

Article

Oxygen Vacancy-Engineered Cu₂O@CuS p–p Heterojunction Gas Sensor for Highly Sensitive n-Butanol Detection

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Abstract

The sensitive detection of n-butanol is of high scientific and practical importance for ensuring safety in industrial production. In this study, hollow Cu₂O@CuS core–shell nanocubic heterostructures were fabricated via a multistep templating method. The Cu₂O@CuS heterostructures demonstrated exceptional performance, with an ultrahigh Brunauer–Emmett–Teller specific surface area that provided abundant active sites and a unique hollow architecture that enhanced mass transport and improved gas adsorption/desorption kinetics. High-density surface oxygen vacancies on the Cu₂O@CuS nanocubic heterostructures provide a key structural basis for the preferential adsorption of n-butanol molecules on its surface. The p–p heterojunction configuration further enhanced selective sensor response by optimizing the charge carrier separation and band structure modulation. The developed sensor achieved a detection limit of 3.18 ppm while exhibiting outstanding sensitivity, stability, and response time, meeting the stringent requirements for n-butanol detection in both industrial and agricultural settings. This work provides new insights on how to design materials for gas sensors.

Keywords: n-butanol; gas sensor; functional Cu₂O@CuS nanocube nanocomposite; p–p heterojunction



Received: 29 July 2025

Revised: 27 August 2025

Accepted: 29 August 2025

Published: 1 September 2025

Citation: Zhang, D.; Qu, Z.; Li, C.; Wang, H.; Zhang, Y.; Ren, X.; Xu, R. Oxygen Vacancy-Engineered Cu₂O@CuS p–p Heterojunction Gas Sensor for Highly Sensitive n-Butanol Detection. *Chemosensors* **2025**, *13*, 324. <https://doi.org/10.3390/chemosensors13090324>

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1. Introduction

As an important organic solvent and chemical raw material [1,2], n-butanol is highly flammable, explosive, and strongly corrosive, posing risks to production safety and to the health of workers who are exposed to excessive concentrations for extended periods [3]. Therefore, trace-level and sensitive detection of n-butanol is essential to promptly monitor whether its concentration exceeds safety limits [4,5], prevent harm to personnel or explosion hazards, and ensure emissions meet environmental standards, thus safeguarding production safety, worker health, and environmental sustainability.

Among various gas-sensing platforms, semiconductor-type detectors occupy a dominant position, with their working mechanism rooted in surface redox chemistry that modulates charge carrier concentrations [6]. In gas sensors based on chemiresistive mechanisms, the chemical reactions induced by target gas molecules function as sensing mechanisms that trigger measurable changes in electrical resistance [7,8]. In semiconductor gas sensors heated to operational stability, the adsorbed gas molecules remove electrons from the semiconductor surface and undergo negative ion adsorption, forming a charged surface

layer [9]. Semiconductor gas sensors can reliably detect multiple gas species, such as CO, NO₂, and freons, with high sensitivity, despite requiring specific work function conditions where the work function of the semiconductor must be lower than the electron affinity of adsorbed molecules [10,11].

Studies have focused on optimizing gas sensor performance by incorporating different dopants, such as noble metals and metal oxides, and by engineering structural features utilizing layered, hollow, and porous architectures [12,13]. Different engineering strategies can produce materials with distinct geometric shapes, large surface areas, and abundant unsaturated active sites, making them suitable for sensing and catalytic applications.

In the field of semiconductor gas sensors, research on gas-sensing properties has long focused on n-type semiconductor materials as the core. However, p-type semiconductor sensors have also gradually demonstrated their application potential in various scenarios due to their distinct resistance change characteristics in applications. Nano-sized p-type semiconductors, including those fabricated using NiO [14,15], Cr₂O₃ [16], Co₃O₄ [17,18], ZnO [19], CuS [20], CuO [21], and Cu₂O [22], have attracted growing interest due to their promising functionalities in fields other than gas sensing. Nanosized p-type semiconducting materials are applied in diverse technologies, including gas detection, energy devices, and catalytic and electrochromic systems. In particular, Cu₂O exhibits p-type semiconducting properties with a bandgap of 2.17 eV, and its electrical conductivity and catalytic activity are influenced by the exposed surface areas [23]. Cu₂O in various morphologies, including nanowires, nanospheres, octahedral structures, nanorods, and nanocubes, has been evaluated for gas-sensing applications. Notably, Cu₂O with (111) surface planes exhibits excellent electrical conductivity [24]. However, improving the gas-sensing performance of Cu₂O, a narrow-bandgap p-type semiconductor, is difficult owing to its inherent properties. One effective strategy for enhancing the gas-sensing capability of Cu₂O is to design and construct a heterojunction. The p–p heterojunctions prepared via interface engineering strategies can provide strong support for the research and development of high-performance gas-sensing systems, significantly enhancing their performance stability and reliability. Recently, Azmoodeh et al. reported on p–p heterojunction-based ZnMn₂O₄/polypyrrole nanocomposites, with substantially enhanced hydrogen sensing performance under ambient conditions. The advantageous properties of p–p heterostructures present novel opportunities for hydrogen detection applications [25]. As a typical p-type semiconductor, CuS is widely studied for its exceptional optoelectronic properties [26]. Thus, fabricating heterojunctions by combining Cu₂O and CuS for gas-sensing applications holds significant research potential; however, no studies have been reported on heterojunctions between Cu₂O and CuS.

In this study, hollow Cu₂O@CuS core–shell (core made of Cu₂O and a shell of CuS) nanocubic heterostructures were prepared using a controllable multistep templating strategy. The highly anoxic Cu₂O and defect-rich surface of CuS were anticipated to provide additional centers for n-butanol gas reactions. After the optimization of sensing conditions, the fabricated gas sensor based on Cu₂O@CuS nanocubic heterostructures exhibited excellent sensing performance. In this study, a mechanism behind the sensing reaction on the surface of the fabricated gas sensor has been discussed in detail. The prepared p–p heterojunctions exhibited superior sensitivity to n-butanol compared with other volatile organic compounds (VOCs), demonstrating a successful fabrication of a highly responsive n-butanol gas sensor.

