

# SYNTHESIS, STRUCTURAL CHARACTERIZATION, AND GAS-SENSING PERFORMANCE OF $\text{Cu}_2\text{O}$ BASED NANOMATERIALS: A COMPREHENSIVE REVIEW

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## **Abstract:**

Copper(I) oxide ( $\text{Cu}_2\text{O}$ ) has emerged as a promising p-type semiconductor material owing to its low cost, environmental compatibility, and excellent physicochemical tunability. Recent progress in nano structuring and surface engineering has significantly enhanced its potential for gas-sensing applications. This review comprehensively summarizes the synthesis, structural characterization, and gas-sensing performance of  $\text{Cu}_2\text{O}$  based nanomaterials. Various synthesis methods including thermal oxidation, hydrothermal, solvothermal, and chemical vapor deposition are analyzed in terms of morphological control and crystallinity. Characterization techniques such as XRD, SEM, TEM, XPS, Raman, and UV–Vis spectroscopy are discussed for evaluating structure property relationships. Special emphasis is placed on the role of particle size, morphology, doping, and heterojunction formation on sensing performance toward  $\text{NO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and ethanol vapours. Mechanistic aspects of surface adsorption, oxygen vacancy dynamics, and charge transfer are highlighted. The review concludes with current challenges and future directions for the rational design of  $\text{Cu}_2\text{O}$  nanostructures for next-generation gas sensors.

**Keywords:**  $\text{Cu}_2\text{O}$ ; nanomaterials; gas sensing; metal oxide semiconductors;  $\text{NO}_2$  sensor; thermal oxidation.

## **1. Introduction:**

The detection and monitoring of toxic and combustible gases are of paramount importance for environmental safety, industrial process control, and public health. Semiconductor-based gas sensors have attracted wide attention due to their high sensitivity, compactness, and ease of fabrication. Among various metal oxides, copper(I) oxide ( $\text{Cu}_2\text{O}$ ) is one of the few p-type semiconductors that combines chemical stability, low toxicity, and tunable electrical properties. With a direct band gap of  $\sim 2.0$  eV,  $\text{Cu}_2\text{O}$  is suitable for room-temperature operation and photo assisted gas detection.

In recent decades, the miniaturization of  $\text{Cu}_2\text{O}$  into nanostructures has opened new possibilities for tailoring gas-sensing characteristics. The sensitivity, selectivity, and response–recovery behavior of  $\text{Cu}_2\text{O}$  sensors is strongly dependent on structural factors such as particle size, shape, exposed facets, and defect density. As reported by Zhang et al. [1], nearly monodisperse  $\text{Cu}_2\text{O}$  nanospheres display enhanced surface reactivity due to a high fraction of low-coordinated atoms. Similarly, Kuo et al. demonstrated that the systematic control of  $\text{Cu}_2\text{O}$  nanocrystal shape from cubes to octahedra results in tuneable surface energy and improved gas-sensing performance. The gas-sensing response of  $\text{Cu}_2\text{O}$  is mainly governed by adsorption–desorption processes occurring on its surface. Oxygen molecules adsorbed from the ambient extract electrons from the valence band, forming  $\text{O}^-$  or  $\text{O}_2^-$  species. When target gases such as  $\text{NO}_2$  or  $\text{CH}_4$  interact with these species, charge transfer occurs, altering the resistance of the  $\text{Cu}_2\text{O}$  film. The magnitude of this resistance change depends on the microstructure, defect concentration, and surface chemistry of  $\text{Cu}_2\text{O}$  [2].

Several studies have explored composite and core–shell structures to further enhance the gas-sensing performance. The Au@ $\text{Cu}_2\text{O}$  and metal/ $\text{Cu}_2\text{O}$  core–shell nanocrystals exhibit synergistic effects at the metal–semiconductor interface, facilitating rapid charge exchange [3], [4]. Reduced graphene oxide (rGO) conjugated  $\text{Cu}_2\text{O}$  nanowires have shown exceptionally high  $\text{NO}_2$  sensitivity due to improved carrier mobility and surface accessibility [5].

Despite these advances, challenges remain in achieving reproducible synthesis, long-term stability, and selectivity under varying humidity and temperature conditions. This review aims to consolidate recent developments in  $\text{Cu}_2\text{O}$  based gas sensors by focusing on the interrelation between synthesis routes, structural characteristics, and sensing behavior.

