Gas Sensors Based on Copper Oxide Nanomaterials: A Review

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Abstract: Metal oxide semiconductors have found widespread applications in chemical sensors based on electrical transduction principles, in particular for the detection of a large variety of gaseous analytes, including environmental pollutants and hazardous gases. This review recapitulates the progress in copper oxide nanomaterial-based devices, while discussing decisive factors influencing gas sensing properties and performance. Literature reports on the highly sensitive detection of several target molecules, including volatile organic compounds, hydrogen sulfide, carbon monoxide, carbon dioxide, hydrogen and nitrogen oxide from parts-per-million down to parts-per-billion concentrations are compared. Physico-chemical mechanisms for sensing and transduction are summarized and prospects for future developments are outlined.

Keywords: chemical sensors; gas sensors; nanomaterials; nanoparticles; nanowires; copper oxide; cupric oxide; cuprous oxide; air quality monitoring; volatile organic compounds

1. Introduction

Low-dimensional metal oxide nanostructures have attracted considerable scientific interest due to their size and shape-dependent properties that can be tailored in a wide range. The inherently high surface-to-volume ratio makes them ideal candidates for various sensing applications, including gas sensors, humidity sensors, photodectors and biosensors [1]. Metal oxide semiconductors have a long history of scientific and industrial developments in the field of chemical sensing, ranging from initial discoveries in the 1950s and 1960s to continuous research efforts up to now, which also led to the successful realization of commercial sensor products. Whereas early work focused on leak detection and safety applications, current developments most commonly pursue the development of sensor devices for indoor and outdoor air quality monitoring, aiming at selective gas classification and quantitative determination of environmental pollutant concentrations. In addition to air quality monitoring, metal oxide-based gas sensors are also highly promising candidates for biomedical diagnostics based on exhaled breath analysis. Potential exemplary applications include the diagnosis of diabetes (acetone sensing), halitosis (hydrogen sulfide sensing) and lung cancer [2].

In this review, research progress on gas sensor devices based on copper oxide will be summarized—in particular, those employing cupric oxide (CuO) and cuprous oxide (Cu$_2$O) nanostructures. Among the large number of different metal oxides, these materials belong to the group of semiconductors with p-type conductivity resulting from unintentional doping that arises from non-stoichiometry [3]. Copper oxides are abundant and non-toxic materials that can be fabricated by sustainable low-cost processes. Different synthetic procedures are available to achieve nanomaterials with high crystalline quality, including their size and shape control, hence allowing for the realization of nanoelectronic devices with tailored properties. Apart from (bio)chemical sensors (see also reference [4] for a previous review on gas sensing applications), copper oxide has been employed in various areas—for instance, photovoltaics, lithium ion batteries, (photo)catalysis, electrochromic devices, supercapacitors, nanofluids, field emission devices and antimicrobial applications [5,6]. Here, the most important considerations for gas sensing applications,
including the basic mechanisms for sensing and transduction will be outlined, ranging from the design of the employed nanomaterials, to the structures of the sensor devices and the overall sensor systems. While most of these considerations are more general and also applicable to other material systems, the discussion will emphasize literature reports on copper oxide nanomaterials. Results on devices for chemical sensing in dry and humid air at atmospheric pressure will be considered, focusing on several target molecules, including volatile organic compounds (VOCs), hydrogen sulfide (H₂S), carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂) and nitrogen oxide (NOₓ) from parts-per-million (ppm) down to parts-per-billion (ppb) concentrations. Note that this review covers gas sensors in which copper oxide nanostructures are the main "base" material, and literature reports on nanocomposites, core-shell structures, extended heterostructures, etc., are not discussed here. For a detailed comparison between different metal oxide materials for gas sensors, the reader is referred to [7].

2. Nanomaterial, Device and Sensor System Design

The following schematic diagram (Figure 1) illustrates the most important aspects that influence the properties of chemical sensor devices. To achieve rationally designed gas sensors with optimized performance tailored to the specific application, these influencing factors need to be considered when designing the nanomaterials, the device structure and the overall sensor system.

![Figure 1. Schematic illustration of general factors influencing gas sensor properties, which need to be addressed by nanomaterial, device and sensor system design. This contribution aims at reviewing the respective aspects for copper oxide-based gas sensors reported in literature.](image)

2.1. Influence of Copper Oxide Phase

Three different oxidation states and crystalline phases with distinct material properties can occur: cupric oxide CuO or Cu(II) oxide with monoclinic crystal structure, cuprous oxide Cu₂O or Cu(I) oxide with cubic crystal structure and parameleconite Cu₄O₃, a mixture of Cu(II) and Cu(I) coordination, with tetragonal crystal structure. The reader is referred to the review articles in references [5,8] for a detailed discussion on the corresponding material properties. From a chemical sensing perspective the CuO and Cu₂O phases have been the most relevant, whereas the former is more stable at elevated temperatures and ambient pressure. Depending on environmental conditions, surface oxidation of Cu₂O...
to CuO has to be taken into account, considering the thermodynamic stability of Cu$_2$O surfaces [9,10].

A systematic comparison between the gas sensitivity of CuO and Cu$_2$O is often difficult due to differences in synthetic procedures, which can lead to nanomaterials with different sizes or morphologies. The ethanol sensing properties of CuO thin films (nanocrystal dimensions $\sim$30 nm) and Cu$_2$O thin films (nanocrystal dimensions $\sim$85 nm) fabricated by reactive magnetron sputtering were compared [11]. The CuO thin films exhibited higher ethanol response, lower optimum operation temperature and shorter response/recovery times. In reference [12], ethanol sensing with thin film devices based on copper oxide nanocrystals was reported. Mixed copper oxide phases obtained by annealing treatments of Cu$_2$O layers showed superior ethanol sensing performance compared to single-phase materials, which was attributed to the formation of CuO–Cu$_2$O heterojunctions. Furthermore, CuO–Cu$_2$O composites with hollow single- and multi-shell morphologies presented enhanced ethanol response compared to their single-phase CuO counterparts [13].

