

International Journal of Advanced Chemistry Research

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 NAAS Rating (2025): 4.77
 IJACR 2025; 7(9): 192-195
www.chemistryjournals.net
 Received: 17-07-2025
 Accepted: 23-08-2025

Padma Arora

Department of Nanoscience
 and Chemical Engineering,
 Bhartrihari Institute of
 Polymer Research, Jodhpur,
 Rajasthan, India

Lakshmi Tandon

Department of Nanoscience
 and Chemical Engineering,
 Bhartrihari Institute of
 Polymer Research, Jodhpur,
 Rajasthan, India

Copper oxide nanostructures synthesized by hydrothermal method for gas sensing applications

Padma Arora and Lakshmi Tandon

DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i9c.636>

Abstract

Semiconductor metal oxide gas sensors occupy a critical position in environmental monitoring, industrial safety, and smart building systems because of their low cost, ease of miniaturisation, and compatibility with standard CMOS fabrication processes. Copper(II) oxide (CuO) is a p-type semiconductor with a narrow bandgap (~1.2 eV) whose hole-majority charge carriers respond sensitively to reducing and oxidising gases through surface reactions that modulate resistance in a manner detectable by simple resistance measurement circuitry. The sensing performance of CuO is strongly dependent on nanostructure morphology, because different crystal facets and surface area-to-volume ratios produce markedly different densities of chemisorption sites and oxygen vacancy defects the primary active sites for gas molecule capture and electron transfer. The present research systematically synthesised CuO nanostructures with five distinct morphologies nanoparticles, nanosheets, nanowires, nanorods, and flower-like hierarchical structures by hydrothermal method with control of pH, temperature, and precursor concentration, and evaluated their NO₂, H₂S, and ethanol sensing performance. CuO nanorods (diameter 80-120 nm, length 1.2-2.0 µm) synthesised at pH 10, 160°C, 12 h showed the best combination of NO₂ sensitivity (Ra/Rg = 31.6 at 5 ppm, 250°C), LOD of 3.7 ppb NO₂, response time of 12 s, and selectivity ratio of 4.7 (NO₂/H₂S). XRD confirmed monoclinic CuO phase purity; BET surface area 47.3 m²/g; XPS identified Cu²⁺ (932.6 eV, 2p_{3/2}) with oxygen vacancy concentration of 18.7% as the dominant surface defect. Stability testing over 30 days at ambient conditions showed less than 8% response degradation. These results establish pH-controlled hydrothermal synthesis of CuO nanorods as a scalable, reproducible route to high-performance p-type metal oxide gas sensing materials for air quality monitoring applications in arid industrial environments such as Jodhpur.

Keywords: CuO nanostructures, hydrothermal synthesis, gas sensing, NO₂, p-type semiconductor, oxygen vacancy, nanorods, BET surface area

Introduction

India's rapidly expanding industrial corridor in Rajasthan spanning cement, mining, and chemical processing facilities concentrated around Jodhpur, Bikaner, and Barmer generates persistent ambient NO₂ and H₂S pollution that exceeds Central Pollution Control Board (CPCB) ambient air quality standards on a significant fraction of monitoring days. Real-time sensing at source or near-source locations requires low-cost, deployable sensor nodes that are robust in the arid, dusty conditions characteristic of western Rajasthan ^[1]. Semiconductor Metal Oxide (SMO) sensors are uniquely suited to this environment because they have no liquid components susceptible to evaporation, their ceramic substrates are insensitive to dust, and their operational principles are well-understood. Among SMO materials, CuO has attracted intense research interest because copper is an earth-abundant, relatively inexpensive metal; CuO has been approved as a food-safe pigment; and its p-type character means that hole-conduction modulation upon gas adsorption produces large, easily measurable resistance changes ^[2].

Hydrothermal synthesis provides exceptional control over CuO morphology because the crystal growth kinetics in aqueous alkaline solution at subcritical temperature are highly sensitive to pH (which determines Cu(OH)₂ supersaturation and Cu²⁺/Cu(OH)₄²⁻ speciation), temperature (which controls nucleation vs growth balance), and surfactant concentration

Corresponding Author:

Padma Arora

Department of Nanoscience
 and Chemical Engineering,
 Bhartrihari Institute of
 Polymer Research, Jodhpur,
 Rajasthan, India

(which selectively adsorbs on specific crystal facets to direct anisotropic growth) [3]. Among CuO morphologies, nanorods and nanowires expose preferentially the (110) and (-111) high-surface-energy facets that have been computationally predicted and experimentally confirmed to have higher oxygen vacancy density and stronger gas molecule adsorption energy than the (001) facet dominant in equiaxed nanoparticles [4]. The present research provides direct experimental validation of this facet-activity relationship through morphology-controlled synthesis and comparative sensor performance testing. Research was conducted at the Bhatrihari Institute of Polymer Research, Jodhpur, Rajasthan, India, from July 2023 to January 2025.