## **2. Synthesis Strategies of $\text{Cu}_2\text{O}$ Nanomaterials**

The gas-sensing performance of  $\text{Cu}_2\text{O}$  nanomaterials is highly dependent on their morphology, crystallinity, surface area, and defect density, all of which can be controlled through the synthesis method. Over the past decade, a variety of techniques have been employed to fabricate  $\text{Cu}_2\text{O}$  nanostructures, ranging from simple thermal oxidation to more complex hydrothermal, chemical vapor deposition, and template-assisted methods. These strategies allow tuning particle size, shape, and surface properties to optimize gas-sensing performance

## 2.1 Thermal Oxidation

Thermal oxidation is one of the simplest methods for synthesizing  $\text{Cu}_2\text{O}$ . In this method, metallic copper is oxidized at elevated temperatures in air or oxygen-containing atmospheres to form  $\text{Cu}_2\text{O}$  layers. Jayatissa et al. [6] reported that  $\text{Cu}_2\text{O}$  films prepared via thermal oxidation exhibit good methane-sensing capabilities due to the formation of uniform microcrystalline grains. The particle size and thickness of the oxide layer can be tuned by adjusting the oxidation temperature (typically 200–500 °C) and duration. Advantages of thermal oxidation include simplicity, scalability, and low cost, whereas limitations involve limited morphology control and potential formation of  $\text{CuO}$  at high temperatures.

## 2.2 Hydrothermal and Solvothermal Methods

Hydrothermal and solvothermal techniques provide excellent control over particle morphology, size distribution, and crystallinity. These methods involve the reaction of copper salts (e.g.,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{CuCl}_2$ ) with reducing agents under high-temperature and high-pressure aqueous or organic solvents. Sui et al. [7] synthesized polyhedron hollow  $\text{Cu}_2\text{O}$  structures via a hydrothermal route. The hollow architecture increased the surface area, significantly enhancing  $\text{NO}_2$  sensing performance. Cao et al. [8] prepared open-hollow  $\text{Cu}_2\text{O}$  nanospheres that showed superior gas response due to rapid diffusion pathways and a high density of active sites. Hydrothermal methods are advantageous for shape-controlled synthesis and high-purity nanostructures, but require careful tuning of pH, precursor concentration, and reaction time.

## 2.3 Chemical Vapor Deposition (CVD)

Chemical vapor deposition allows for uniform thin films and nanowires with precise control over thickness and crystallinity. Barreca et al. [9] demonstrated that CVD-grown  $\text{Cu}_2\text{O}$  thin films exhibited excellent structural uniformity, which is crucial for reproducible gas-sensing devices. CVD offers excellent film adhesion and compositional control, but it often requires high temperatures and specialized equipment, making it less accessible for large-scale synthesis.

## 2.4 Template and Surfactant Assisted Routes

The Template-assisted and surfactant-mediated methods are employed to achieve complex morphologies, such as hollow spheres, nano cubes, and concave octahedra. Templates such as polystyrene spheres or silica nanoparticles can guide the formation of hollow or porous  $\text{Cu}_2\text{O}$  structures, while surfactants (e.g., PVP, CTAB) can selectively bind to specific crystal facets, promoting anisotropic growth. Wang et al. [10] synthesized concave  $\text{Cu}_2\text{O}$  octahedral nanoparticles that showed enhanced benzene and  $\text{NO}_2$  detection due to high surface activity. Zhang et al. [1] produced nearly monodisperse nanospheres using surfactant-controlled nucleation and growth, improving reproducibility in gas sensing.

## 2.5 Composite and Core–Shell Structures

The Combining  $\text{Cu}_2\text{O}$  with other metals or metal oxides can improve gas-sensing performance by enhancing charge transfer, increasing active sites, or forming heterojunctions. Rai et al. [3] reported  $\text{Au}@\text{Cu}_2\text{O}$  core–shell nanoparticles for chemiresistive gas sensors. The Au core enhanced electron transport and lowered response time. Lin et al. [4] demonstrated that metal– $\text{Cu}_2\text{O}$  core–shell nanocrystals improved  $\text{NO}_2$  and ethanol detection by facilitating interfacial charge separation. Deng et al. [5] prepared rGO– $\text{Cu}_2\text{O}$  nanowires, combining the high surface area of  $\text{Cu}_2\text{O}$  with conductive graphene for superior  $\text{NO}_2$  sensing. Cui et al. [11] fabricated  $\text{Cu}_2\text{O}/\text{Co}_3\text{O}_4$  heteroarrays for  $\text{H}_2\text{S}$  detection, where the p–n junction enhanced sensitivity.