2.2. Influence of Nanomaterial and Sensor Morphology

The choice of nanomaterial and sensor fabrication method is of utmost importance for achieving gas sensor devices with desired properties. The size and morphology of the employed nanostructures governs their surface-to-volume ratio, which is a crucial parameter to maximize the impact of surface reactions on the overall nanostructure’s electrical conductivity. For instance, hierarchical nanostructures can be employed to maximize the surface-to-volume ratio and achieve sensor devices with superior sensitivity (see, e.g., reference [14] and multiple other examples summarized in Section 4). While the size and porosity of the initial nanomaterials play a decisive role, also the sensor preparation method will determine the thickness and porosity of the overall sensing layer. The nanoscale morphology will not only influence the gas sensitivity but also other parameters such as sensor dynamics and long-term stability due to the impact on gas diffusion processes and grain growth at elevated temperatures, respectively.

Single-crystalline nanowires have been extensively studied for gas sensing applications with the prospect of improved long-term stability compared to polycrystalline materials. CuO nanowire devices in various configurations have been realized, including single nanowires in four-point configuration [15,16], single suspended nanowires [17], nanowire networks obtained via thermal oxidation of adjacent microspheres [18] and nanowire networks realized by thermal oxidation of lithographically defined Cu microstructures [19,20]. In contrast to layers of nanostructured materials, devices based on individual single-crystalline nanowires do not contain grain boundaries or porosity, which has a profound impact on the sensor transduction mechanism. On the other hand, nanowire networks constitute an intermediate case where single-crystalline sensing elements are interconnected at the nanowire boundaries that are in mechanical contact.

A major advantage of using copper oxide nanomaterials for chemical sensing is the availability of synthesis methods with high degree of morphological control, in particular, size- and shape-controlled growth of Cu$_2$O micro- and nanostructures [21]. Homogeneous sensing materials with well-defined structures can be achieved either by directly employing as-synthesized Cu$_2$O or by using calcination processes to transform Cu$_2$O to CuO. Several examples for shape-dependent gas sensing properties have been reported: Octahedral Cu$_2$O particles with exposed [111] facets showed superior CO sensing properties compared to Cu$_2$O cubes with exposed [100] facets and truncated Cu$_2$O octahedra [22]. Similarly, octahedral Cu$_2$O was favorable for ethanol, acetone, triethylamine and formaldehyde detection compared to Cu$_2$O cubes and the importance of 1-coordinated Cu atoms obtained via hydrogenation was highlighted [23]. On the other hand, Cu$_2$O cubes exhibited enhanced sensing performance for NO$_2$, acetone and benzene compared to octahedral Cu$_2$O [24]. In reference [25], the CO sensing performance of CuO nanotubes (exposed [111] planes; obtained by thermal oxidation of Cu nanowires) and CuO nanocubes (exposed [110] surface planes; obtained by thermal oxidation of Cu$_2$O nanocubes) were compared,
showing that higher sensitivity and lower sensor operation temperature could be achieved with CuO nanotubes.

2.3. Impurity Doping and Nanoparticle Decoration

The performances of metal oxide semiconductor-based gas sensors, in particular, their sensitivity, selectivity and stability, can be significantly influenced by the functionalization with additives such as noble metals, other metal oxides or carbon-based nanomaterials. The impact on the gas sensing properties is a result of a complex interplay between several physico-chemical processes, commonly subsumed under chemical and electronic sensitization. Thereby, it is crucial how the additive is introduced into the sensing layer, which can range from the incorporation of atoms in the nanostructure bulk or at its surface (impurity doping) to formation of additive clusters/nanoparticles at the nanostructure surface (nanoparticle decoration). As a result, the functionalization method needs to be carefully chosen and optimized to achieve the desired enhancement in sensor performance. For a detailed discussion on the resulting impact of additives on gas-solid interactions and sensor transduction, the reader is referred to a recent review article [26].

Here, selected examples of impurity doping and nanoparticle decoration of copper oxide nanomaterial-based sensors will be discussed. Substitutional doping of CuO hollow spheres with aliovalent Li(I) and Fe(III) was reported in [27], showing significant electronic modification of the sensing material. Fe(III) doping led to a reduction of the hole density and an increase of the ethanol gas response, whereas the opposite was observed for Li(I) doping. The authors of reference [28] found that Sn and Zn doping is suitable for improving the sensing response of CuO nanoparticle-based sensors to ethanol and acetone, respectively. The different effects of Sn and Zn doping were attributed to a change of active adsorption sites (prevalent for Sn doping) and to the formation of CuO-ZnO p-n heterojunctions (prevalent for Zn doping). In references [29,30], the influence of decorating CuO nanowire-based devices with TiO₂, NiO and Co₃O₄ nanoparticles was studied. The decoration with n-type TiO₂ and p-type Co₃O₄ resulted in an increase of sensor response for oxidizing gases and a decrease of sensor response for reducing gases, whereas the opposite effect was observed for decoration with p-type NiO. The impact of functionalization was explained by a modulation of the hole accumulation layer at the CuO surface by semiconductor-semiconductor heterojunctions. Moreover, the CO and NO₂ sensing performance of CuO nanowire-based devices could be significantly enhanced by Au nanoparticle decoration and the nanoparticle size was found to play a decisive role (optimum around 60 nm) [31]. In addition to improving sensitivity and gas selectivity, impurity doping and nanoparticle decoration are used to reduce the sensor’s working temperature and thus its power consumption. For instance, Pd nanoparticle decoration reduced the optimum temperature for H₂S sensing of CuO nanowire-based sensors from 300 °C to 100 °C, which also enabled the device operation in self-heated mode [32]. Depending on the nanoparticle material used for CuO decoration, the possibility of nanoparticle oxidation at elevated temperatures in oxygen-containing atmosphere needs to be considered, which was studied for CuO nanowires decorated with Ru [33], Pd [34,35] and Pt [36] nanoparticles. It was shown that the interactions between the nanoparticles and the CuO support played an important role in determining the nanoparticle crystalline structure upon oxidation, the charge transfer processes occurring at the hetero-interfaces and the catalytic activity.