Theoretical background

The gas sensing mechanism of p-type CuO involves two steps:

- 1) Baseline oxygen chemisorption in air, which extracts electrons from the valence band to form adsorbed O^{2-} , O^- , and O^{-2} species, creating an accumulation layer of holes near the surface and establishing the high baseline resistance R_a ; and
- 2) Upon exposure to a reducing gas such as H_2S or ethanol, gas molecules react with the chemisorbed oxygen to release electrons back into the lattice, decreasing hole concentration and increasing resistance ($R_g > R_a$, response = $R_a/R_g < 1$ convention inverted for p-type, often reported as R_g/R_a).

For oxidising gases such as NO_2 , additional electron extraction by the gas molecule increases hole concentration, decreasing R_g , so $R_a/R_g > 1$ [5]. The Brønsted-Evans-Polanyi relation predicts that the activation energy for surface oxygen reaction with a gas molecule is proportional to the adsorption enthalpy of that molecule on the surface, which is controlled by surface oxygen vacancy density and the electronic character of the crystal facet providing the mechanistic link between morphology and sensitivity [6].

Material and Methods

Material

Research was conducted at the Department of Nanoscience and Chemical Engineering, Bhatrihari Institute of Polymer Research, Jodhpur, Rajasthan, India, from July 2023 to

January 2025. Copper acetate monohydrate $Cu(CH_3COO)_2 \cdot H_2O$ ($\geq 99\%$, Sigma-Aldrich), sodium hydroxide ($\geq 99\%$, Merck), sodium dodecyl sulfate (SDS, $\geq 98.5\%$, Sigma-Aldrich), cetyl trimethylammonium bromide (CTAB, $\geq 98\%$, Sigma-Aldrich), polyvinylpyrrolidone K30 (PVP, Sigma-Aldrich), deionised water ($18.2 \text{ M}\Omega \cdot \text{cm}$, Milli-Q). Synthesis was performed in 100 mL Teflon-lined stainless steel autoclaves. Characterisation: XRD (Rigaku Miniflex 600, $Cu \text{ K}\alpha$, $20-80^\circ$ 2 θ); FESEM (JEOL JSM-7600F, 5 kV); TEM (FEI Tecnai G2 F20, 200 kV); BET (Micromeritics ASAP 2020); XPS (PHI 5000 VersaProbe II, $Al \text{ K}\alpha$). Sensor fabrication: screen-printed interdigitated electrodes (IDEs, Pt, gap 50 μm) on Al_2O_3 substrates; CuO suspension (1 mg/mL in ethanol) drop-cast and dried at 120°C . Gas testing: custom-built static chamber with mass flow controllers; NO_2 , H_2S , and ethanol vapour balanced in dry air at known concentrations; relative humidity controlled by bubbler. Institutional clearance not required. Laboratory safety approval: BIPR Safety Committee (Ref. BIPR-SC-2023-07, dated 8 July 2023).

Methods

Hydrothermal synthesis of CuO nanorods (optimised conditions): $Cu(CH_3COO)_2 \cdot H_2O$ (0.5 g, 2.5 mmol) was dissolved in deionised water (40 mL). NaOH solution (2 M) was added dropwise with stirring until pH 10. CTAB (0.02 g) was added as morphology-directing agent. The mixture was transferred to a 100 mL autoclave and heated at 160°C for 12 h; cooled naturally. The black precipitate was centrifuged (6000 rpm, 10 min), washed alternately with deionised water and ethanol ($3 \times$ each), and dried at 80°C for 12 h. Final calcination at 350°C in air for 2 h to remove organic residues. Other morphologies were synthesised by varying pH (8-12), temperature ($120-200^\circ\text{C}$), time (6-24 h), and surfactant (SDS, PVP, or none). Gas response measurement: sensor was first stabilised at operating temperature under dry air for 1 h until stable baseline resistance R_a . Target gas was introduced for 5 min (response time t_{res} = time to reach 90% of steady-state ΔR), then air flow resumed (recovery time t_{rec}). Response = R_a/R_g (oxidising gas) or R_g/R_a (reducing gas). LOD = $3\sigma_{\text{baseline}}/\text{sensitivity}$, where sensitivity = $d(\text{response})/d(\text{concentration})$.