2. Experimental Section

2.1. Apparatus

X-ray diffraction (XRD, Model Smart Lab SE, Rigaku, Japan) determined the crystal structure of the sample with a Cu-K α radiation source ($\lambda = 1.54 \text{ \AA}$) at a voltage of 40 kV and a current of 40 mA. The scanning range was 10° – 90° , the step size was 0.02, and the speed was $10^\circ \text{ min}^{-1}$. The morphology and structure of the as-prepared samples were characterized by a field emission scanning electron microscope (FE-SEM Quanta FEG 250) and TEM (JEOL JEM 2100), facilitated with energy-dispersive X-ray spectroscopy (EDS). More information on the crystal structure and crystallinity can also be obtained by high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL). Information about the material elements and surface states was obtained by X-ray photoelectron spectroscopy (XPS, Smart Lab SE, Rigaku, Tokyo, Japan) analysis.

2.2. Preparation of Materials

First, a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.5 mmol), trisodium citrate (0.5 mmol), and deionized water (80 mL) was mixed with aqueous NaOH (20 mL, 1.25 mol/L). Next, a water-based solution of l-ascorbic acid (50 mL, 0.03 mol/L) was mixed into the reaction system, stirred for an additional 3 min, and then aged for 1 h. Subsequently, a Na_2S solution (40 mL, 6.25 mmol/L) was added to a suspension of the Cu_2O nanocubes (100 mg) in deionized water (60 mL) for sulfation over 30 min, followed by a centrifugation and washing cycle. The obtained $\text{Cu}_2\text{O}@\text{CuS}$ core-shell nanocubes were suspended in a 1:1 water-ethanol mixed solvent (40 mL). The produced suspension was treated with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (16 mL, 1.0 mol/L) to etch Cu_2O nuclei. After allowing the treated suspension to rest for 30 min, hollow $\text{Cu}_2\text{O}@\text{CuS}$ nanocubes were collected by performing multiple centrifugation and washing cycles [27].

2.3. Construction and Testing of Gas Sensor

The performance of the fabricated gas sensors was characterized using a gas-sensing measurement system. Measurement of the target gas concentration was carried out using a dynamic gas-dispersion approach. First, hollow $\text{Cu}_2\text{O}@\text{CuS}$ nanocube powder was mixed with ethanol to improve the stability of the fabricated devices, producing a suspension. The prepared suspension was uniformly applied to the surface of alumina tubes to obtain a homogeneous coating. Subsequently, the residual solvents were removed by heating and aging at an appropriate temperature for 3 h. A piece of Ni–Cr alloy wire, used as a heating element, was inserted into a ceramic tube and soldered to the base of six probes, along with four platinum wires (Figure S1). The working temperature of the fabricated thermocouple was regulated by adjusting the applied heating voltage. The produced contaminating gases were obtained by evaporating liquid ammonia, ethanol, acetone, toluene, formaldehyde, and n-butanol. The relative humidity level was maintained at 20% during the experiment. The resistance ratio $R = R_a/R_g$ was used to quantify the gas response. R_a and R_g represent the sensor resistance in air and in the test gas, respectively. The response and recovery times of the gas sensor were determined by monitoring the time it takes for the signal to reach a 90% stabilization threshold during gas switching cycles. Different VOC concentrations were then calculated using the following formula:

$$C = \frac{\rho V R T P}{M \times 1 \text{ atm} \times 18 \text{ L}} \quad (1)$$

In Equation (1), the parameters are defined as follows: C denotes the target gas concentration (ppm), ρ represents the reagent density (g/mL), V stands for the liquid volume (L), R is the gas constant ($0.082 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}$), T is the temperature (K, 298 K), M

indicates the molecular weight of the gas (g/mol), and P is the purity factor, where p is 0.25 for NH_3 calculation and 0.37 for HCHO calculation. The source solutions of the other gases ($\text{CH}_3\text{CH}_2\text{OH}$, $\text{C}_4\text{H}_{10}\text{O}$, $\text{C}_3\text{H}_6\text{O}$, and C_7H_8) are of AR with P set to 1, and CO is supplied by a gas cylinder with a purity of 99.9%. The purities of gas source liquids and gas used in this study are presented in Table 1.

Table 1. Gas source liquids and gas purity.

	$\text{CH}_3\text{CH}_2\text{OH}$	NH_3	HCHO	$\text{C}_4\text{H}_{10}\text{O}$	$\text{C}_3\text{H}_6\text{O}$	C_7H_8	CO
Source	liquid	liquid	liquid	liquid	liquid	liquid	gas cylinder
Purity	AR	25%	37%	AR	AR	AR	99.9%