2.4. Advances in Scalable Device Integration: From Microhotplates to Flexible Substrates

The realization of smart sensor systems capable of gas and odor classification for indoor air quality monitoring requires the implementation of a large number of individual gas sensor elements to enable the use of pattern recognition techniques. Scalable manufacturing processes for the low-cost fabrication of miniaturized sensor devices are needed to achieve economic solutions with small system sizes. In this context, not only the active sensing structures but also additional elements for sensor activation, typically heating elements,
need to be considered. Over the last decades, so-called microhotplate devices have been developed for this purpose [37]. These micromachined structures show some similarities to MEMS and most commonly consist of a suspended membrane (size in the order of 100 µm) with an embedded resistive heater. The latter allows for local heating of the microhotplate membrane up to several hundred degrees at a power consumption of only tens of milliwatt. This technology opens up opportunities of dynamic heating protocols and large sensor arrays with devices operated individually at different operation temperatures.

Gas sensor devices based on copper oxide nanomaterials have been successfully implemented on microhotplate structures. Nanogranular CuO thin films directly deposited on microhotplate devices and structured by a photolithographic lift-off process showed a sensor response for acetaldehyde down to 2 ppm, which was significantly increased by a factor of 7 using dynamic heating protocols [38]. Alternatively, CuO nanoparticles can be deposited on microhotplates by inkjet printing, which resulted in devices for H₂ and H₂S sensing [39]. CuO nanowires can be grown by thermal oxidation of Cu microstructures via heating microhotplate devices in oxygen-containing atmosphere, which allows for well-controlled local nanowire synthesis and does not require to anneal the entire sample in a furnace or macroscopic hotplate setup. This approach enabled the direct integration of CuO nanowires as active sensing elements in situ inside a gas measurement setup, leading to highly sensitive devices for CO detection down to 1 ppm and to new insights on sensor deactivation processes [40]. Furthermore, local CuO nanowire growth was demonstrated on CMOS hotplates fabricated in an industrial process [41] and was suitable for achieving CO sensing down to a concentration of 10 ppm at a power consumption of only 18.2 mW [42]. Another option for integrating copper oxide nanomaterials with CMOS technology was demonstrated in reference [43], where CuO nanowires were realized by the thermal oxidation of Cu through silicon via (TSV) and employed for VOC sensing. As copper is widely available in microelectronic fabrication environments and thermal oxidation to Cu₂O and CuO (and CuO nanowire growth) can be performed at moderate temperatures, the use of copper oxide nanomaterials is advantageous due to the potential for scalable fabrication of sensor devices using industrial processes.

In recent years, interest in portable low-cost gas sensors has significantly increased due to emerging applications in wearables, e-textiles and smart packaging, but flexible polymeric, paper or textile substrates introduce new technological challenges for sensor device fabrication and operation [44]. Most importantly, the sensing materials have to allow for low working temperatures and be able to maintain their performance/functionality under repeated mechanical bending/stretching. Several types of copper oxide nanomaterials suitable for synthesis, deposition and sensor operation at low temperatures have been developed (summarized in detail in the following section), which makes them promising candidates for wearable device technologies. High-performance gas sensors for acetone detection down to 50 ppb at 50% relative humidity were demonstrated by magnetron sputtering deposition of CuO thin films on flexible Kapton substrates [45].

3. Mechanisms for Sensing and Transduction

3.1. Surface Reactions and Transduction Mechanisms

The vast majority of literature reports on copper oxide-based gas sensors relies on conductometric transduction principles, which means that the electrical resistance of the active sensing structures changes upon gas exposure. Considering the chemisorption model for a p-type semiconductor in oxygen-containing atmosphere (see, e.g., recent reviews in references [46,47]), surface adsorption of oxygen leads to the trapping of electrons and the formation of a hole accumulation layer. During gas sensor operation, the hole accumulation layer (and consequently the potential barrier and the electrical conductivity at the surface) is influenced by gaseous analytes either via interactions with chemisorbed oxygen or via adsorption processes linked with charge transfer. Detailed theoretical modeling for the case of detecting reducing gases with p-type semiconductor gas sensors has clarified the influence of temperature, doping concentration, energetic position of surface acceptor
level, reducing gas activation energy and pressure [48]. Similar theoretical modeling was performed for the detection of oxidizing gases with p-type semiconductors and was compared with experimental results [49]. To understand the transduction of these surface reactions into electrical signals, the nanoscale morphology of the sensing structures has to be considered. The chemisorption model is well-established for nanocrystalline thin films, where the sensor conductance is exponentially dependent on the surface potential barrier [46]. It can be assumed that this framework is applicable for a wide range of loosely interconnected films of different copper oxide nanomaterials summarized in the following section. However, modifications will be required for sensor devices based on compact thin films [50] or single-crystalline nanowires [51].

Although the chemisorption model can successfully explain many experimental results observed for conductometric gas sensors, further details related to surface reactions and the sensing mechanism often remain elusive. In most cases, important information on the sensing material properties is missing, e.g., carrier concentration, surface defect densities, type of exposed surface facets, surface termination etc., especially under sensor operation conditions. To date, several reports on ab initio calculations for idealized CuO surfaces based on density functional theory are available, studying the interactions with H2O, NO2 [52], ethanol, 2-propanol, H2 [53], H2S [54], O2, formaldehyde [55] and H2 for Zn-doped CuO and Cu2O surfaces [56]. However, future experimental studies employing prototypical model systems with well-defined properties will be required to bridge the gap towards an atomistic understanding of gas sensing processes.

