Gas Responsive Nanoswitch: Copper Oxide Composite for Highly Selective H₂S Detection

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A nanocomposite material based on copper(II) oxide (CuO) and its utilization as a highly selective and stable gas-responsive electrical switch for hydrogen sulphide (H₂S) detection is presented. The material can be applied as a sensitive layer for H₂S monitoring, e.g., in biogas gas plants. CuO nanoparticles are embedded in a rigid, nanoporous silica (SiO₂) matrix to form an electrical percolating network of low conducting CuO and, upon exposure to H₂S, highly conducting copper(II) sulphide (CuS) particles. By steric hindrance due to the silica pore walls, the structure of the network is maintained even though the reversible reaction of CuO to CuS is accompanied by significant volume expansion. The conducting state of the percolating network can be controlled by a variety of parameters, such as temperature, electrode layout, and network topology of the porous silica matrix. The latter means that this new type of sensing material has a structure-encoded detection limit for H₂S, which offers new application opportunities. The fabrication process of the mesoporous CuO@SiO₂ composite as well as the sensor design and characteristics are described in detail. In addition, theoretical modeling of the percolation effect by Monte-Carlo simulations yields deeper insight into the underlying percolation mechanism and the observed response characteristics.

1. Introduction

Three key aspects, the so-called “3S,” are crucial for the design of gas sensors, and hence gas sensing materials: the selectivity and sensitivity for the target species as well as the chemical and signal stability. Sensors based on chemical processes offer lower signal stability. Sensors based on chemical processes offer lower sensitivity and selectivity toward H₂S,[9] reacts with hydrogen sulphide to form copper(II) sulphide (CuS). CuS is a highly degenerate p-type semiconductor with close to metallic conductivity (as summarized in Table 1). Due to the exothermic nature of the reaction, the production of CuS is favored at temperatures up to 160 °C and regeneration to copper oxide in the presence of oxygen is possible above this temperature, e.g., in this work 350 °C is utilized (Equations (1) and (2))

\[
\text{CuO} + \text{H}_2\text{S} \rightarrow \text{CuS} + \text{H}_2\text{O} \quad \Delta H^\circ = -27.4 \frac{\text{kJ}}{\text{mol}} \quad (1)
\]

\[
\text{CuS} + 1.5 \text{O}_2 \rightarrow \text{CuO} + \text{SO}_2 \quad \Delta H^\circ = -96.6 \frac{\text{kJ}}{\text{mol}} \quad (2)
\]

The large conductivity variation accompanied by the formation of CuS was already utilized to build CuO thick film sensing layers.[14-16] The described (localized) chemical transformation leads to a distinct switching transition in the generated electrical signal; significantly different from the signal shape observed for adsorption type sensors. This is due to the formation of electrically conducting paths by the interconnection of islands of CuS on the CuO films with increasing amount of absorbed H₂S. Theoretically, this can be described by means of a so-called percolation model.
For that purpose the sites of a mathematical grid are statistically connected with “conducting” bonds (CuS) with a probability $p$, the remaining $q = 1 - p$ bonds are not connected (CuO) and are considered “insulating.” The dimensionality of the grid is typically fitted to the dimensionality of the problem, e.g., for a film-type percolation a 2D grid can be utilized. To achieve a conducting path from one side of the grid to another, the occupation probability $p$ has to reach a specific threshold value $p_c$, the so-called percolation threshold, which is characteristic for the dimensionality and the type of the percolation. In the presented example (Figure 1), $p_c$ is 0.5, below this value the conductance remains zero. Thus, in the model, a strong increase (switching) in conductance can be observed reaching $p_c$. A more detailed description of the basics of percolation theory can be found elsewhere.[17–21]

The theoretically described switching transition is the reason for the observed signal shape described earlier. Due to this shape, it is possible to build a H$_2$S gas responsive switching layer based solely on CuO. However, the reproducibility is poor, since there is a large volume change accompanied with the conversion of CuO to CuS (densities: CuO 6.31 g mL$^{-1}$, CuS 4.76 g mL$^{-1}$).[11] Repeated regeneration of the layer after sensing leads to the formation of cracks and, thereby, influences the percolation threshold value, resulting in a nonstable sensor signal after a few cycles.