3. Results and Discussion

3.1. Characterization of $\text{Cu}_2\text{O@CuS}$

The XRD data in Figure 1a shows characteristic Cu_2O crystal diffraction peaks with no detectable impurities from other copper compounds [27]. The diffraction peaks align perfectly with the standard Cu_2O data (PDF #05-0667). The highest intensity peak, centered at approximately 36.418° , is attributable to the (111) plane of Cu_2O . The XRD pattern of $\text{Cu}_2\text{O@CuS}$ confirms the presence of both Cu_2O and CuS . Specifically, diffraction peaks attributable to Cu_2O are observed, along with peaks corresponding to the (103), (105), and (110) crystal planes of CuS (PDF #06-0464). Furthermore, the peak at 46.136° is assigned to the (220) crystal plane of Cu_{2-x}S , which is understood as an indication of the presence of a heterostructure interface during the sulfidation process. In general, Cu_2O with (111) crystalline surfaces exhibits high electrical conductivity, which is advantageous in various scenarios [28]. Scanning electron microscopy (SEM) imaging results in Figure 1b reveal that the Cu_2O nanocubes were successfully formed, with their average size measured to be around 400 nm. Figure 1c,d show the SEM images of the hollow $\text{Cu}_2\text{O@CuS}$ nanocubes synthesized via ion exchange with a Na_2S solution, followed by selective etching using sodium thiosulfate. Figure 1c,d also show that the nanocubes have a uniform size of approximately 400 nm and a relatively rough surface, endowing them with a large specific surface area. Note that an increase in the specific surface area offers more active sites for gas molecules to interact with the sensing material, enhancing gas-sensing capabilities. The transmission electron microscopy (TEM) image of the $\text{Cu}_2\text{O@CuS}$ nanocubes in Figure 1e shows a relatively brighter middle region, indicating that the prepared nanocubes are hollow.

Energy-dispersive X-ray spectroscopy (EDS) elemental mapping was used to analyze the spatial distribution of Cu, S, and O on the hollow $\text{Cu}_2\text{O@CuS}$ nanocubes. According to Figures 1f and S2, all elements (Cu, S, and O) are uniformly distributed on the surfaces of the hollow $\text{Cu}_2\text{O@CuS}$ nanocubes. EDS analysis of the data presented in Table S2 reveals the weight ratio of Cu_2O to CuS is 1:2.48, meaning Cu_2O constitutes 28.8% and CuS 71.2% of the composite. A negligible excess of oxygen (0.86 atoms) was disregarded, confirming the material is primarily composed of these two phases.

To examine the interactions between active sites and carriers, electronic state analysis was performed. The electronic states and charge transport behavior of Cu_2O and hollow $\text{Cu}_2\text{O@CuS}$ nanocubes were studied using X-ray photoelectron spectroscopy (XPS). In Figure 2a, the XPS survey scans of Cu_2O and hollow $\text{Cu}_2\text{O@CuS}$ nanocubes reveal that no impurities were introduced during synthesis. In Figure 2b, the Cu 2p XPS core-level spectra show peaks at 950.90 eV (Cu 2p_{1/2}) and 931.08 eV (Cu 2p_{3/2}) attributable to Cu^+ , along with peaks at 932.88 eV (Cu 2p_{3/2}) and 952.96 eV (Cu 2p_{1/2}) attributable to Cu^{2+} , indicating the presence of the two primary oxidation states of Cu in both Cu_2O and $\text{Cu}_2\text{O@CuS}$.

Furthermore, the Cu (II) peak suggests the existence of a very thin oxide layer on the Cu_2O surface. Notably, both the Cu 2p and O 1s XPS spectra provide complementary information about the surface chemistry of Cu_2O and $\text{Cu}_2\text{O}@\text{CuS}$. The results of Figure 2c confirm the existence of oxygen species related to oxygen vacancies, and thus infer the existence of oxygen vacancies, which can significantly enhance the catalytic reactivity of $\text{Cu}_2\text{O}@\text{CuS}$ [29,30]. Typically, oxygen vacancies on the material surface (including active sites generated by surface reconstruction) can enhance catalytic performance, promote oxygen adsorption, and thereby improve gas-sensing performance [31]. According to the values listed in Table 2, the proportion of oxygen vacancies in $\text{Cu}_2\text{O}@\text{CuS}$ (43.48%) is higher than that in Cu_2O (31.3%), indicating that CuS promotes the detachment of oxygen atoms from the Cu_2O lattice, thereby promoting oxygen molecule adsorption on the surface. In the S 2p XPS spectra in Figure 2d, the peaks at 160.39 and 161.56 eV are attributable to S $2p_{1/2}$ and S $2p_{3/2}$, respectively. The synergistic results of XPS and XRD confirmed the successful preparation of $\text{Cu}_2\text{O}@\text{CuS}$.

Surface area and pore architecture represent crucial material characteristics [32]. Typically, a larger surface area in gas sensors offers greater availability of active sites, enhancing gas detection sensitivity. The porous properties of Cu_2O and $\text{Cu}_2\text{O}@\text{CuS}$ were examined using nitrogen adsorption/desorption isotherm analysis. Figure 2e,f show the corresponding adsorption/desorption isotherms, pore size distributions, and summed porosity volumes. The Brunauer–Emmett–Teller (BET) surface area of $\text{Cu}_2\text{O}@\text{CuS}$ is determined as $83.1 \text{ m}^2/\text{g}$, which is a relatively high value for promoting gas adsorption. According to the Barrett–Joyner–Halenda method, the cumulative pore volume and average pore size of $\text{Cu}_2\text{O}@\text{CuS}$ are $0.145 \text{ cm}^3/\text{g}$ and 6.99 nm , respectively. A large surface area allows for rapid gas molecule adsorption/desorption kinetics, enabling swift sensor response/recovery while improving the sensitivity.