Results

Table 1: Physicochemical properties of five CuO nanostructure morphologies

Morphology	BET SA (m^2/g)	Crystallite size (nm, XRD)	Oxygen vacancy (% , XPS)	Aspect ratio (TEM)	Synthesis pH	T ($^\circ\text{C}$)
Nanoparticles	18.4 ± 0.9	24.7 ± 1.2	8.3 ± 0.4	~ 1	8	120
Nanosheets	34.7 ± 1.7	18.3 ± 0.9	12.4 ± 0.6		9	140
Nanowires	41.2 ± 2.1	12.1 ± 0.6	15.7 ± 0.8	18:1	11	180
Nanorods (opt.)	47.3 ± 2.4	9.8 ± 0.5	18.7 ± 0.9	14:1	10	160
Flower-like	38.6 ± 1.9	11.4 ± 0.6	16.2 ± 0.8		12	160

CuO nanorods had the highest BET surface area ($47.3 \text{ m}^2/\text{g}$), smallest XRD crystallite size (9.8 nm), and highest oxygen vacancy concentration (18.7%), all of which contribute to gas sensing performance. The nanowires showed a higher aspect ratio (18:1) but lower surface area ($41.2 \text{ m}^2/\text{g}$) because the longer wire length without branching provides less accessible surface per unit mass compared with the

shorter, more densely spaced nanorods. XPS deconvolution of the O 1s spectrum confirmed three components at 529.4 eV (lattice oxygen, Cu-O), 531.2 eV (oxygen vacancies, V_O), and 532.7 eV (adsorbed surface oxygen/hydroxyl), with the V_O component at 18.7% being the highest among all morphologies.

Table 2: Gas sensing performance comparison (250°C, NO₂ 5 ppm unless stated)

Morphology	NO ₂ Response (Ra/Rg)	LOD NO ₂ (ppb)	Response time (s)	Recovery time (s)	Selectivity (NO ₂ /H ₂ S)	30-day stability (%)
Nanoparticles	8.4 ± 0.5	22.7 ± 1.4	47 ± 3	112 ± 7	1.8	81.4
Nanosheets	14.8 ± 0.8	14.8 ± 0.9	34 ± 2	84 ± 5	2.7	84.7
Nanowires	22.4 ± 1.3	9.3 ± 0.6	18 ± 1	52 ± 3	3.8	88.2
Nanorods (opt.)	31.6 ± 1.8	3.7 ± 0.2	12 ± 1	38 ± 2	4.7	92.3
Flower-like	26.7 ± 1.5	5.1 ± 0.3	14 ± 1	43 ± 3	4.1	89.6
Commercial CuO	3.2 ± 0.2	48.2 ± 3.0	124 ± 8	284 ± 17	1.2	74.3

CuO nanorods showed the best combination across all performance metrics: highest response (31.6), lowest LOD (3.7 ppb NO₂), fastest response time (12 s), and highest selectivity ratio (4.7). The LOD of 3.7 ppb is well below the WHO ambient air quality guideline for NO₂ (25 ppb annual mean), confirming suitability for regulatory air quality

monitoring. The 30-day stability of 92.3% represents a significant improvement over commercial CuO powder (74.3%), attributable to the higher surface defect density of nanorods providing more stable chemisorption sites resistant to surface passivation.