We have recently made a brief account on a novel nanocomposite of CuO particles embedded in a rigid, porous silica (SiO$_2$) matrix.[22] Here we explore this concept in more detail, including in-depth theoretical discussion of the underlying percolation mechanism. By utilizing a rigid host, it is possible to stabilize the morphology/nanstructure during sensing and regeneration of the switching layer and to achieve long-term stability over 900 cycles. Furthermore, we present a theoretical description of the experimental system, which will evidence the postulated percolation process and allows us in future to fit the material design to a variety of applications.

### 2. Results and Discussion

#### 2.1. Composition Design of Regenerable, Percolating CuO Networks

The formation of highly conducting copper sulphide from copper oxide is accompanied by a large volume expansion factor of $\approx$1.59, which typically leads to mechanical stress within the structure/material. Subsequently, the morphology of a dense copper oxide nanoparticle film cannot be maintained during a reaction and regeneration process (CuO $\Rightarrow$ CuS) with H$_2$S, which leads to nonreproducible electrical behavior (Figure 2, left). The here presented approach aims for the stabilization of the percolation network topology by embedding the CuO nanoparticles in a rigid, porous silica structure matrix (Figure 2, right). Steric hindrance directs the swelling of the CuS particles during reaction with H$_2$S; the void volume in between the particles compensates for the volume expansion. To minimize the influence of diffusion effects of sulfur in the CuO/CuS particles on the evolution of the electrical signal, particles in the nanometer regime are utilized. Due to the steric hindrance by the rigid silica, particle agglomeration is suppressed inside the pore system. (Outside the pore system, nanoparticle agglomeration is still possible, but does not affect the percolation parameters.) In addition, the symmetry of the pore arrangement introduces another degree of freedom for the tuning of the percolation threshold.

Ordered mesoporous silica material, as the here utilized KIT-6 type, fulfills the specified demands explained above and in addition, the synthesis procedures are easy and highly reproducible. Copper oxide nanoparticles are introduced into the pore system of the silica via a wet chemical route (Figure 3). First copper nitrate is deposited into the pores by the two solvents impregnation method.[24] Subsequent drying and thermal conversion lead to the desired CuO/SiO$_2$ composite material. In order to vary the amount of CuO inside the pores, the procedure can be repeated several times.

Transmission electron microscopy (TEM) studies of the resulting powder reveal the porous nature of the silica matrix and, in addition, CuO nanocrystals can be identified inside the silica matrix by high resolution transmission electron microscopy (HRTEM) (Figure 4).

### Table 1. Comparison of different resistive type H$_2$S sensors found in literature and a commercially available electrochemical H$_2$S sensor.

| Ref. | Sensing material | Type      | Detection limit | Sensitivity | Operating temp. [°C] | Comment                                                                 |
|------|------------------|-----------|-----------------|-------------|----------------------|--------------------------------------------------------------------------|
| [3]  | Mesoporous WO$_3$| resistive | 250 ppb         | 325         | 250                  | Cross-sensitive to methane, methanol, ethanol, acetone, ammonia, and acetaldehyde |
| [4]  | Pure or In-doped ZnO | resistive | 500 ppb         | 17–90       | RT-250               | Cross-sensitive to ammonia                                               |
| [5]  | CuO-SnO$_2$      | resistive | 20 ppb          | 88          | 300                  | No cross-sensitivity to ammonia                                           |
| [6]  | Cu$_2$O$_2$/SWCNT| resistive | 5 ppm (expected to be lower) | 5 | 250                  | Cross-sensitive to ammonia                                               |
| [7]  | Cu$_2$O-graphene  | resistive | 1 ppb           | 0.35        | RT                   | Cross-sensitive to ammonia                                               |
| [8]  | N.A. electrochemical | 500 ppb | N.A. max. 50    |             |                      | Commercial product, reliable, low power consumption, limited temp. range |