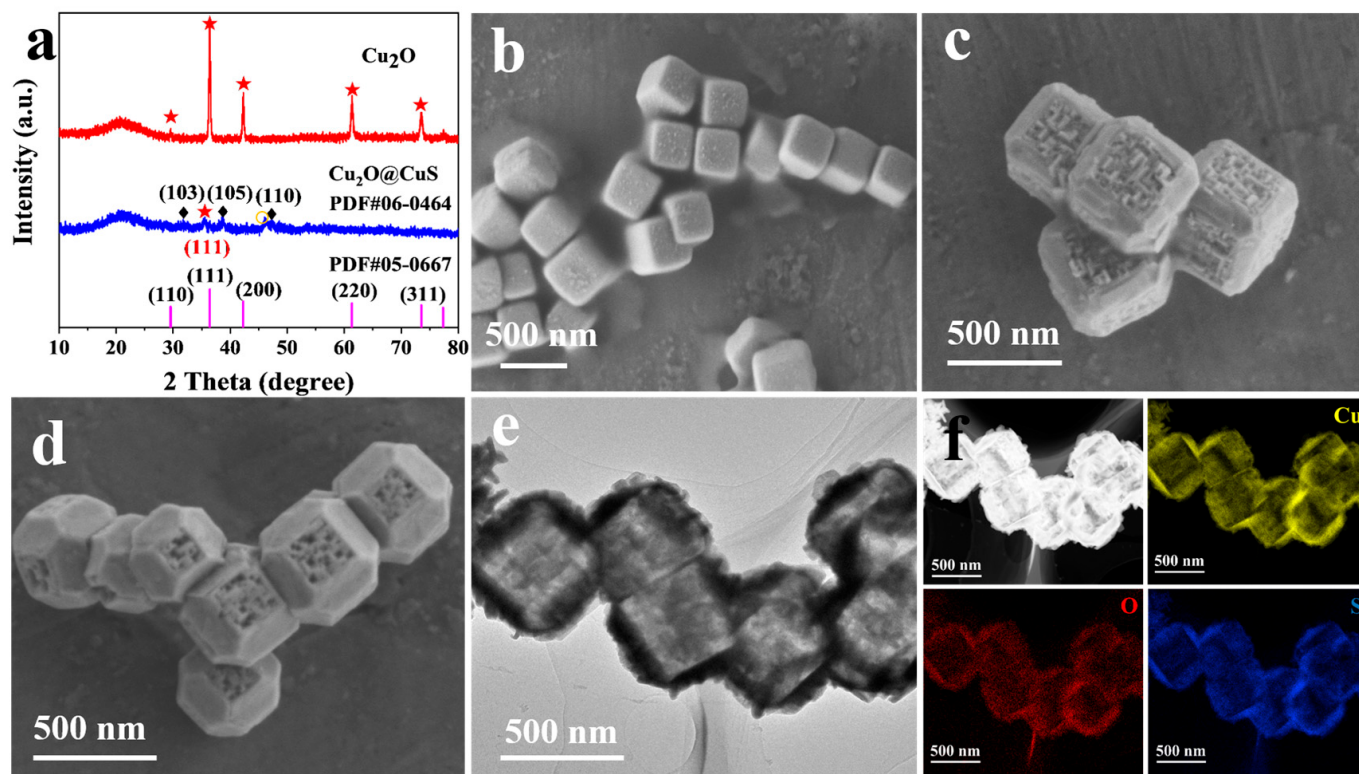


Figure 1. (a) XRD patterns of Cu_2O and $\text{Cu}_2\text{O}@\text{CuS}$. SEM images of (b) Cu_2O and (c,d) $\text{Cu}_2\text{O}@\text{CuS}$. (e) TEM image of $\text{Cu}_2\text{O}@\text{CuS}$. (f) EDS images of $\text{Cu}_2\text{O}@\text{CuS}$.

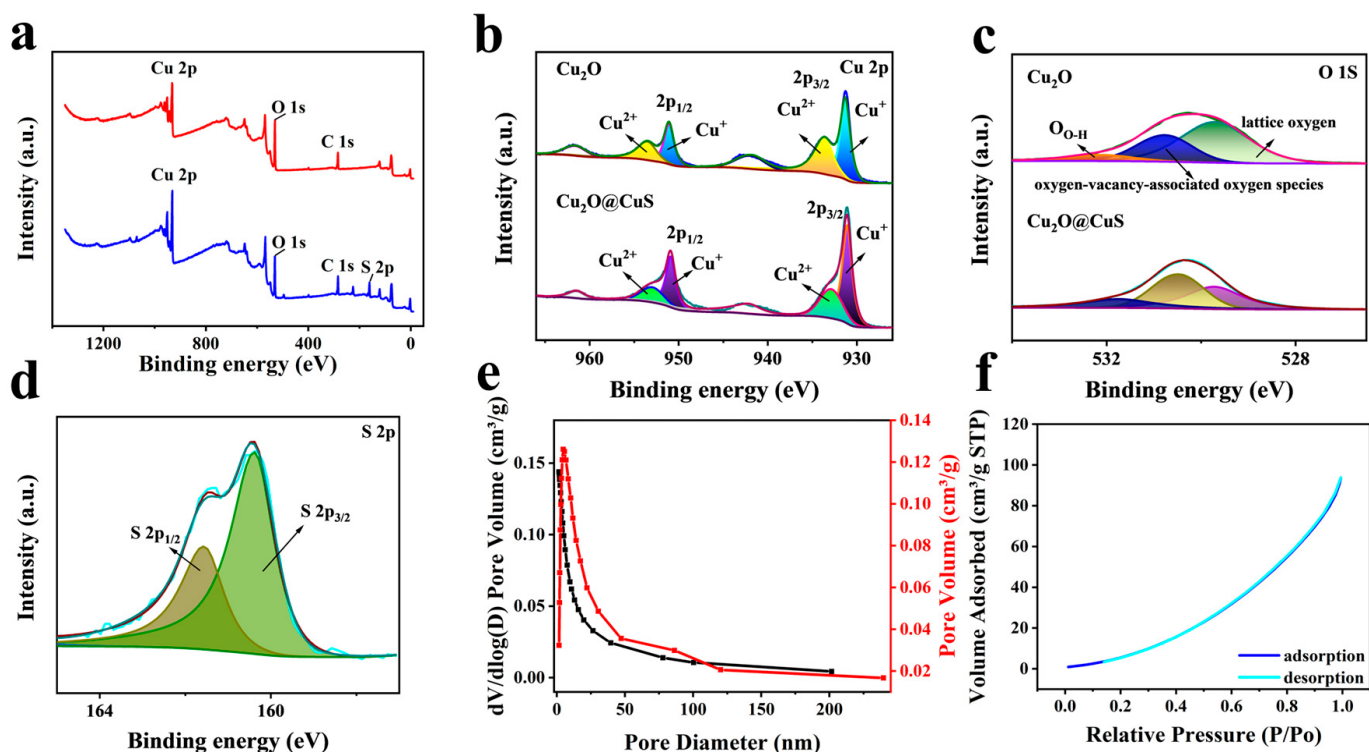


Figure 2. (a) XPS survey scans, (b) Cu 2p spectra, and (c) O 1s spectra of Cu₂O and Cu₂O@CuS. (d) S 2p spectrum, (e) pore size distribution and cumulative pore volume, and (f) N₂ adsorption/desorption isotherms of Cu₂O@CuS.