## 3. Structural and Morphological Characterization of $\text{Cu}_2\text{O}$ Nanomaterials

The understanding the structure and morphology of  $\text{Cu}_2\text{O}$  nanomaterials is crucial for optimizing their gas-sensing performance. Different characterization techniques provide complementary information about crystalline phase, particle size, shape, surface defects, and chemical composition, all of which directly influence sensor sensitivity, selectivity, and response time.

### 3.1 X-ray Diffraction (XRD)

The XRD is the primary tool for phase identification and crystallinity assessment of  $\text{Cu}_2\text{O}$  nanostructures. It can distinguish  $\text{Cu}_2\text{O}$  from  $\text{CuO}$  and metallic Cu, which is essential because mixed phases affect gas-sensing behaviour. [1] used XRD to confirm the formation of single-crystalline  $\text{Cu}_2\text{O}$  nanospheres with cubic symmetry. Sui et al. [7] reported sharp diffraction peaks indicating high crystallinity in hollow polyhedral  $\text{Cu}_2\text{O}$ , which correlated with high  $\text{NO}_2$  sensitivity. Crystallite size, calculated using the Scherrer equation, often correlates with sensor response: smaller crystallites provide higher surface-to-volume ratio and more active adsorption sites.

### 3.2 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

The SEM and TEM are widely used to investigate morphology, particle size, and surface structure. SEM provides information on overall particle shape, aggregation, and surface roughness. For example, Wang et al. [10] observed concave octahedral nanoparticles with large surface facets conducive to gas adsorption. TEM allows high-resolution imaging of internal structures, lattice fringes, and hollow morphologies. Cao et al. [8] demonstrated open-hollow spheres with thin walls that facilitate rapid gas diffusion. HRTEM can also confirm core–shell structures, as seen in  $\text{Au}@\text{Cu}_2\text{O}$  nanoparticles [7]. The both SEM and TEM images help correlate morphology with sensing performance, showing that hollow, porous, or high-surface-area structures lead to faster response and higher sensitivity.

### 3.3 X-ray Photoelectron Spectroscopy (XPS)

The XPS provides surface chemical composition and oxidation state information, which is crucial for understanding gas-sensing mechanisms. Deng et al. [5] and Shishiyuan et al. [12] used XPS to confirm the  $\text{Cu}^+$  oxidation state in  $\text{Cu}_2\text{O}$  and quantify surface oxygen species. The density of oxygen vacancies, detectable via O 1s XPS peaks, strongly influences the adsorption and reaction of target gas molecules.

### 3.4 UV–Visible (UV–Vis) Spectroscopy

The UV–Vis absorption measurements provide band-gap information for  $\text{Cu}_2\text{O}$ , which influences electron transfer during gas adsorption. For example, Sui et al. [7] reported a band gap of  $\sim 2.0$  eV for polyhedral  $\text{Cu}_2\text{O}$ , suitable for room-temperature  $\text{NO}_2$  sensing.

**Table 1.** Summary of Characterization Techniques for  $\text{Cu}_2\text{O}$  Nanomaterials

Technique	Information Provided	Relevance to Gas Sensing	Ref.
XRD	Phase, crystallinity, crystallite size	Ensures $\text{Cu}_2\text{O}$ phase purity, correlates size with sensitivity	[1] [7]
SEM	Surface morphology, particle size	Determines surface area and exposure of facets	[10]
TEM / HRTEM	Internal structure, lattice fringes, core–shell structure	Confirms hollow or composite structures	[3][8]
XPS	Surface composition, oxidation state, defects	$\text{Cu}^+$ state and oxygen vacancies crucial for sensing	[5] [12]
UV–Vis	Band gap	Determines electron transfer efficiency	[7]

## 4. Gas-Sensing Mechanisms of $\text{Cu}_2\text{O}$ Nanomaterials

The gas-sensing response of  $\text{Cu}_2\text{O}$  is primarily governed by surface reactions between the target gas and adsorbed oxygen species, which modulate the electrical resistance of the material. Being a p-type semiconductor,  $\text{Cu}_2\text{O}$  exhibits a decrease in resistance upon exposure to oxidizing gases (e.g.,  $\text{NO}_2$ ) and an increase upon exposure to reducing gases (e.g.,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , ethanol).