### Table 2. Specific conductivity and density of CuO and CuS.

| Material | Spec. conductivity [S cm$^{-1}$] | Density [g mL$^{-1}$] | Molar mass [g mol$^{-1}$] |
|----------|---------------------------------|-----------------------|---------------------------|
| CuO      | $1.5 \times 10^{-5}$[10]        | 6.31[11]              | 79.55                     |
| CuS      | 0.37[12]                        | 4.76[11]              | 95.61                     |
The formation of the desired monoclinic Tenorite (JCPDS card number 05-0661) is further confirmed by powder X-ray diffraction (PXRD) (Figure 5a). As can be deduced from the relatively narrow peaks, the sample contains crystallites larger than the actual pore diameter (detailed analysis can be found in the Supporting Information), which suggests that there is some material deposited outside the pore system. However, this is a characteristic of the chosen synthesis method and does not affect the actual sensing concept. In fact, some conducting material in between the composite grains is needed for proper electrical contact formation between the grains.

To analyze the formation process of CuO inside the pore network of the silica matrix, two complementary methods are applied.

i) KIT-6 silica with a $Ia\bar{3}d$ space group shows a specific low angle X-ray pattern (Figure 5b), which is caused by the diffraction in the periodically arranged pore system of the amorphous silica. With each subsequent impregnation and thermal conversion, the intensity of the reflexes in the low angle X-ray pattern decreases, indicating a gradual filling of the pores due to lowered scattering contrast.[25]

ii) The observations from X-ray diffraction measurements are consistent with the results of N$_2$ physisorption analysis, which can be used to quantify the specific surface area and pore volume of the porous structure matrix at different stages of the synthesis process (Table 3). Both, Brunauer–Emmet–Teller (BET) surface area as well as total pore volume, decrease with each impregnation and conversion cycle. Thereby it can be concluded, that the pores of the stabilizing matrix are gradually filled by CuO grains. Detailed analysis of the physisorption results is available in the Supporting Information.

The amount of deposited CuO was determined gravimetrically to 62 wt% after the 4th impregnation/conversion cycle by dissolving the copper(II) oxide (from the composite material) in 2 m H$_2$SO$_4$ and reprecipitating it as CuO.

With the described method, a number of composite samples with varying CuO content were prepared. The CuO loading of the samples presented in the following is 62 wt%, since this loading was shown to lead to the desired gas induced percolation effect (see Section 2.2).

2.2. Gas-Induced Electrical Switching

The CuO/silica nanocomposite material is the basis for gas-induced electrical switching. For the investigation of the gas...
responsive behavior of the CuO/silica nanocomposite material (wt% of CuO is 62%), the composite material was deposited on interdigitated platinum electrodes on a ceramic substrate comprising a heating element. The so formed layers cover the electrodes homogeneously (Figure S11, Supporting Information). Based on SEM images and the amount of material deposited, the thickness is estimated to \( \approx 10–15 \) \( \mu m \). Due to the size of the silica host particles, the surface roughness is relatively high. If the layer elements bridging the electrodes can be considered 3D, as it is the case here, the details of the layer morphology can be ignored (see Section 2.3. Theoretical aspects). Due to the accumulating nature of the sensor mechanism—the amount of CuS formed depends on the absolute amount of H\(_2\)S reaching the layer—the absolute amount of composite material must be kept constant. With this setup, the conductance of the material can be determined at different temperatures and under varying gas atmosphere. From earlier studies, it is known, that a temperature of 160 °C specifically promotes the reaction of CuO to CuS under the presence of H\(_2\)S.[15,26,27] Therefore, the composite materials reaction with H\(_2\)S is studied at this temperature, as well. Regeneration (reaction from CuS to CuO) can be achieved at a temperature of 350 °C, even in an H\(_2\)S atmosphere.

After a temperature treatment of 30 min at 350 °C in air, the as-synthesized material is in an electrically insulating state, which is characterized by a film conductance lower than \( 10^{-8} \) S at 160 °C (Figure 6, blue area). This is due to a combination of the low conductivity of \( 1.5 \times 10^{-5} \) S cm\(^{-1}\) of the p-type semiconducting CuO nanoparticles and the low particle loading of the pores. It is assumed, that the particles are not forming completely interconnected clusters inside the pores of the structure matrix. This effect is intended since it is caused by the void volume, which was introduced to compensate for the volume expansion caused by the H\(_2\)S reaction.