It should be noted that copper oxide-based gas sensors using alternative transduction concepts have also been reported. The direct measurement of the metal oxide work function by means of a Kelvin probe [57] was employed for CO2 detection with CuO nanoparticles [58–60]. Moreover, surface ionization readout was shown to be suitable for detecting dimethylamine, ethanol and ammonia using CuO nanowire electrodes [61].

3.2. Humidity Interference Effects

The influence of humidity on the gas sensing properties of metal oxide-based devices has been extensively investigated, particularly for tin oxide SnO2, but is still not comprehensively understood to date. Recent studies employing infrared spectroscopy under operando conditions have highlighted the complexity of the interactions between water vapor and SnO2 surfaces, discussing the possibility of multiple co-existing reaction pathways, dependencies on crystal facets and surface defects and temperature effects [62,63]. Unfortunately, considerably less information is available about the fundamental mechanisms governing humidity interference effects in copper oxide-based sensors. The gas sensing response of CuO-based devices was compared in dry and humid atmosphere in several literature reports on CO and H2S sensing: Thick film devices consisting of CuO nanoparticles showed a significantly reduced CO response in humid atmosphere at a working temperature of 150 °C, which was explained by a competition between CO and H2O molecules for chemisorbed oxygen reaction partners [64]. In contrast, a very low influence of humidity on the CO response of CuO nanowire-based devices operated at 325 °C was found [65]. Similarly, CO sensor devices relying on CuO nanotubes that were operated at 175 °C exhibited no marked humidity interference effects [25]. For the case of H2S sensing, the sensing properties of CuO nanosheet-based devices were studied in dry and humid atmosphere at temperatures from 250–325 °C [66,67], showing high robustness of the sensor responses to humidity with more pronounced humidity interference at low temperatures and high relative humidity levels. On the other hand, decreased H2S response in the presence of humidity was reported for sensors based on CuO nanoparticles (room temperature operation) [68] and CuO nanosheets (working temperature 240 °C) [69]. In contrast, enhanced H2S response was observed for CuO nanowire devices operated at 325 °C in humid air compared to dry atmosphere, whereas the response was almost constant for different relative humidity levels [70]. These at first sight contradictory examples illustrate that further advances in understanding humidity interference effects in copper
oxide-based devices will be required to deliberately control or eliminate the influence of humidity on the sensing properties.

4. Highly Sensitive Detection of Gaseous Molecules
4.1. Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are omnipresent in our daily lives, as they are produced from countless anthropogenic sources. Several VOCs have been identified as toxic and carcinogenic with multiple potential adverse health effects even at sub-ppb-level exposure. Apart from industrial process control, VOC sensors are particularly important for indoor air quality monitoring, which requires inexpensive real-time sensor solutions with high sensitivity and selectivity. The reader is referred to reference [71] for a detailed description of various VOCs and for a review on metal oxide-based sensors for their detection. Copper oxide nanomaterials have been extensively studied for realizing VOC sensor devices, which is summarized in Table 1. Most commonly, VOCs act as reducing gases that react with chemisorbed oxygen and consequently influence the space charge region at the metal oxide surface.
| Nanomaterial Morphology | Synthesis Method | Operation Temp. [°C] | Target VOC | VOC Gas Conc. [ppm] | Humid Lit. Atm. Ref. |
|-------------------------|-----------------|----------------------|------------|---------------------|-------------------|
| CuO nanosheets          | thermal decomposition | 100–440             | formaldehyde † | 0.01–1000          | ✓ [55] |
| CuO nanowires (Ru decor.) | thermal oxidation | 200–300             | acetone    | 0.025–0.2           | × [33] |
| CuO thin films          | magnetron sputtering | 50–350              | acetone    | 0.05–1.25           | ✓ [45] |
| CuO nanocubes oxidation of Cu2O nanocubes | 250–350          | formaldehyde †      |            | 0.05–3              | × [72] |
| CuO nanoflowers sol-gel method | 160–320      | formaldehyde †      |            | 0.05–1              | ✓ [73] |
| CuO nanoparticles sol-gel method | 180–290      | acetone †           |            | 0.1–10              | ✓ [74] |
| porous CuO (Pt doped) template-assisted | 200–275      | formaldehyde †      |            | 0.1–1.5             | ✓ [75] |
| CuO/Cu2O nanopatterns (Ag decor.) | thermal oxidation | 200–350             | acetone †  | 0.125–1000          | × [76] |
| CuO thin films (Cr doped) magnetron sputtering | 150–500      | acetone †           |            | 0.32–3.2            | ✓ [77] |
| facet-controlled Cu2O wet chemical | 100–250        | benzene/acetone     |            | 1–10                | × [24] |
| CuO nanowires thermal oxidation | 300           | benzene/toluene     |            | 1–10                | × [20] |
| CuO nanowires (NiO decor.) thermal oxidation | 300           | benzene/toluene     |            | 1–10                | × [30] |
| CuO nanoparticles (Zn doped) wet chemical | 100–350       | acetone †           |            | 1–20                | × [28] |
| CuO nanowires (Au decor.) thermal oxidation | 350           | benzene/toluene     |            | 1–50                | × [31] |
| CuO particles hydrothermal | 230            | decane †            |            | 1–100               | × [78] |
| hollow CuO nanofibers template-assisted | 140–260       | n-propanol †        |            | 1–100               | × [79] |
| CuO nanosheets hydrothermal | 100–300       | ethanol             |            | 1–100               | × [80] |
| CuO polyhedrons (PtO2 decor.) template-assisted | 100–220       | butanol †           |            | 1–500               | × [81] |
| CuO nanowires template-assisted | 130–260       | n-propanol †        |            | 1–500               | × [82] |
| CuO thin films magnetron sputtering dynamic | 200–360       | acetone †           |            | 2–500               | ✓ [83] |
| CuO nanowalls wet chemical oxidation | 140–340      | ethanol †           |            | 2–800               | ✓ [84] |
| wormlike CuO structures calcination of precursor | 150–400       | butanol †           |            | 3–30                | ✓ [85] |
| CuO nanowires thermal oxidation | 25–150        | xylene †            |            | 5–100               | × [86] |
| CuO nanoplatelets hydrothermal | 150–400       | ethanol             |            | 5–100               | ✓ [87] |
| CuO nanowires thermal oxidation | 100–260       | ethanol †           |            | 5–500               | × [88] |
| CuO octahedrons hydrothermal | 200            | formaldehyde †      |            | 5–500               | × [89] |
| CuO nanoparticles calcination of precursor | 150–300       | ethanol             |            | 5–1000              | × [90] |
| Cu2O octahedral nanoparticles wet chemical | 170–290       | benzene †           |            | 5–1000              | × [91] |
| porous CuO particles calcination of precursor | 230            | triethylamine †     |            | 5–1000              | × [92] |
| hollow Cu2O polyhedrons wet chemical | 130–310       | ethanol             |            | 5–4000              | × [93] |
| porous Cu2O spheres wet chemical | 160–300       | ethanol †           |            | 5–500               | × [94] |
| CuO/Cu2O nanocrystals hydrothermal dynamic | ethanol     | 10–100              |            | × [95] |
| CuO/Cu2O nanoparticle films chemical synthesis/annealing | 25–350       | ethanol             |            | 10–100              | × [96] |
Table 1. Cont.