Table 2. Different oxygen, Cu (II), and Cu (I) contents in the prepared samples.

Materials	Lattice Oxygen	Vacant Oxygen	Adsorbed Oxygen	Cu (I)	Cu (II)
Cu ₂ O	59.34	31.3	9.36	47.24	42.31
Cu ₂ O@CuS	35.86	43.48	20.66	56.29	33.73

3.2. Gas-Sensing Properties

A series of gas-sensing tests were performed to evaluate the gas-sensing performance of the hollow Cu₂O@CuS nanocube-based gas sensor, particularly its ability to detect various VOCs, with a focus on n-butanol. Note that the operating temperature of a gas sensor significantly affects its sensing performance. In general, sensors require a specific operating temperature to enable optimal activity of the sensing material because target molecules often lack sufficient energy to surpass the activation barriers at relatively lower temperatures. When the operating temperature exceeds the optimal range, the sensor signal decreases. The core cause of this phenomenon is primarily the reduced reaction efficiency induced by n-butanol desorption [3]. A perfect balance between the adsorption and desorption dynamics of a target molecule on the sensor surface is achieved only at the optimal operating temperature, maximizing reaction kinetics. Furthermore, the working temperature influences both the nature of chemisorbed oxygen species and the mobility of charge carriers. Figure 3a shows that both Cu₂O- and Cu₂O@CuS-based sensors exhibit a temperature-dependent response toward 100 ppm n-butanol at temperatures ranging from 160 to 300 °C. Both sensors exhibit a similar response curve: initially increasing with temperature, reaching a peak at the optimal operating temperature of 260 °C, and then decreasing. Comparative analysis of the sensor responses reveals that the response of the hollow Cu₂O@CuS nanocube-based sensor (58.944) toward 100 ppm n-butanol at 260 °C exceeds that of the pure Cu₂O-based sensor (2.856). The superior response of the Cu₂O@CuS

nanocube-based sensor can be attributed to the catalytic properties of CuS nanoparticles, the presence of a heterojunction between Cu₂O and CuS, a large BET-specific surface area, and high concentration oxygen vacancies. Figure 3b illustrates that the response of the hollow Cu₂O@CuS nanocube-based sensor improves with the concentration of n-butanol, reaching a maximum value of 58.944 at 100 ppm. Notably, at a low concentration of 1 ppm n-butanol, the Cu₂O@CuS nanocube-based sensor produces a measurable response of 2.9717. In addition, the dynamic response curve in Figure 3b demonstrates good reversible cycling properties of the Cu₂O@CuS nanocube-based sensor at both low and high concentrations of incoming and outgoing n-butanol molecules. The resistance response curve in Figure 3c shows that the Cu₂O@CuS nanocube-based sensor exhibits a stable baseline. The dynamic and resistive response curves in Figure 3e,f, respectively, show that the Cu₂O nanocube-based gas sensor exhibits good reversible cyclability with low responses.