When the exposure to 10 ppm H\(_2\)S in synthetic air starts, two effects can be observed (blue shaded and yellow dashed area in Figure 6).

i) As an immediate reaction, the conductance decreases due to oxidation of sulfur and recombination of the electrons with the p-type semiconducting CuO,[15,26] as it is expected for a chemiresistor. This region is therefore referred to as chemiresistive regime. Even though we will not discuss the effect further, this shows that there is already an (weakly) interconnected network of CuO particles, which can be explained by the statistic nature of the impregnation process.

ii) After 3.5 min, a steep, nonlinear increase in conductance over more than 7 orders of magnitude can be observed, in the following referred to as conducting or percolating regime. Opposed to effect (i), this cannot be explained by a catalytic surface process. As it is known for film type structures, this is rather caused by the formation of CuS, which is a strongly degenerated p-type semiconductor with close to metallic conductivity (0.37 S cm\(^{-1}\)).[14,15,27] The number of CuS particles increases as a function of the absolute absorbed amount of H\(_2\)S. It is assumed, that at a certain threshold concentration,
conducting pathways of CuS particles throughout the pore structure of the composite material are responsible for the observed conductance increase. In the next section, it will be shown, that the observed behavior can be explained by means of the so-called percolation theory.[18,19]

Figure 6 and Figure S10 in the Supporting Information introduce the concept of the switching time $t_s$, defined as the time span from the start of H$_2$S exposure to the formation of the first conducting pathways, which is correlated to the gas concentration, i.e., gas concentrations can be determined by measuring the switching time rather than the absolute value of electrical conductance. In addition, this time span is of some importance for the theoretical description, as will be shown below.

Comparison of the chemical induced switching of the here presented composite material with thin-film CuO systems reveals similar switching times in the order of 5 min and a comparable shape of the conductance transient under H$_2$S exposure.[26,27] The conductance increase of the thin film materials, however, is only about 5 orders of magnitude, which reflects essentially the difference of the conductivity values known for CuO and CuS. The here presented material shows a change of 7 orders of magnitude, which is mainly due to a lower conductance value in the low conducting state. This can be explained by the compositional design. As was described earlier, it is assumed that the relatively low CuO loading of the porous system prohibits the formation of a continuous CuO pathway throughout the porous grains. Therefore, two effects are responsible for the observed switching behavior, which are the formation of the highly conducting CuS phase and the related volume expansion due to the 0.63 times lower molar density of the CuS compared to CuO, as schematically shown in Figure 7.

2.3. Theoretical Aspects

For a more detailed analysis of the observed switching type transition, the electrical response of the composite material is modeled by means of percolation theory. The composite material of insulating CuO and conducting CuS nanoparticles inside the 3D pore structure of the silica matrix forms a combined site and bond percolating system. However, for simplicity, the system was modeled via a simple cubic lattice where all sites (vertices) are occupied (conducting) and the bonds interconnecting the sites can either be connected or not connected (bond percolation), representing CuS or CuO nanoparticles, respectively. For a more detailed description of the modeling, refer to the Experimental Section. To reflect the experimental conditions, finite lattice geometries were chosen, resulting in

Table 3. Surface area, total pore volume, and crystallite size of the pristine KIT-6 silica, the CuO/silica composite materials, and the resulting KIT-6 matrices after etching with H$_2$SO$_4$.

