Electrical Measurement

Morphology, composition, and crystal structure were analyzed using SEM, EDS, and XRD, respectively. Gas sensing performance toward NO was tested under controlled concentrations using a custom impact system (Fig. 2), and electrical outputs (V–ppm and sensitivity) were recorded to evaluate device response..

3 Result and Discussions

A. Material Characteristic of 1-D ZnO and Ce-doped ZnO NRs.

Fig. 3 shows SEM images of ZnO and Ce-doped ZnO nanorods grown on ITO/PET substrates. Both samples exhibit uniform hexagonal structures with vertically aligned nanorods. The average height decreased from $\sim 1.75\text{ }\mu\text{m}$ for ZnO to $\sim 1.3\text{ }\mu\text{m}$ for Ce:ZnO, attributed to lattice strain from the ionic radius mismatch between Ce^{3+} ($1.01\text{ }\text{\AA}$) and Zn^{2+} ($0.74\text{ }\text{\AA}$), which limits axial growth and refines nanorod morphology. EDS analysis confirmed the presence of Zn, O, and Ce elements without impurities, indicating successful Ce incorporation and high sample purity. XRD patterns (Fig. 4) revealed dominant (002) peaks for both samples, consistent with hexagonal wurtzite structures and preferred c-axis orientation. The reduction in (002) intensity upon Ce doping suggests minor lattice distortion without phase alteration, confirming substitutional incorporation of Ce ions into the ZnO lattice.

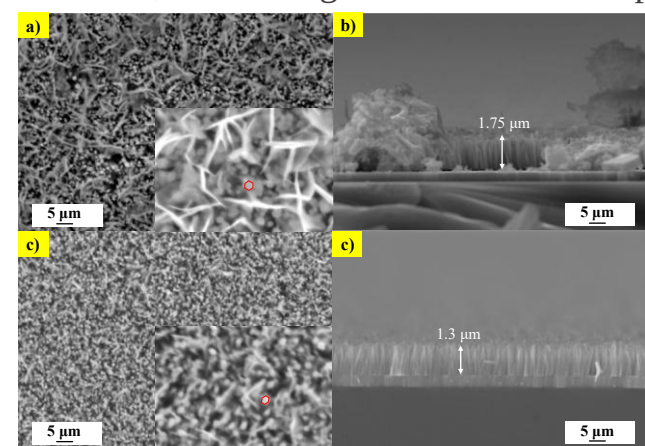


Fig.3: (a) (c): top-view and (b) (d) side-view SEM images of the 1-D ZnO and Ce:ZnO NR arrays. (e) EDS result of the 1-D Ce:ZnO NRs.

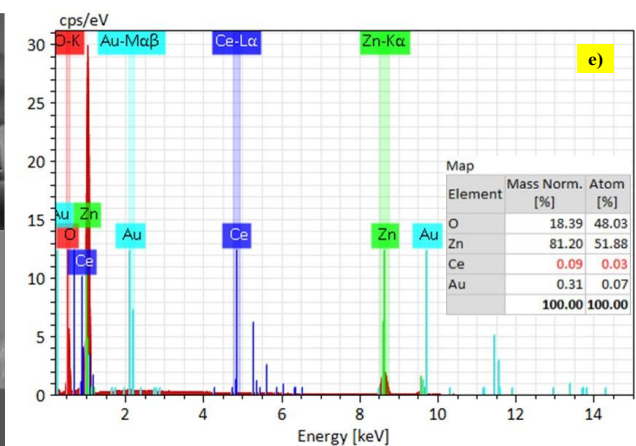


Fig.4: XRD pattern measured from the as-grown 1-D ZnO and Ce:ZnO NR samples.

B. Electrical Performances of PENG devices.

Under ambient air, the pure ZnO PENG produced an average output voltage of 0.451 V , while the Ce-doped ZnO PENG generated a higher output of 0.668 V , confirming enhanced piezoelectric performance. When exposed to NO gas, the Ce-doped ZnO device showed a clear voltage increase with concentration, reaching 1.191 V at 100 ppm (Figs. 5 – 6).