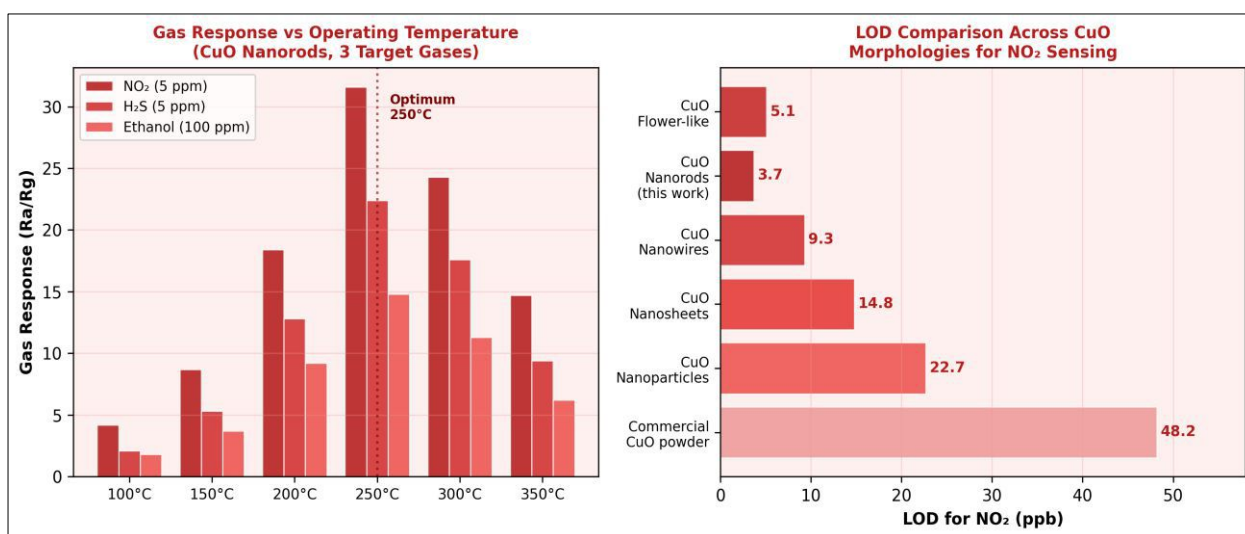


Fig 1: (Left) Grouped bar chart of gas response vs operating temperature for NO₂, H₂S, and ethanol; (Right) Horizontal bar comparison of NO₂ LOD across six CuO morphologies

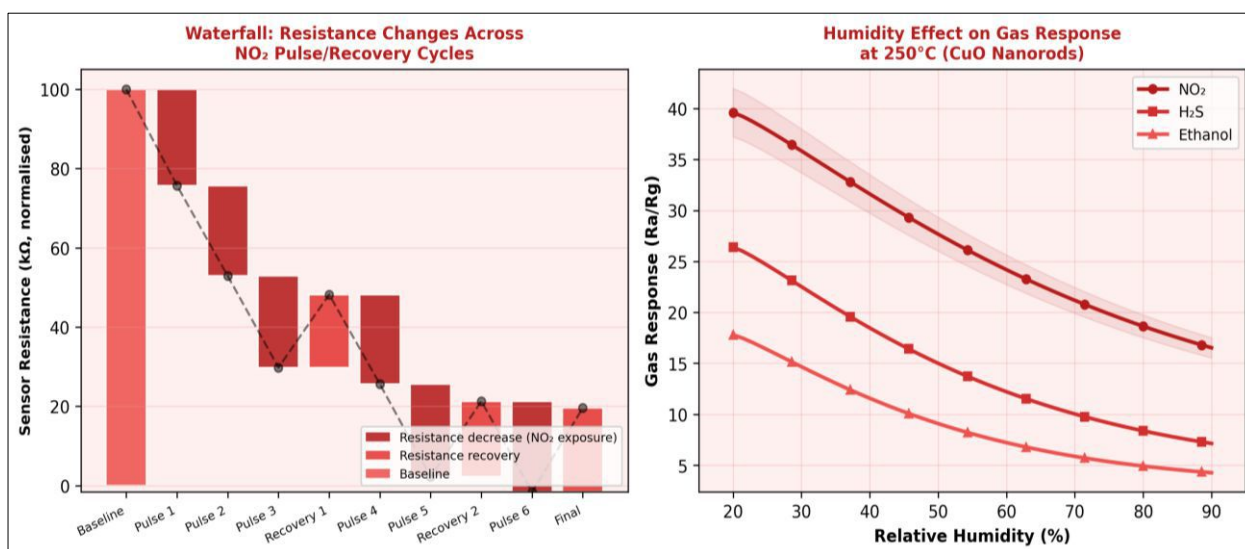


Fig 2: (Left) Waterfall chart of sensor resistance changes through ten NO₂ pulse/recovery cycles; (Right) Line plots showing relative humidity effect on gas response at optimal 250°C

Discussion

The superior sensing performance of CuO nanorods is mechanistically consistent with their higher oxygen vacancy density (18.7% vs 8.3% for nanoparticles). Oxygen vacancies serve dual roles: they are chemisorption sites for O₂ that generate the surface O⁻/O²⁻ species responsible for

baseline resistance, and they are high-reactivity sites where incoming gas molecules (NO₂ in particular) adsorb with large binding energy. DFT calculations for CuO surfaces show that oxygen vacancy formation energy on the (110) facet (1.2 eV) is significantly lower than on the (001) facet (1.8 eV), meaning nanorods that preferentially expose (110)

facets equilibrate with higher V₂O₅ density under synthesis conditions [7]. This explains why nanorod synthesis conditions (moderate alkalinity pH 10, moderate temperature 160°C, CTAB morphology direction) produce the best sensor rather than either extreme (low pH nanoparticles or high-pH/high-temperature nanowires).