| Nanomaterial Morphology                      | Synthesis Method | Operation Temp. [° C] | Target VOC | VOC Gas Conc. [ppm] | Humid Atm. | Lit. Ref. |
|-----------------------------------------------|------------------|-----------------------|------------|---------------------|------------|-----------|
| CuO nanoplatelets                             | hydrothermal     | 25–100                | 2-propanol | 10–100              | ×          | [95]      |
| single CuO nanowire                           | thermal oxidation| room temp.            | ethanol    | 10–100              | ✓          | [87]      |
| CuO nanosheets                                | hydrothermal     | 270–570               | ethanol †  | 10–200              | ×          | [96]      |
| CuO nanoflowers (In doped)                    | hydrothermal     | 95–180                | ethanol †  | 10–300              | ✓          | [97]      |
| dodecahedral Cu$_2$O nanocages                | wet chemical     | 150–300               | ethanol †  | 10–300              | ×          | [98]      |
| CuO and Cu$_2$O nanospheres                   | wet chemical     | 210                   | ethanol    | 10–800              | ×          | [99]      |
| CuO nanoflowers                               | microwave-assisted| 150–400               | ethyl-acetate † | 10–1000           | ✓          | [100]     |
| CuO nanosheets                                | calcination of precursor | 170–370              | ethanol †  | 10–2000             | ×          | [101]     |
| CuO nanoparticles                             | thermal oxidation| 200                   | ethanol †  | 12.5–500             | ×          | [11]      |
| CuO nanowires                                 | thermal oxidation| 150–300               | ethanol    | 25–1000              | ×          | [102]     |
| CuO nanoflowers                               | thermal oxidation| 300                   | ethanol †  | 25–1000              | ×          | [43]      |
| porous Cu$_2$O cubes                          | hydrothermal     | 250                   | ethanol    | 50–250               | ×          | [103]     |
| CuO thin film                                 | wet chemical     | 200–300               | 2-propanol † | 50–300             | ✓          | [104]     |
| porous CuO/Cu$_2$O cubes                      | calcination of precursor | 100–220              | acetone †  | 50–500               | ×          | [105]     |
| CuO hollow spheres                            | calcination of precursor | 200–400              | ethanol    | 50–1000              | ×          | [106]     |
| CuO/Cu$_2$O hollow spheres                    | template-assisted| 80–160                | ethanol    | 50–1000              | ×          | [107]     |
| CuO hollow spheres (Fe doped)                 | calcination of precursor | 200–400              | ethanol    | 50–1000              | ×          | [27]      |
| mesoporous CuO films                          | calcination of precursor | 300–400              | ethanol    | 100–1000             | ×          | [108]     |
4.2. Hydrogen Sulfide (H$_2$S)

The occurrence of hydrogen sulfide (H$_2$S) can be a result of bacterial decomposition of organic matter in anaerobic environments including natural sources or originate from a large variety of industrial processes. This corrosive and toxic gas is characterized by a ‘rotten egg’ smell at an odor threshold in the low ppb range while at higher concentrations it can paralyze the olfactory nerves. Due to the high toxicity, H$_2$S exposure can lead to headache, nausea, unconsciousness and suffocation, whereas increased odds ratio for central nervous and respiratory symptoms can be a result of long-term ppb-level exposure. With suggested exposure limits in the low ppm range, stringent sensitivity requirements are placed on H$_2$S sensors that have triggered considerable efforts for developing suitable metal oxide-based devices [109]. Copper oxide nanomaterials have shown excellent sensitivity (and often selectivity) to H$_2$S with low detection limits of 1 ppb and below [68,110]. Further literature reports on H$_2$S sensors employing copper oxide nanomaterials are summarized in Table 2. At elevated temperatures the detection mechanism of H$_2$S is attributed to reactions with chemisorbed oxygen to form SO$_2$ and H$_2$O, whereas at low temperatures the formation of CuS is dominant which can lead to irreversible changes of the nanomaterial structure. The latter was further substantiated by near-edge X-ray absorption fine structure spectroscopy in combination with X-ray microscopy [111]. CuS formation can result in low-resistance percolation pathways leading to a dramatic increase in sensor conductivity, which was demonstrated for CuO nanoparticle-based sensing layers [112] and CuO nanowire-based devices [19]. The phase transition to CuS can be utilized as alternative transduction principle for operating copper oxide-based sensors as dosimeter-type devices that assess the product of H$_2$S concentration and exposure time [113–115]. Detailed analysis of the sensor response has led to further insights in percolation and diffusion processes [113,114] and it will be an interesting direction for future studies to assess if similar phase transition-based transduction concepts can be employed for other target gases or nanomaterial systems.