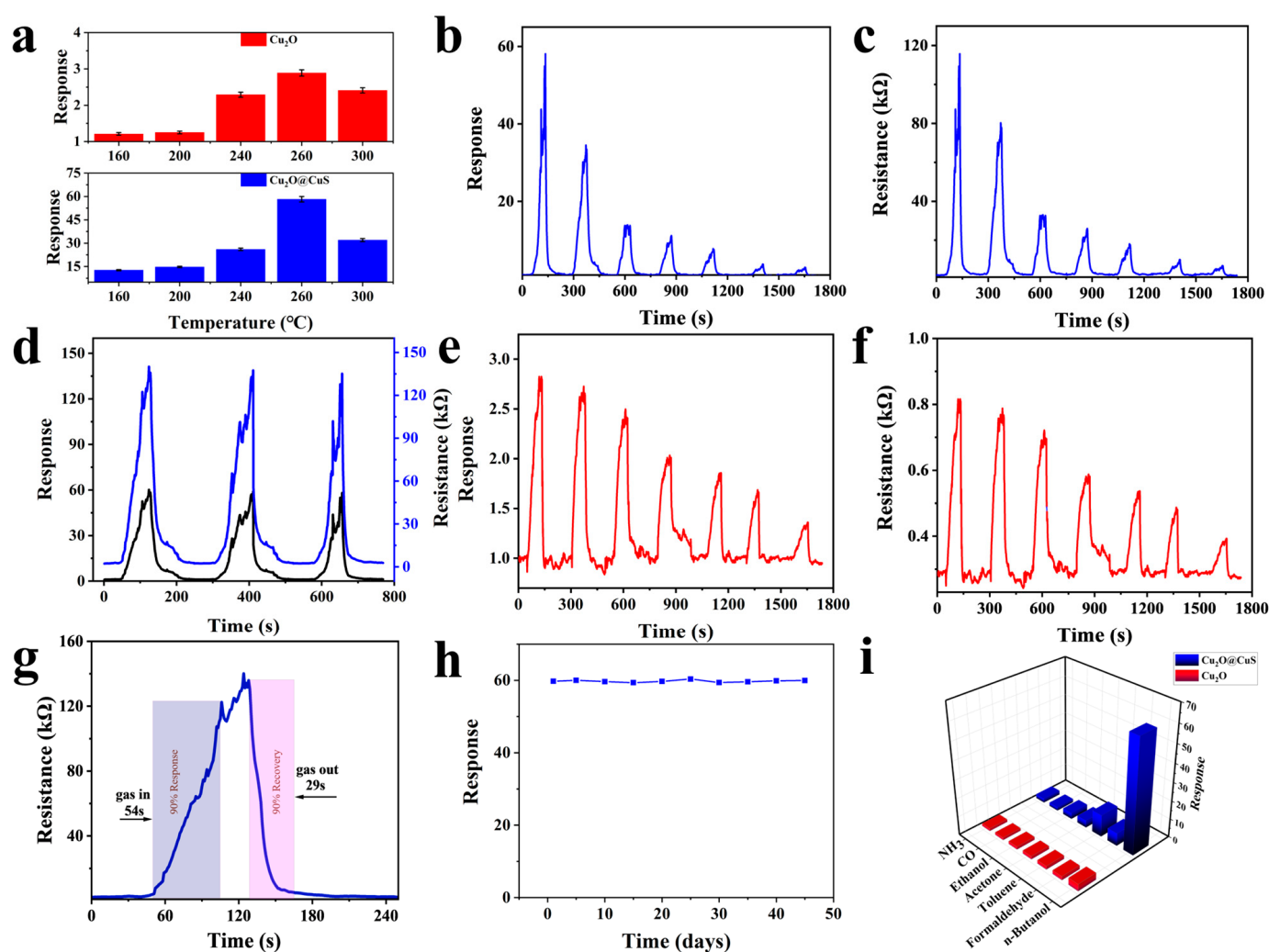


Figure 3. (a) Responses of different sensors to 100 ppm n-butanol measured at different operating temperatures. (b) Dynamic response curve of the hollow Cu₂O@CuS nanocube-based sensor obtained by varying the n-butanol concentration at 260 °C. (c) Resistance response of the hollow Cu₂O@CuS nanocube-based sensor at different n-butanol concentrations at 260 °C. (d) Cyclic repeatability of the hollow Cu₂O@CuS-based sensor at 260 °C. (e) Dynamic and (f) resistive response curves of the Cu₂O-based sensor at different n-butanol concentrations at 260 °C. (g) Response–recovery curve of the Cu₂O@CuS-based sensor at 260 °C. (h) Long-term response stability of the Cu₂O@CuS-based sensor to 100 ppm n-butanol over 45 d at 260 °C. (i) Selectivity of the hollow Cu₂O@CuS nanocube-based sensor toward different VOCs at a concentration of 100 ppm at 260 °C.

Stability is one of the important parameters for the practical application of gas sensors because it determines how reliably they perform over time and under varying conditions [33]. In Figure 3d, the cyclic repeatability test results show that, under the conditions of 100 ppm n-butanol and 260 °C, the hollow Cu₂O@CuS nanocube-based gas sensor exhibits small differences in response peaks during multiple cycles; moreover, after each cycle ends, the sensor resistance can fall back to near the initial baseline without obvious baseline elevation, depression, or intensified fluctuation. These characteristics indicate that the sensor has a stable cyclic response and stable baseline resistance. In Figure 3h, the long-term stability test results show that the Cu₂O@CuS nanocube-based gas sensor exhibits a relatively stable response over a period of 45 d, implying that the sensor possesses high long-term stability and is suitable for use in practical applications. Additionally, the Cu₂O@CuS nanocube-based gas sensor exhibits a response recovery time of 54/29 s after detecting 100 ppm n-butanol, as shown in Figure 3g. Thus, the hollow Cu₂O@CuS nanocube-based gas sensor is effective for applications where high response and fast recovery are needed.

Effective selectivity is a decisive factor in determining the practical utility and reliability of gas sensors under real operational conditions. The selectivity of the Cu₂O@CuS nanocube-based sensor was assessed for n-butanol in the presence of several interfering gases (NH₃, CO, ethanol, acetone, toluene, and formaldehyde) at a uniform concentration of 100 ppm at a sensor operating temperature of 260 °C. Notably, the Cu₂O@CuS nanocube-based sensor exhibited a relatively stronger response toward 100 ppm n-butanol (Figure 3i). The excellent gas-sensing selectivity of the Cu₂O@CuS heterostructure toward n-butanol stems from the synergistic effect between its surface structure and the molecular properties of n-butanol. Surface oxygen vacancies, acting as active adsorption sites, can interact with the –OH groups of n-butanol molecules to enhance adsorption. Compared with short-chain alcohols and carbonyl-containing molecules, the longer carbon chain and higher polarizability of n-butanol further stabilize adsorption through strong van der Waals forces. This synergistic effect can promote electron transfer and regulate the interfacial charge distribution, thereby significantly enhancing the sensing response. Differences in chemical affinity, molecular polarity, and adsorption–desorption kinetics enable the sensor to distinguish n-butanol from interferents to a certain extent [34]. This indicates that the sensor exhibits favorable performance in n-butanol detection and holds potential for practical applications.

Detection data were analyzed based on the classical Formula (2) for gas sensors. Figure 4a presents the correlation characteristics between the logarithm of the response value of the hollow Cu₂O@CuS nanocube-based gas sensor and the logarithm of the n-butanol concentration. Through linear fitting, the relational expression $\lg G_{\text{gas}} = 0.42 + 0.64 \lg p$ was obtained; further, the formula $G_{\text{gas}} = 2.63 p^{0.64}$ can be derived.

$$G_{\text{gas}} = A p^n \quad (2)$$

To conduct an in-depth analysis of the sensing mechanism and performance limits of the hollow Cu₂O@CuS nanocube gas sensor for n-butanol, the limit of detection (LOD) was calculated based on the aforementioned classical formula and fitting parameters, yielding an LOD of 3.18 ppm. This LOD index can meet the requirements of practical application scenarios for n-butanol gas detection, highlighting the excellent practical potential and certain commercial application value of the gas sensor based on this hollow-structured nanomaterial.