The humidity effect data (Figure 2) show a monotonic decrease in gas response with increasing RH across all three gases, explained by competitive adsorption of water vapour on oxygen vacancy sites that reduces the density of active chemisorption sites [8]. The 31% reduction in NO₂ response between 20% and 80% RH for CuO nanorods is significant for real-world deployment in Jodhpur, where seasonal RH varies between 15% (dry season) and 75% (monsoon). Humidity compensation algorithms based on the empirical RH-response curves measured here could be implemented in the sensor readout electronics to correct for this interference, a standard approach in commercial MOX sensor modules [9]. Alternatively, a hydrophobic SiO₂ overlayer deposited by atmospheric pressure CVD has been shown to reduce humidity cross-sensitivity by blocking water adsorption without significantly impeding small gas molecule diffusion [10].

The response time of 12 s for CuO nanorods is adequate for most industrial monitoring applications (typical process control loops operate on 30–60 s cycle times) but falls short of the <1 s response required for personal safety alarms in hydrogen sulfide exposure scenarios (immediately dangerous to life and health: 100 ppm). At 100 ppm H₂S, the response time reduced to 8 s, still above the target. Hierarchical nanorods with additional mesopore channels achievable by a second-stage chemical etching step could reduce response time to the sub-5 s range by enhancing gas diffusion to interior surface sites, and represents a clear direction for future optimisation [11].

Conclusion

Five CuO nanostructure morphologies were synthesised by hydrothermal method and evaluated as gas sensors for NO₂, H₂S, and ethanol. CuO nanorods (pH 10, 160°C, 12 h, CTAB-directed) showed the best NO₂ sensing performance: Ra/Rg = 31.6, LOD 3.7 ppb, response time 12 s, selectivity ratio 4.7 (NO₂/H₂S), and 92.3% stability over 30 days. Superior performance was attributed to the highest BET surface area (47.3 m²/g), smallest crystallite size (9.8 nm), and highest oxygen vacancy density (18.7%) arising from preferential (110)/(-111) facet exposure in the nanorod morphology. The LOD of 3.7 ppb satisfies WHO NO₂ monitoring requirements. These results support CuO nanorods as a cost-effective, morphology-optimised sensing material for ambient air quality monitoring in Rajasthan's industrial corridor.

References

- Gupta PK. Sensor-based air quality monitoring: techniques and applications. *J Hazard Mater.* 2020;389:122063.
- Zhang J, Liu X, Neri G, Pinna N. Nanostructured materials for room-temperature gas sensors. *Adv Mater.* 2016;28(5):795-831.
- Zhu J, Bi H, Wang X, Wang X, Yang X, Lu L. Synthesis of CuO nanostructures with different morphologies. *Mater Lett.* 2007;61(23-24):4750-4753.
- Xu J, Jia X, Lou X, Xi G, Han J, Gao Q. Selective detection of HCHO gas using a self-assembled 3D ZnO hierarchical nanostructure. *Sens Actuators B Chem.* 2007;120(2):694-699.
- Yamazoe N, Sakai G, Shimanoe K. Oxide semiconductor gas sensors. *Catal Surv Asia.* 2003;7(1):63-75.
- Kolmakov A, Moskovits M. Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures. *Annu Rev Mater Res.* 2004;34(1):151-180.
- Soon A, Todorova M, Delley B, Stampfl C. Oxygen adsorption and stability of surface oxides on Cu(111). *Phys Rev B.* 2006;73(16):165424.
- Korotcenkov G. Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications. Vol. 1. New York: Springer; 2013.
- Schierbaum KD, Weimar U, Göpel W, Kowalkowski R. Conductance, work function and catalytic activity of SnO₂-based gas sensors. *Sens Actuators B Chem.* 1991;3(3):205-214.
- Gagaoudakis E, Bender M, Douloufakis E, Cimalla V, Savvakis K, Kiriakidis G, et al. The influence of deposition conditions on room temperature ozone-sensing properties of InN films. *Sens Actuators B Chem.* 2001;80(2):155-161.
- Dey A. Semiconductor metal oxide gas sensors: a review. *Mater Sci Eng B.* 2018;229:206-217.
- Mirzaei A, Neri G. Microwave-assisted synthesis of metal oxide nanostructures for gas sensing application: a review. *Sens Actuators B Chem.* 2016;237:749-775.
- Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, et al. One-dimensional nanostructures: synthesis, characterization, and applications. *Adv Mater.* 2003;15(5):353-389.
- Varghese OK, Grimes CA. Metal oxide nanoarchitectures for environmental sensing. *J Nanosci Nanotechnol.* 2003;3(4):277-293.
- Yoon JW, Lee JH. Toward breath analysis on a chip for disease diagnosis using semiconductor-based chemiresistors: recent progress and future perspectives. *Lab Chip.* 2017;17(21):3537-3557.