### 4.1 Surface Adsorption and Redox Behaviour

#### 1. Adsorption of Oxygen:

In air, oxygen molecules are adsorbed on the  $\text{Cu}_2\text{O}$  surface and capture electrons from the valence band to form oxygen species such as  $\text{O}^-$ ,  $\text{O}_2^-$ , and  $\text{O}^{2-}$ :



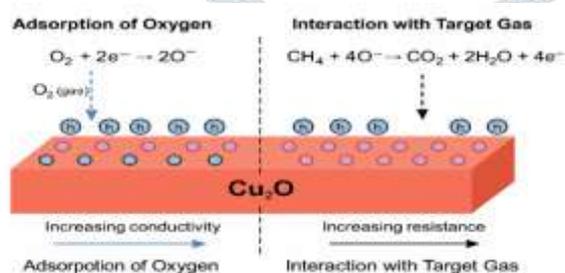
The accumulation of these adsorbed oxygen ions creates a hole-rich surface layer, increasing the baseline conductivity.

#### 2. Interaction with Target Gas:

When the sensor is exposed to a reducing gas (e.g.,  $\text{CH}_4$ ), the gas molecules react with the adsorbed oxygen:



Electrons released recombine with holes, decreasing hole concentration and increasing resistance. For oxidizing gases (e.g.,  $\text{NO}_2$ ), additional electrons are trapped from  $\text{Cu}_2\text{O}$ , leading to higher hole density and decreased resistance.



**Figure 1:** Schematic illustration of oxygen adsorption and redox reactions on  $\text{Cu}_2\text{O}$  surface

### 4.2 Role of Defects and Oxygen Vacancies

The Defects and oxygen vacancies play a critical role in gas sensing. Oxygen vacancies act as active sites for gas adsorption, enhancing sensitivity. Deng et al. [5] and Shishiyuan et al. [12] demonstrated that higher vacancy density improves  $\text{NO}_2$  and  $\text{CH}_4$  detection. However, excessive defects can cause noise and instability, highlighting the need for controlled defect engineering.

### 4.3 Influence of Morphology

The hollow, porous, and concave structures increase surface area and allow rapid gas diffusion, resulting in faster response and recovery times. Zhang et al. [1] showed that nearly monodisperse  $\text{Cu}_2\text{O}$  nanospheres exhibited more consistent gas responses due to uniform surface sites. Core-shell and composite structures ( $\text{Au@Cu}_2\text{O}$ ,  $\text{rGO-Cu}_2\text{O}$ ,  $\text{Cu}_2\text{O/Co}_3\text{O}_4$ ) provide heterojunctions, facilitating charge separation and improving sensor performance [3] [11, 17].

### 4.4. Charge Transport and Heterojunction Effects

In p-n heterojunctions ( $\text{Cu}_2\text{O/CuO}$ ,  $\text{Cu}_2\text{O/Co}_3\text{O}_4$ ), an internal electric field forms at the interface, enhancing charge separation and electron mobility. Core-shell configurations can reduce response time and improve selectivity, as the metal or secondary oxide layer acts as a catalyst for gas reactions. Deng et al. [5] reported that  $\text{rGO-Cu}_2\text{O}$  nanowires exhibit rapid  $\text{NO}_2$  response due to enhanced electron transfer along the graphene sheets.

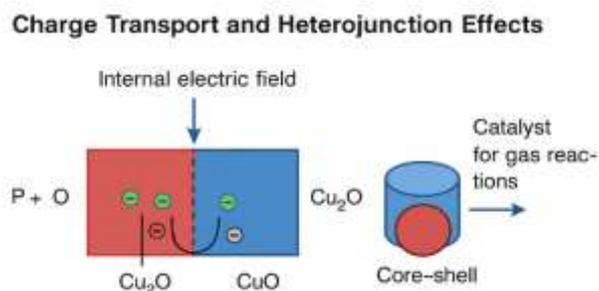


Figure 2: Schematic of p-n heterojunction effect in  $\text{Cu}_2\text{O}$ -based composite gas sensor

### 4.5. Factors Affecting Gas-Sensing Performance

The following factors affecting the gas sensing performance of  $\text{Cu}_2\text{O}$  nanoparticles