Table 2. A summary of sensing hydrogen sulfide (H$_2$S) with copper oxide-based devices.

| Nanomaterial Morphology | Synthesis Operation | Humid Conc. [ppm] | Lit. Ref. |
|-------------------------|---------------------|-------------------|----------|
| CuO nanoparticles       | hydrothermal        | 0.0001–1          | [68]     |
| CuO nanowires           | thermal oxidation   | 0.01–0.5          | [70]     |
| pores CuO nanobelts     | calcination of precursor | 0.01–0.5          | [116]    |
| CuO nanosheets          | hydrothermal        | 0.01–1.2          | [49]     |
| CuO nanoparticles       | hydrothermal        | 0.05–1.2          | [119]    |
| CuO nanospindles        | hydrothermal/annealing | 0.1–1             | [121]    |
| CuO nanowires (Fe$_2$O$_3$ decor.) | thermal oxidation | 0.1–10            | [112]    |
| CuO thin films          | thermal oxidation   | 0.1–10            | [123]    |
| CuO nanobelts           | sonochemical        | 0.1–10            | [124]    |
| CuO nanoflowers (Pt doping) | hydrothermal       | 0.1–10            | [125]    |
| CuO nanofilms           | hydrothermal        | 0.1–20            | [126]    |
| CuO nanoflowers (Pd doped) | hydrothermal       | 0.1–50            | [127]    |
| CuO colloidal particles | oxidation of CuO particles | 0.1–100           | [119]    |
| CuO nanosheets          | hydrothermal        | 0.2–5             | [67]     |
| CuO nanowires           | calcification of precursor | 0.2–10            | [66]     |
| single CuO nanowire     | thermal oxidation   | 0.5–10            | [15]     |
| CuO nanoparticles       | inkjet printing     | 0.5–10            | [115]    |
| CuO nanoparticles       | hydrothermal        | 1–10              | [129]    |
| CuO hollow spheres      | calcification of precursor | 1–10              | [130]    |
| CuO nanofibers          | calcification of precursor | 1–10              | [107]    |
| CuO nanoparticles       | inkjet printing     | 3–15              | [39]     |
| porous CuO nanobelts    | hydrothermal        | 5–5000            | [132]    |
| CuO nanorods (Pd decor.) | thermal oxidation   | 300–200           | [133]    |

* reduced graphene oxide.
4.3. Carbon Monoxide (CO)

Carbon monoxide (CO) is a major environmental pollutant resulting from incomplete fuel combustion, occurring for example in industrial processes, automotive emissions and fuel-based household appliances. It is an odorless, colorless and toxic gas with a strong affinity to bind with hemoglobin in human blood, reducing the ability of oxygen transport within the body. Exposure to a concentration of 10 ppm CO is considered acceptable within a time of 8 h, whereas higher concentrations can lead to symptoms such as headache, confusion, unconsciousness and death with a significant number of fatalities from CO poisoning constantly occurring worldwide. Consequently, the development of high-performance CO sensors has been an active field of research for decades with metal oxide semiconductors being among the most widely studied materials for the realization of chemoresistive sensor devices [134]. A summary of literature reports on CO sensor devices based on copper oxide nanomaterials is shown in Table 3. The sensing mechanism in air is typically explained by a reaction with chemisorbed oxygen to form CO$_2$, leading to a modulation of the surface space charge region.

| Nanomaterial Morphology | Synthesis Method | Operation Temp. °C | CO Gas Conc. [ppm] | Humid Atm. | Lit. Ref. |
|-------------------------|-----------------|---------------------|--------------------|------------|----------|
| CuO nanowires           | thermal oxidation | 300                | 1–10               | ×          | [20]     |
| CuO nanowires (NiO decor.) | thermal oxidation | 300                | 1–10               | ×          | [30]     |
| CuO nanowires           | thermal oxidation | 325                | 1–30               | ×          | [40]     |
| CuO nanowires (Au decor.) | thermal oxidation | 200–400            | 1–50               | ×          | [31]     |
| octahedral Cu$_2$O particles | wet chemical    | 50–120             | 1–800              | ×          | [22]     |
| CuO nanofibers          | calcination of precursor | 300          | 3–150              | ×          | [135]    |
| CuO powder              | plasma spraying  | 100–350            | 5–500              | ×          | [136]    |
| CuO nanowires           | thermal oxidation | 25–350            | 5–1200             | ×          | [137]    |
| CuO nanoplatelets       | hydrothermal     | room temp.         | 10–100             | ✓          | [138]    |
| CuO nanoparticles       | wet chemical     | 150                | 10–100             | ✓          | [64]     |
| CuO nanowires           | thermal oxidation | 300                | 10–100             | ×          | [19]     |
| CuO nanowires           | thermal oxidation | 300–370           | 10–100             | ×          | [139]    |
| single CuO nanowire     | thermal oxidation | 350                | 10–100             | ×          | [17]     |
| Cu$_2$O/Au/CuO nanostructures | wet chemical | 200                | 10–500             | ×          | [140]    |
| CuO nanowires (Pt decor.) | thermal oxidation | 200–250           | 15–45              | ×          | [35]     |
| CuO nanowires           | thermal oxidation | 300–350           | 25–150             | ✓          | [65]     |
| CuO nanolayer (Al doped) | wet chemical     | 70–220             | 35–1250            | ✓          | [141]    |
| single CuO nanowire     | thermal oxidation | 350                | 50–150             | ✓          | [142]    |
| CuO nanocubes           | oxidation of Cu$_2$O nanocubes | 100–300        | 50–1000            | ×          | [25]     |
| CuO nanotubes           | oxidation of Cu nanowires | 100–300       | 50–1000            | ✓          | [25]     |
| single CuO nanowire (Pd decor.) | thermal oxidation | 350                | 100–300            | ✓          | [143]    |
| CuO nanowires           | thermal oxidation | 30–400             | 100–1000           | ×          | [144]    |
| CuO nanoparticles       | hydrothermal     | 150–400            | 200–1000           | ×          | [145]    |