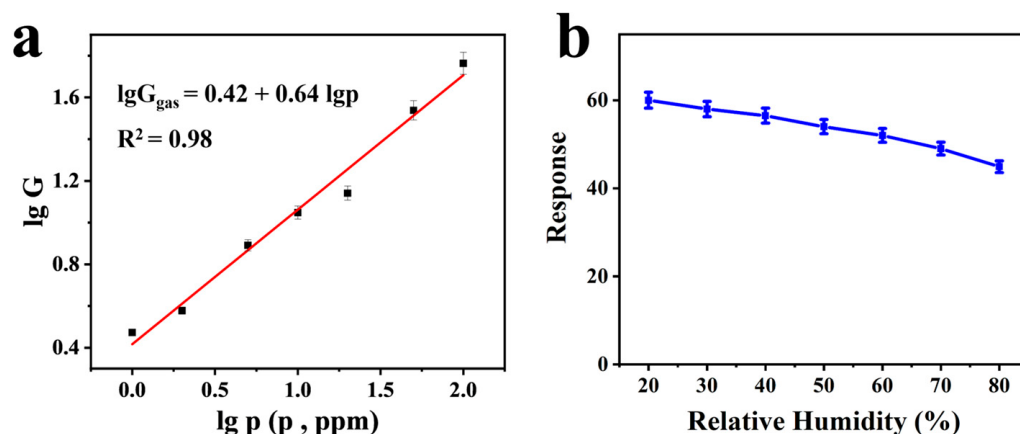


Figure 4. (a) Effect of the concentration of n-butanol on the response of the hollow $\text{Cu}_2\text{O}@\text{CuS}$ nanocube-based gas sensor at $260\text{ }^\circ\text{C}$. The straight solid line represents the line of best fit. (b) Effect of different relative humidity (at ambient temperature $25\text{ }^\circ\text{C}$) on the response of the sensor to 100 ppm n-butanol at $260\text{ }^\circ\text{C}$. The solid line has been added to serve as a visual guide.

Under conditions of elevated humidity, adsorbed water molecules occupy the active oxygen sites on the sensor surface, thereby reducing its response. Therefore, the effects of different relative humidity (RH) conditions (the range of the RH is from 20% to 80% at ambient temperature $25\text{ }^\circ\text{C}$) on the resistance changes and response of the fabricated sensor were investigated at the optimal working temperature of $260\text{ }^\circ\text{C}$ for 100 ppm n-butanol [35]. As shown in Figure 4b, the $\text{Cu}_2\text{O}@\text{CuS}$ -based gas sensor exhibits a considerably high response toward n-butanol at a relative humidity below 60%. When the ambient humidity exceeds 60%, the sensor performance slightly degrades; however, the sensor response still remains considerably high.

To demonstrate the sensor performance in this work, a comparison was conducted with previously reported n-butanol sensors. As shown in Table S3, the $\text{Cu}_2\text{O}@\text{CuS}$ sensor demonstrates superior performance, confirming that the $\text{Cu}_2\text{O}@\text{CuS}$ core-shell nanocubic heterostructure enables excellent n-butanol detection performance through the synergistic effects of ultrahigh specific surface area, hollow transport architecture, preferential adsorption by oxygen vacancies, and carrier regulation via p-p heterojunction.

3.3. Plausible Gas-Sensing Mechanism

A space charge layer model can be used to interpret the macroscopic resistance changes of the sensor. Note that the resistance of a gas sensor changes due to various processes, such as gas adsorption and desorption on the surface.

Both Cu_2O (energy gap (E_g) = 1.50 eV) and CuS (E_g = 1.12 eV) are typical p-type semiconductors. The Cu atoms in the Cu_2O (111) plane are asymmetrically coordinated [36]; thus, each pair of copper atoms has a dangling bond oriented perpendicular to the (111) face. Notably, compared to the (100) face, the (111) face of Cu_2O has a greater number of terminal Cu atoms per unit surface area. Consequently, a higher adsorption of negative oxygen ions on the (111) face considerably improves the sensing performance of the $\text{Cu}_2\text{O}@\text{CuS}$ nanocube-based gas sensor.

The integration of CuS with Cu_2O results in a p-p heterojunction, enabling carrier flow from CuS to Cu_2O under the influence of a steep work function gradient until Fermi level equilibrium is reached (Figure 5). When the $\text{Cu}_2\text{O}@\text{CuS}$ heterostructure is exposed to air, O_2 molecules are chemisorbed onto the material's oxygen vacancies, with these vacancies including the active sites generated by surface reconstruction; this process further leads to the formation of oxygen anion species ($\text{O}^{\alpha-}$), such as O_2^- , O^- , and O^{2-} . During the process of anion generation, the adsorbed oxygen species function as providers of

hole carriers, enhancing the hole concentration in the sensing material and expanding the hole-accumulation layer at the heterojunction while thinning the depletion layer. In p-type semiconductor sensor materials, holes can flow along the grain boundaries and through the hole-accumulation layer. Therefore, potential barriers do not significantly impede the flow of holes in p-type semiconductor sensor materials, resulting in a lower baseline resistance [37]. The reaction processes involved during oxygen adsorption and anion generation are described by the following equations [38,39]:

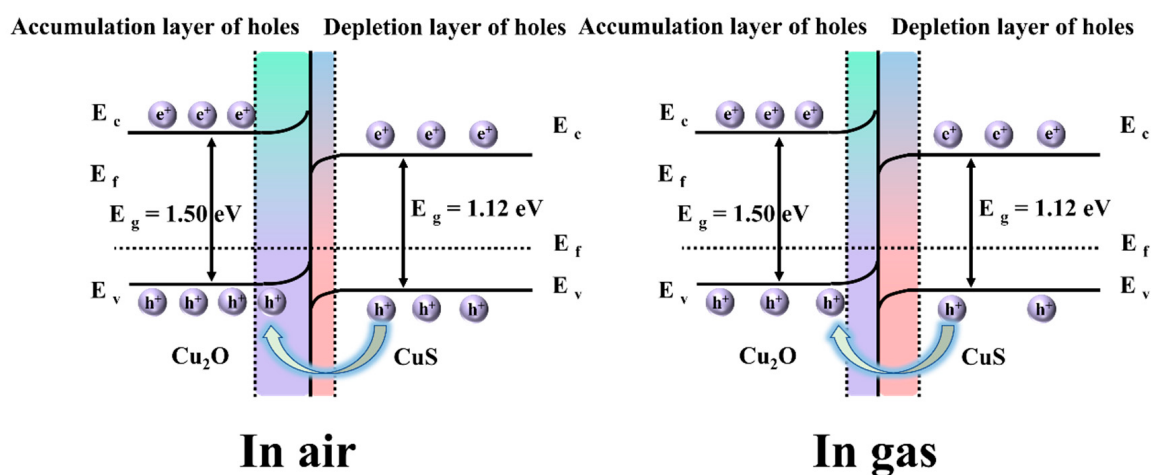
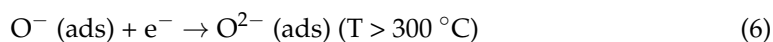
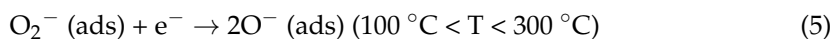
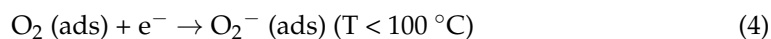
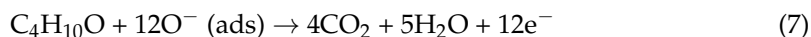


Figure 5. Schematic showing the sensing mechanism of the hollow Cu₂O@CuS nanocube-based gas sensor in air and n-butanol gas.

In the presence of n-butanol, a redox reaction occurs between the gas molecules and the previously adsorbed oxygen anions on the Cu₂O@CuS p-p heterojunction, releasing electrons to the sensor surface. The recombination of released electrons with holes leads to a decrease in the charge carrier concentration within the sensing layer. Subsequently, the produced electron-hole complexes reduce the hole density in the nanocomposite and break the dynamic carrier equilibrium between Cu₂O and CuS. Consequently, the hole accumulation layer thickness diminishes at the Cu₂O interface while the hole depletion layer expands at the CuS interface, significantly increasing the resistance in the n-butanol environment. The following equation describes the reaction pathway between n-butanol and oxygen anions [40]:



To summarize, hollow Cu₂O@CuS nanocubes, due to their relatively high specific surface area, provide numerous active sites for negative oxygen ion adsorption. Highly anoxic Cu₂O and defect-rich CuS surfaces in Cu₂O@CuS nanocubes enhance their gas-sensing performance by providing abundant centers for gas reactions. The presence of a heterojunction, along with synergistic electronic effects, further improves the performance of the n-butanol sensor based on Cu₂O@CuS nanocubes.

4. Conclusions

This study successfully fabricated hollow Cu₂O@CuS core-shell nanocubic heterostructures and applied them to construct a gas sensor for the detection of n-butanol. The prepared sensor exhibited a low detection limit of 3.18 ppm and rapid response/recovery times of 54/29 s, respectively, enabling trace-level monitoring and quantitative analysis of n-butanol in various environments. The sensor's excellent performance stems from multiple synergistic effects. The high specific surface area offers abundant active sites for gas adsorption; the hollow structure promotes mass transfer and accelerates adsorption/desorption kinetics; the high-density surface oxygen vacancies facilitate the preferential adsorption of n-butanol molecules, suppressing interference from other analytes; and the p-p heterojunction optimizes charge carrier separation and band structure modulation, further enhancing the selective response. During a 45-day stability test, the sensor maintained stable performance and exhibited good responsiveness under 20–80% humidity. These characteristics make the Cu₂O@CuS nanocube-based sensor an ideal candidate for industrial n-butanol detection. This work highlights the great potential of heterostructure design and defect engineering in developing high-performance gas-sensing materials.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemosensors13090324/s1>, Table S1. Reagents used in the experiments; Figure S1. Physical schematic diagram of sensor core device; Figure S2. EDS analysis of hollow Cu₂O@CuS nano-cube; Table S2. EDS analysis of hollow Cu₂O@CuS nano-cube; Table S3. Comparison of n-butanol gas sensors based on other sensing materials in previous reports [41–46].

Author Contributions: Conceptualization, D.Z., Z.Q. and C.L.; Data curation, C.L.; Formal analysis, R.X.; Funding acquisition, Y.Z.; Investigation, D.Z. and Z.Q.; Methodology, D.Z. and Z.Q.; Project administration, H.W.; Software, X.R.; Supervision, H.W. and Y.Z.; Visualization, R.X.; Writing—original draft, D.Z.; Writing—review and editing, Y.Z. All authors have read and agreed to the published version of the manuscript.

Funding: The authors appreciate the support of the National Natural Science Foundation of China (No. 22264025), the Applied Basic Research Foundation of Yunnan Province (No. 202401AS070033), the National Key R&D Program of China (No. 2024YFD1700200), the Yunnan Provincial Department of Education Scientific Research Fund (No. 2025Y0299), and the Reserve talents for young and middle-aged academic and technical leaders project of Yunnan Province (No. 202405AC350071, Yong Zhang).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data will be made available upon request.

Conflicts of Interest: The authors declare no conflicts of interest.

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