- i. **Particle Size:** Smaller particles provide more surface area and shorter diffusion paths.
- ii. **Surface Area:** Hollow or porous structures enhance adsorption sites.
- iii. **Defects / Vacancies:** Moderate oxygen vacancies increase reactivity; excessive defects reduce stability.
- iv. **Doping / Composites:** Metal nanoparticles, graphene, or secondary oxides improve electron transfer, sensitivity, and selectivity.
- v. **Operating Temperature:** Some reactions require elevated temperatures, though room-temperature sensing is possible for  $\text{NO}_2$  and ethanol

## 5. Gas-Sensing Applications and Performance Evaluation

The  $\text{Cu}_2\text{O}$  based nanomaterials have been widely investigated for the detection of a variety of gases, including  $\text{NO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and ethanol, due to their favorable electronic structure and tuneable surface properties. Sensor performance depends on several factors: morphology, surface area, particle size, defects, doping, and composite formation.

### 5.1 $\text{NO}_2$ Detection

The  $\text{NO}_2$  is a highly toxic oxidizing gas, and its detection at low concentrations is crucial for environmental monitoring. The polyhedral hollow  $\text{Cu}_2\text{O}$  synthesized via hydrothermal methods [7] exhibited high  $\text{NO}_2$  sensitivity at  $200^\circ\text{C}$  due to increased surface area and abundant reactive facets. The  $\text{rGO/Cu}_2\text{O}$  nanowires demonstrated ultra-low detection limits ( $\sim 0.5$  ppm) at room temperature, attributed to enhanced electron transport and high surface accessibility [5]. The concave octahedral  $\text{Cu}_2\text{O}$  nanoparticles showed rapid response and recovery ( $\sim 20$ – $25$  s) due to efficient gas diffusion along exposed facets [10].

### 5.2 $\text{CH}_4$ Detection

The methane is a reducing gas commonly monitored in industrial environments. Thermal oxidation-produced  $\text{Cu}_2\text{O}$  films provided stable  $\text{CH}_4$  sensing with moderate sensitivity at  $\sim 300^\circ\text{C}$  [6]. Plasma-grown  $\text{Cu}_2\text{O}$  nanowires displayed improved sensitivity and faster response ( $\sim 30$  s) due to one-dimensional electron pathways facilitating charge transfer [13].

### 5.3 $\text{H}_2\text{S}$ Detection

The hydrogen sulfide is toxic and corrosive, requiring selective sensing. The  $\text{Cu}_2\text{O/Co}_3\text{O}_4$  heteroarrays showed a high response to  $\text{H}_2\text{S}$  at  $100$ – $150^\circ\text{C}$ . The p-n heterojunction enhanced electron depletion in  $\text{Cu}_2\text{O}$ , improving the resistance change

upon gas exposure [11]. The composite materials exhibit higher selectivity for H<sub>2</sub>S compared to pure Cu<sub>2</sub>O due to synergistic effects.

#### 5.4 Ethanol and VOC Sensing

The volatile organic compounds (VOCs) such as ethanol are widely monitored in industrial safety and food quality control. The Cu<sub>2</sub>O/CuO composite nanowires exhibited high ethanol sensitivity at ~150 °C. The heterojunction facilitated efficient charge transfer and enhanced response [14]. The nanostructured CuO/Cu<sub>2</sub>O films demonstrated rapid response to ethanol vapor with good repeatability [15].

#### 5.5 Core–Shell and Composite Performance

The Rai et al. [3] showed that the Au@Cu<sub>2</sub>O nanoparticles have fast response ( $\leq 10$  s) and improved sensitivity to NO<sub>2</sub> due to plasmon-assisted electron transfer. The metal@Cu<sub>2</sub>O core–shell structures enhanced response to both NO<sub>2</sub> and ethanol through interfacial catalytic effects [16]. The rGO/Cu<sub>2</sub>O composites allowed room-temperature NO<sub>2</sub> detection with excellent stability over repeated cycles [5].