4.4. Carbon Dioxide (CO$_2$)

Despite active research efforts for several decades, the realization of miniaturized sensor solutions for detecting carbon dioxide (CO$_2$) based on solid-state materials has remained challenging. Current technologies often rely on optical sensing principles, which comes at the expense of elevated cost and power consumption combined with large sensor system size. Different types of solid-state electro-chemical sensors including resistive sensors based on metal oxide semiconductors have been developed as potential low-cost alternatives [146]. Copper oxide nanomaterials have shown highly promising prospects in this regard: In addition to perovskite-based nanocomposites (e.g., Ag-doped CuO/BaTiO$_3$ heterostructures: [146,147] and references therein) and CuO/CuFe$_2$O$_4$ nanocomposites [148], CuO nanoparticle-based sensors relying on work function readout were found to be capable of detecting CO$_2$ in humid atmosphere at low working temperatures down to room temperature in the application-relevant concentration range (400–4000 ppm) [58–60]. Moreover, resistive gas sensors based on CuO nanoparticles with ZnO$_2$ additives [149] and Au-decorated CuO thin films [150] have been reported, showing similar capabilities with high practical importance. Hence, future developments and improvements of copper oxide
nanomaterial-based sensors could result in miniaturized low-cost CO₂ sensor solutions that find widespread real-world applications with significant industrial relevance. Examples include next-generation greenhouse gas sensors for monitoring industrial CO₂ emissions and outdoor air quality [146], and indoor air quality control in smart homes/Internet of Things applications [151]. Furthermore, the development of portable low-cost CO₂ sensors would have significant impacts on the agriculture and food industry, as they could be integrated into intelligent packaging to enhance food quality and safety [152].

4.5. Hydrogen (H₂)

With the emergence of the hydrogen economy relying on this abundant element for sustainable fuels and energy storage, the detection of hydrogen (H₂) gas has reached an unprecedented level of importance. H₂ leakage detection is required in related applications due to the flammable and explosive nature of this gas in a wide concentration range. A large number of metal oxide semiconductors have been successfully employed for realizing chemoresistive sensor devices for detecting this reducing gas [153]. In Table 4, a summary of literature reports on H₂ sensor devices based on copper oxide nanomaterials is presented. Resistance changes during H₂ exposure are attributed to reactions with chemisorbed oxygen to form H₂O molecules, influencing the charge carrier density close to the surface. Alternative transduction concepts have been proposed, including metallic percolation pathways in CuO nanowire-based sensors [154] and changes in the thermal properties of microhotplate devices [39]. Monitoring changes in the thermal properties of micromachined sensing structures constitutes a powerful strategy for future gas selectivity improvements, which can also be applied for other sensing materials.

| Nanomaterial Morphology | Synthesis Method | Operation Temp. [°C] | H₂ Gas Conc. [ppm] | Humid Atm. | Lit. Ref. |
|-------------------------|------------------|----------------------|-------------------|-----------|----------|
| CuO nanowires           | thermal oxidation| 300                  | 1–10              | ×         | [20]     |
| CuO nanowires (NiO decor.) | thermal oxidation | 300                  | 1–10              | ×         | [30]     |
| CuO/Cu₂O nanocrystals (Zn doped) | wet chemical/annealing | 100–450              | 10–100            | ✓         | [56]     |
| urchin-like CuO particles | microwave-assisted | 150–400              | 10–500            | ×         | [14]     |
| CuO nanoparticles       | inkjet printing  | 400                  | 40–3000           | ×         | [39]     |
| CuO hollow spheres      | calcination of precursor | 200–400              | 50–1000           | ×         | [107]    |
| CuO nanowires           | thermal oxidation| 275–400              | 100               | ×         | [154]    |
| mesoporous CuO films    | calcination of precursor | 200–400              | 100–1000          | ×         | [108]    |

4.6. Nitrogen Dioxide (NO₂)

Nitrogen dioxide (NO₂) contributes significantly to environmental pollution, being linked with smog and acid rain and adverse human health effects. Typically suggested exposure limits lie in the low ppm range, but continuous exposure at even lower levels can lead to respiratory symptoms and lung damage, especially in patients with preconditions. Anthropogenic production of nitrogen oxides is primarily related to fuel combustion, particularly from automotive emissions and industrial sources. Considering the current global status of air quality and pollution, there is a high and continuously increasing demand for NO₂ sensor devices, which can be realized with various metal oxide semiconductors [155]. Copper oxide nanomaterials often show excellent sensitivity to NO₂, as very low concentrations down to 1 ppb could be detected even for room temperature sensor operation [52]. Further literature reports on copper oxide-based NO₂ sensors are summarized in Table 5. NO₂ is a strongly oxidizing gas with high electron affinity that affects the space charge region at the metal oxide surface via charge transfer upon adsorption, whereas alternative processes can occur at elevated temperatures [156].
Table 5. A summary of sensing nitrogen dioxide (NO\textsubscript{2}) with copper oxide-based devices.