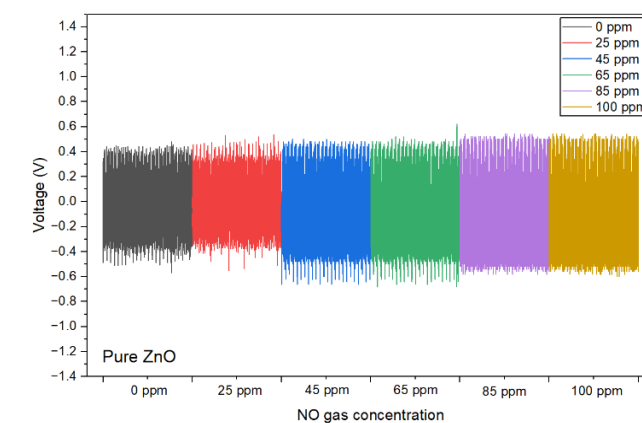


Fig.5: Voltage of Pure ZnO in the presence of different NO gas concentrations

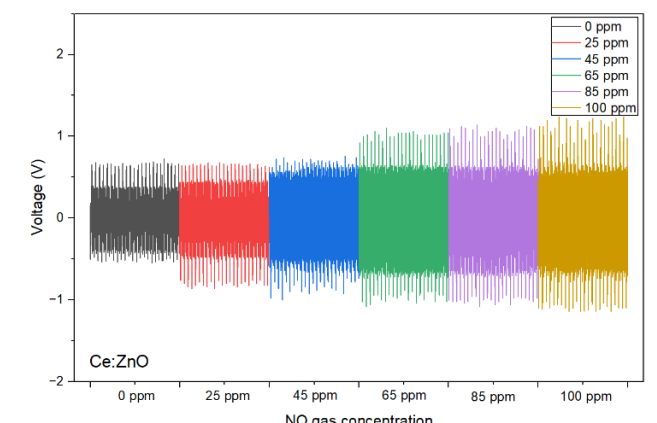
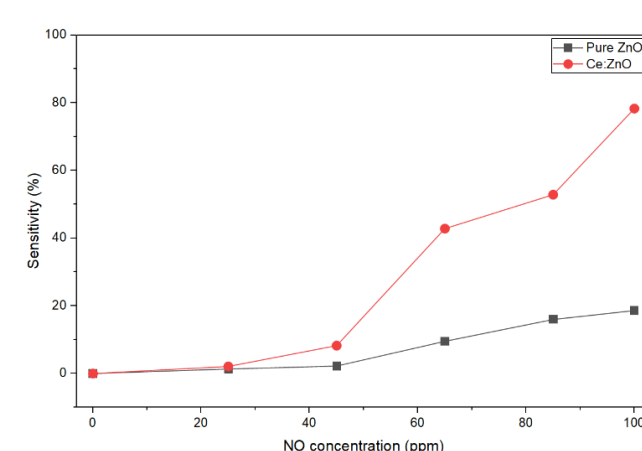


Fig.6: Voltage of Ce:ZnO in the presence of different NO gas concentrations

The sensing performance of Ce-doped ZnO nanorod PENGs was evaluated by the relative change in output voltage: $S\% = |V_a - V_g|/V_a \times 100\%$