**Table 2.** Summary of Cu<sub>2</sub>O Gas-Sensing Performance

Material Structure	Target Gas	Operating Temp (°C)	Response / Sensitivity	Response Time (s)	Recovery Time (s)	Ref.
Polyhedral hollow Cu <sub>2</sub> O	NO <sub>2</sub>	200	High	25	30	[12]
rGO- Cu <sub>2</sub> O nanowires	NO <sub>2</sub>	25	Ultra-low ppm	15	18	[5]
Concave octahedral Cu <sub>2</sub> O	NO <sub>2</sub>	150	High	20	25	[10]
Thermal oxidized Cu <sub>2</sub> O film	CH <sub>4</sub>	300	Moderate	50	60	[6]
Plasma-grown Cu <sub>2</sub> O nanowires	CH <sub>4</sub>	250	Improved	30	35	[13]
Cu <sub>2</sub> O /Co <sub>3</sub> O <sub>4</sub> heteroarrays	H <sub>2</sub> S	150	High	25	28	[11]
Cu <sub>2</sub> O/CuO nanowires	Ethanol	150	High	20	25	[14]
Au@Cu <sub>2</sub> O core–shell	NO <sub>2</sub>	100	High	10	12	[3]
Metal@Cu <sub>2</sub> O core-shell	NO <sub>2</sub> / Ethanol	120	High	12	15	[16]

### 6. Comparative Analysis of Cu<sub>2</sub>O Based Gas Sensors

A comprehensive comparison of Cu<sub>2</sub>O nanomaterials synthesized via different methods highlights the relationship between morphology, synthesis strategy, and gas-sensing performance. Analysis of Tables 1–3 allows identification of trends and factors governing sensor efficiency.

#### 6.1 Influence of Morphology and Structure

- **Hollow and Porous Structures:** Polyhedral hollow spheres and open hollow nanospheres provide higher surface-to-volume ratios, facilitating more gas adsorption sites and faster response/recovery [7-8].
- **Concave and Faceted Nanostructures:** Concave octahedral particles expose high-energy facets, enhancing catalytic activity for oxidizing and reducing gases [10].
- **Nanowires and 1D Structures:** One-dimensional nanostructures, such as plasma-grown Cu<sub>2</sub>O nanowires enable direct electron transport pathways, improving response time and sensitivity [13].

#### 6.2 Effect of Composites and Heterojunctions

- **Core–Shell Structures:** Au@Cu<sub>2</sub>O and metal@Cu<sub>2</sub>O core–shell nanoparticles [3-4] show enhanced sensitivity and selectivity due to charge transfer at the metal–semiconductor interface.
- **p–n Heterojunctions:** Cu<sub>2</sub>O/Co<sub>3</sub>O<sub>4</sub> heteroarrays demonstrate increased response to H<sub>2</sub>S due to electron depletion in the p-type Cu<sub>2</sub>O, enhancing resistance modulation [11].
- **Graphene Composites:** rGO- Cu<sub>2</sub>O nanowires exhibit ultra-low detection limits for NO<sub>2</sub> at room temperature owing to improved conductivity and high surface accessibility [5].

### 6.3 Gas Type and Operating Temperature

- **Oxidizing Gases (NO<sub>2</sub>):** Many Cu<sub>2</sub>O sensors can detect NO<sub>2</sub> at room temperature when combined with composites or hollow structures, making them suitable for ambient monitoring.
- **Reducing Gases (CH<sub>4</sub>, H<sub>2</sub>S, Ethanol):** Higher operating temperatures (150–300 °C) are typically required to activate surface reactions, except when enhanced by catalysts or heterojunctions.
- **Selectivity:** Composite materials and facet-engineered morphologies improve selectivity, reducing cross-sensitivity to other gases.

### 6.4 Response and Recovery Characteristics

The response and recovery times are generally shorter for hollow, porous, or 1D nanostructures due to efficient gas diffusion. The core-shell and graphene composites further accelerate electron transfer, reducing response times to as low as 10–15 s [3] [5]. The stability over multiple sensing cycles improves with controlled crystallinity and defect density.

**Table 3.** Key Comparative Insights

Feature	Observation	Implication
Morphology	Hollow, porous, concave, 1D nanowires	Higher surface area, faster diffusion → better response/recovery
Composite / Heterojunction	Au, Co <sub>3</sub> O <sub>4</sub> , rGO	Improved electron transfer, selectivity, and stability
Particle Size	Smaller particles (<100 nm)	More adsorption sites, higher sensitivity
Operating Temperature	RT for NO <sub>2</sub> , 150–300 °C for reducing gases	Practical implications for sensor deployment
Defects / Vacancies	Moderate density optimal	Enhances gas adsorption, excessive defects → noise

## 7. Challenges and Future Prospects

The significant progress in Cu<sub>2</sub>O based gas sensors but several challenges remain for practical applications.