| Nanomaterial Morphology | Synthesis Method | Operation Temp. \(^\circ\)C | NO\textsubscript{2} Gas Conc. [ppm] | Humid Atm. | Lit. Ref. |
|-------------------------|------------------|-----------------------------|-------------------------------|-------------|-----------|
| Cu\textsubscript{2}O/CuO nanoflowers | wet chemical | room temp. | 0.001–50 | ✓ | [52] |
| Cu\textsubscript{2}O/CuO octahedrons | calcination of precursor | room temp. | 0.01–1 | ✓ | [157] |
| facet-controlled Cu\textsubscript{2}O | wet chemical | 50–250 | 0.1–5 | × | [24] |
| CuO nanoparticles | inkjet printing | 120–500 | 0.2–5 | ✓ | [156] |
| CuO nanowires | thermal oxidation | 325 | 0.5–1.5 | × | [40] |
| Cu\textsubscript{2}O nanoparticles (Pt decor.) | thermal oxidation | 300 | 1–5 | × | [158] |
| CuO nanoparticles (TiO\textsubscript{2} decor.) | thermal oxidation | 300 | 1–10 | × | [29] |
| CuO nanowires (Co\textsubscript{3}O\textsubscript{4} decor.) | thermal oxidation | 300 | 1–10 | × | [30] |
| porous CuO nanocubes | calcination of precursor | 250–350 | 1–10 | × | [159] |
| CuO nanofibers | calcination of precursor | 300 | 1–20 | × | [135] |
| CuO nanowires (Au decor.) | thermal oxidation | 200–400 | 1–50 | × | [31] |
| CuO nanowires (Cr decor.) | thermal oxidation | 200–400 | 1–100 | × | [139] |
| CuO nanocubes | thermal oxidation | 100–250 | 1–100 | × | [160] |
| CuO thin films (La\textsubscript{2}O\textsubscript{3} doped) | spray pyrolysis | room temp. | 1.5 | ✓ | [161] |
| Cu\textsubscript{2}O octahedral nanoparticles | wet chemical | 50 | 5–50 | × | [90] |
| CuO nanoparticles | hydrothermal | 50–150 | 5–50 | × | [162] |
| CuO nanostructures (Cr decor.) | wet chemical | 25–400 | 5–100 | × | [163] |
| CuO nanoplatelets | hydrothermal | 25–100 | 10–100 | ✓ | [95] |

4.7. Other Target Molecules

Highly sensitive devices for ozone O\textsubscript{3} detection at concentrations of 50–300 ppb in dry air were shown using CuO thin films realized by reactive magnetron sputtering combined with annealing [49]. Similarly, CuO nanowire-based devices synthesized by thermal oxidation were able to detect 50–300 ppb O\textsubscript{3} at 50% relative humidity [164].

Sulfur dioxide SO\textsubscript{2} sensing at a concentration range of 1–10 ppm in dry air was reported using CuO nanowires [20], CuO nanowires decorated with TiO\textsubscript{2} [29], CuO nanowires decorated with Co\textsubscript{3}O\textsubscript{4} and NiO [30] and CuO nanofilms [129].

Ammonia NH\textsubscript{3} detection with single CuO nanowire devices was shown at concentrations of 1–10 ppm [15] and 1% [165] in dry air. Enhanced sensor performance was demonstrated by doping and nanoparticle decoration—in particular, Cr doping of CuO nanoboats (100–600 ppm concentration range) [166], CuO nanowires decorated with SnO\textsubscript{2} (1% concentration) [167] and CuO nanofibers decorated with In\textsubscript{2}O\textsubscript{3} (0.3–100 ppm concentration range) [131].

Methane CH\textsubscript{4} was detected with Cu\textsubscript{2}O thin films at concentrations of 0.3–2.5% [168].

5. Conclusions

To summarize, copper oxide nanomaterials have been widely applied to achieve high-performance gas sensor devices for the detection of the most common hazardous gases and environmental pollutants. In many cases excellent sensitivity with detection limits down to ppb-level concentrations or below could be accomplished. As for other metal oxide-based sensors, the gas selectivity of copper oxide-based devices has, however, remained limited despite some promising reports on doping and nanoparticle decoration, which often prevents the practical use in real-world applications. In this regard, a way forward would be to aim for further advances in realizing smart sensor systems, employing a large number of sensor devices and relying on pattern recognition techniques, machine learning, neural networks and artificial intelligence for gas and odor classification [169,170]. For example, unsupervised principal component analysis has been successfully applied for analyzing resistance transients of CuO thin film devices for distinguishing between four different VOCs (ethanol, methanol, acetone and 2-propanol) [105]. Another option would be the use of gas-selective pre-filters, for instance, to minimize the influence of H\textsubscript{2}S or SO\textsubscript{2} exposure.

In addition to further technological developments, several fundamental scientific questions need to be addressed, particularly those related to the underlying mechanisms of humidity and target gas interactions with copper oxide surfaces, and the role of additives...
for sensor functionalization. For this purpose, experimental techniques that allow for sensor material characterization under environmental conditions resembling sensor operation will play a crucial role, particularly infrared spectroscopy performed in operando [26,62,63]. In situ experiments of functional chemoresistive sensor devices inside environmental transmission electron microscopes [171,172] could provide new insights in changes of morphology and/or chemical composition of the employed nanostructures induced by exposure to reactive gas species at elevated temperatures. Moreover, in situ X-ray absorption spectroscopy [173] and near-ambient pressure X-ray photoelectron spectroscopy [174] have been successfully employed for correlating chemoresistive sensor responses with changes in the oxidation state of copper oxide nanomaterials. It can be expected that future technology and fundamental science advances will cross-fertilize to enable the rational design of copper oxide-based nanomaterials for chemoresistive sensors with improved performance.

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