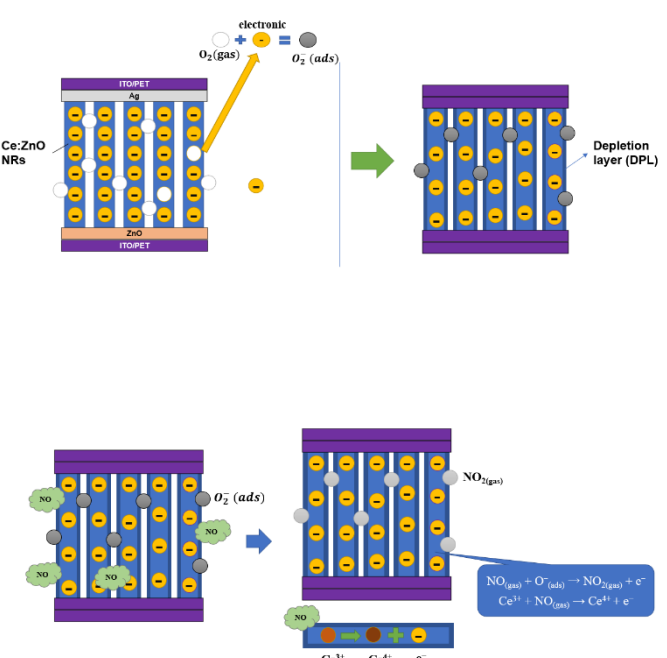
As summarized in Table 1, the device with 0.75 mM Ce doping achieved the highest response of 78.29% at 100 ppm NO, indicating excellent sensitivity and stability. These results demonstrate that Ce-doped ZnO nanorod PENGs are highly effective for self-powered NO gas sensing, as illustrated in Fig. 7.



Material samples	NO (ppm)	Average Voltage (V)	Sensitivity (%)
ZnO PENG	0	0.451	0
	25	0.457	1.33
	45	0.461	2.21
	65	0.494	9.53
	85	0.523	15.96
	100	0.535	18.62
Ce:ZnO PENG	0	0.668	0
	25	0.682	2.09
	45	0.723	8.23
	65	0.954	42.8
	85	1.021	52.84
	100	1.191	78.29

C. Gas-Sensing Mechanisms of PENG in Air and NO gas.

In air, oxygen molecules adsorb on the ZnO surface, capturing electrons to form O_2^- and O^- species, which create a depletion layer and increase resistance. When exposed to NO gas, NO reacts with these adsorbed oxygen ions or directly with Ce^{3+} , producing NO_2 and releasing electrons back to the conduction band. $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycling enhances charge transfer and oxygen vacancy activity, leading to higher piezoelectric output under gas exposure[3]. This dynamic interaction between oxygen species, NO molecules, and cerium ions modulates surface potential and charge screening, resulting in increased output voltage and excellent reversibility of the Ce-doped ZnO PENG sensor.



4 Conclusion

Pure ZnO and Ce-doped ZnO nanorods were synthesized via hydrothermal growth and confirmed by SEM and XRD to form high-density wurtzite arrays with c-axis orientation. EDS verified Ce incorporation ($\sim 0.03\text{ at}\%$), beneficial for gas sensing. Under NO exposure ($0\text{--}100\text{ ppm}$), the PENG output voltage increased due to electron withdrawal and depletion layer expansion; at 0.75 mM Ce doping, the voltage rose from 0.682 V (air) to 1.191 V (100 ppm), yielding a 78.29% response. These results demonstrate excellent self-powered NO sensing capability, highlighting potential for energy-autonomous devices.

References

- Yen-Lin Chu, Liang-Wen Ji, Jun-Hong Xie, and Tung-Te Chu, "High-Sensitivity of Self-Powered Gas Sensors Based on Piezoelectric Nanogenerators With Y-Doped 1-D ZnO Nanostructures," IEEE SENSORS JOURNAL, vol. 24, 2024.
- Ahmad Umar, Sheikh Akbar, Rajesh Kumar, Jesse Nii Okai Amu-Darko, Shahid Hussain, Ahmed A. Ibrahim, Mohsen A. Alhamami, Noura Almebad, Tubia Almas, Amal F. Seliem, "Ce-doped ZnO nanostructures: A promising platform for NO₂ gas sensing," Chemosphere, vol. 349, p. 140383, 2024
- P. Luo, M. Xie, J. Luo, H. Kan, and Q. Wei, "Nitric oxide sensors using nanospiral ZnO thin film deposited by GLAD for application to exhaled human breath," RSC Advances, no. 10, p. 14877, 2020