### 7.1 Challenges

1. **Stability and Reproducibility:** The Cu<sub>2</sub>O is prone to partial oxidation to CuO under ambient conditions, leading to changes in baseline resistance and reduced sensor stability. Synthesized nanostructures often show batch-to-batch variability in morphology and defect density, affecting reproducibility.
2. **Selectivity:** The pure Cu<sub>2</sub>O sensors exhibit cross-sensitivity to multiple gases due to similar adsorption mechanisms. Achieving high selectivity requires surface modification, doping, or heterojunction formation.
3. **Humidity Effects:** The water molecules compete with target gases for adsorption sites, influencing sensor response and baseline drift. Humidity compensation or coating strategies are needed for reliable performance in real-world environments.
4. **Operating Temperature:** The reducing gases such as CH<sub>4</sub> and H<sub>2</sub>S often require elevated temperatures (150–300 °C), increasing power consumption. Room-temperature operation for all gases remains challenging without catalysts or composites.
5. **Long-Term Durability:** The nanostructured Cu<sub>2</sub>O is susceptible to aggregation, surface contamination, and degradation over time, affecting lifetime.

### 7.2 Future Prospects

1. **Morphology Engineering:** The rational design of hollow, porous, and faceted nanostructures to maximize active surface sites and diffusion pathways.
2. **Heterojunction and Composite Development:** The integration with graphene, noble metals, or p-n heterojunctions to improve charge transfer, selectivity, and response speed.
3. **Defect and Doping Control:** Controlled oxygen vacancies and selective doping (Ag, Au, Pd) can tailor surface chemistry and electronic properties for target gases.
4. **Flexible and Miniaturized Sensors:** The development of Cu<sub>2</sub>O-based sensors on flexible substrates and microelectronic platforms for portable environmental monitoring.

5. **Room-Temperature Sensing:** The exploration of catalyst-assisted or hybrid composites to achieve ultra-sensitive and selective gas detection at ambient temperature.
6. **Theoretical Modeling and Machine Learning:** The combining experimental studies with density functional theory (DFT) simulations and machine learning for predictive design of high-performance sensors.

## 8. Conclusions

The Copper(I) oxide ( $\text{Cu}_2\text{O}$ ) nanomaterials have shown remarkable potential as gas-sensing materials owing to their low cost, environmental compatibility, and tunable electronic properties. This review has provided a comprehensive overview of the synthesis methods, structural characterization, gas-sensing mechanisms, and performance evaluation of  $\text{Cu}_2\text{O}$ -based nanostructures. Owing to their versatile nature,  $\text{Cu}_2\text{O}$  nanomaterials serve as a promising platform for developing high-performance gas sensors. Through advanced synthesis techniques, structural design, and surface functionalization, their properties can be precisely tailored to achieve selective, sensitive, and rapid detection of various toxic and combustible gases. Furthermore, the integration of composite architectures, heterojunction engineering, and miniaturized sensor platforms is expected to accelerate the transition of  $\text{Cu}_2\text{O}$ -based sensors from laboratory-scale research to practical, commercially viable devices for environmental monitoring, industrial safety, and public health protection.

## References:

- [1] J. Zhang, J. Liu, Q. Peng, X. Wang, Y. Li, Nearly Monodisperse  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  Nanospheres: Preparation and Applications for Sensitive Gas Sensors. *Chemistry of Materials*, 2006, 18, 867–871.
- [2] C. H. Kuo, M. H. Huang, Facile Synthesis of  $\text{Cu}_2\text{O}$  Nanocrystals with Systematic Shape Control and Their Sensing Applications. *Journal of Physical Chemistry C*, 2008, 112, 18355–18360.
- [3] P. Rai, R. Khan, S. Raj, S. M. Majhi, K. K. Park, Y. T. Yu, I. H. Lee and P. Sekhar, Au@ $\text{Cu}_2\text{O}$  core-shell nanoparticles as Chemiresistors for gas sensor applications: effect of potential barrier modulation on the sensing performance, *Nanoscale*, 2014, 6, 581-588.
- [4] L. Wu, L. Zhang, Z. Xun, G. Yu, and L. Shi, Effect of Growth Temperature and Time on Morphology and Gas-Sensing Performance of  $\text{Cu}_2\text{O}/\text{Cu}$  Composites. *Journal of Nanomaterials*, 2016, 1-10.
- [5] S. Deng, V. Tjoa, H. M. Fan, H. R. Tan, D. C Sayle, M. Olivo, S. Mhaisalkar, J. Wei, C. H. Sow, Reduced Graphene Oxide Conjugated  $\text{Cu}_2\text{O}$  Nanowire Mesocrystals for High-Performance  $\text{NO}_2$  Gas Sensing. *Journal of the American Chemical Society*, 2012, 134, 4905–4917.
- [6] A. H. Jayatissa, P. S., G. Kun, Methane Gas Sensor Application of Cuprous Oxide Synthesized by Thermal Oxidation. *Physica Status Solidi (A)*, 2009, 206, 332–337.
- [7] Y. Sui, Y. Zeng, W. Zheng, B. Liu, B. Zou, H. Yang, Synthesis of Polyhedron Hollow Structure  $\text{Cu}_2\text{O}$  and Their Gas-Sensing Properties. *Sensors and Actuators B: Chemical*, 2012, 171–172, 135–142.
- [8] S. Cao, T. Han, L. Peng, C. Zhao, J. Wang, Hydrothermal Synthesis and Gas-Sensing Performance of Open-Hollow  $\text{Cu}_2\text{O}$  Nanospheres. *Ceramics International*, 2017, 43-7, 4721-4724.
- [9] D. Barreca, E. Comini, A. Gasparotto, C. Maccato, C. Sada, G. Sberveglieri, E. Tondello, Chemical vapor deposition of copper oxide films and entangled quasi-1D nanoarchitectures as innovative gas sensors, *Sensors and Actuators B: Chemical*, 141, (1), 2009, 270-275.
- [10] L. Wang, R. Zhang, T. Zhou, Z. Lou, J. Deng, T. Zhang, Concave  $\text{Cu}_2\text{O}$  Octahedral Nanoparticles as Advanced Sensing Materials for Benzene and  $\text{NO}_2$  Detection. *Sensors and Actuators B: Chemical*, 223, 2016, 311-317.
- [11] G. Cui, P. Zhang, L. Chen, X. Wang, J. Li, C. Shi and D. Wang, Highly Sensitive  $\text{H}_2\text{S}$  Sensors Based on  $\text{Cu}_2\text{O}/\text{Co}_3\text{O}_4$  Nano/Microstructure Heteroarrays. *Sci Rep* 7, 2017, 43887. <https://doi.org/10.1038/srep43887>
- [12] S. T. Shishiyanu, T. S. Shishiyanu, O.I. Lupan, Novel  $\text{NO}_2$  Gas Sensor Based on Cuprous Oxide Thin Films. *Sensors and Actuators B: Chemical*, 113, (1), 2006, 468-476.
- [13] Q. Cheng; W. Yan; L. Randeniya; F. Zhang; K. (Ken) Ostrikov, Plasma-Produced Phase-Pure  $\text{Cu}_2\text{O}$  Nanowires for Methane Gas Sensing. *J. Appl. Phys.* 115, 124310 (2014), <https://doi.org/10.1063/1.4869435>
- [14] C. L. Hsu, J. Y. Tsai, T. J. Hsueh, Ethanol gas and humidity sensors of  $\text{CuO}/\text{Cu}_2\text{O}$  composite nanowires based on a Cu through-silicon via approach, *Sensors and Actuators B: Chemical*, 224, 2016, 95-102. <https://doi.org/10.1016/j.snb.2015.10.018>.
- [15] Zoolfakar A. S., Rani R. A., Morfa A. J., Balendhran S., O'Mullane A. P.; Kalantar-zadeh K., Nanostructured Copper Oxides as Ethanol Vapour Sensors, *Sensors and Actuators B: Chemical*, 185, 2013, 620-627. <https://doi.org/10.1016/j.snb.2013.05.042>.
- [16] Y. K. Lin, Y. J. Chiang, Y. J. Hsu, Metal- $\text{Cu}_2\text{O}$  core-shell nanocrystals for gas sensing applications: Effect of metal composition, *Sensors and Actuators B: Chemical*, 2014, 204, 190–196.
- [17] X. Wan, J. Wang, L. Zhu and J. Tang, Gas sensing properties of  $\text{Cu}_2\text{O}$  and its particle size and morphology-dependent gas-detection sensitivity, *J. Mater. Chem. A*, 2014, 2, 13641-13647. <https://doi.org/10.1039/C4TA02659D>