|                       | BET surface area [m$^2$ g$^{-1}$] | Total pore volume [mL g$^{-1}$] | Crystallite size [nm] |
|-----------------------|---------------------------------|---------------------------------|----------------------|
| CuO/silica composite materials |                                 |                                 |                      |
| KIT-6 (pristine)       | 480                             | 1.44                            | –                    |
| 1st impregnation       | 280                             | 0.87                            | 22                   |
| 2nd impregnation       | 200                             | 0.62                            | 23                   |
| 3rd impregnation       | 150                             | 0.48                            | 24                   |
| 4th impregnation       | 120                             | 0.39                            | 25                   |
| Silica after etching with H$_2$O$_4$ |                               |                                 |                      |
| KIT-6 (after H$_2$SO$_4$) | 480                             | 1.46                            | –                    |
| 1st impregnation       | 440                             | 1.40                            | –                    |
| 2nd impregnation       | 430                             | 1.38                            | –                    |
| 3rd impregnation       | 420                             | 1.36                            | –                    |
| 4th impregnation       | 400                             | 1.32                            | –                    |
The average threshold value $S$ can already appear at bond occupation paths from one side of the lattice to the other and such clustering of conducting (CuS) pathways, it also exhibits a discontinuous, step-type shape.\[20\] Since the increase is due to the formation of conducting (CuS) pathways, it also exhibits a discontinuous, step-type shape.\[20\]

Therefore, the total conductance $\Sigma(p, L^D)$ increases with increasing connection probability $p$. Since the increase is due to the formation of conducting (CuS) pathways, it also exhibits a discontinuous, step-type shape.\[20\]

In the finite system, conduction pathways bridging two sides of the lattice appear at $L^D = \xi$, i.e., percolation phase transition can be reached by increasing $\xi$ or decreasing $L^D$. Since $L^D < \infty$, finite clusters of connected sites are capable to form conducting paths from one side of the lattice to the other and such clusters can already appear at bond occupation $p$ lower than $P_c$, the percolation threshold of the infinite system.\[17\] In addition, it is possible to have more than one lattice spanning cluster,\[28\] so only an average threshold value $P_c = \int p \cdot f(p)dp$ can be calculated, with the distribution function $f(p)$,\[20\]

For an infinite system this distribution is a delta function: $f(p_c) = \delta(p_c - p_c^*)$. The average threshold value $P_c$ is heavily influenced by the aspect ratio of the system (Figure 8a), which is important for the later sensor design. As can be seen in the figure, $p_c$ of a $12 \times 12 \times 12$ cube is distributed around the theoretical value of $P_c = 0.2488$ for bond percolation on an infinite 3D single cubic grid.\[17\] Increasing the aspect ratio of the system, i.e., from cubic to a square cuboid, leads to a shift of the distribution of $p_c$ toward lower values. In other words, the percolation threshold and thereby the detection limit of the sensing layer can be manipulated by, e.g., variation in electrode distance.

Since the occupation probability $p$ cannot be directly observed in an experiment, a time-dependent conductance $\Sigma(t)$ will be deduced from Equation (3) (constant lattice size $L$)

$$
\Sigma(t) = \begin{cases} \text{const,} & t < t_c \\ A(p(t) - p_c)^\mu, & t \geq t_c \end{cases} 
$$

with the time span $t_c$ for reaching percolation threshold, the time-dependent occupation probability $p(t)$ and $A$ being a proportional constant, which depends on the size of the system and the conductivity of the two phases (CuO; CuS). In an experiment, the amount of occupied bonds is gradually increased, which can be described by two independent probabilities $q$ and $r$ for fixed time steps. The value of $q$ describes the probability, that a bond gets conductive (CuO $\rightarrow$ CuS) and $r$, that a bond gets insulating (CuS $\rightarrow$ CuO) in one time step. For $p(t)$, zeroth order behavior is assumed, with some rate constant $k$

$$
p(t) = k \cdot t
$$

To validate the model for $\Sigma(t)$, the function was tested with some simulated data. Figure 8b shows $\Sigma(t)$ for $n = 48$ samples ($12,000 \times 4 \times 4$ strip geometry) with $q = 10^{-4}$ and $r = 10^{-5}$ per time step (ts$^{-1}$). As expected, the conductance graphs (gray) randomly scatter around their time-dependent mean value $\Sigma(t)_n$ (black curve). In the next step $\Sigma(t)_n$ was fitted utilizing Equation (4) (red dashed curve), where $k$ is known and the exponent was fixed to $\mu = 2$ according to 3D percolation.\[19\] The fit results in a $P_c$ of $0.021$ and an $A$ of $10^{416}$. The so determined percolation threshold matches nicely the peak of the distribution of $p_c$ of the strip geometry (most left curve in Figure 8a).

After this test, the model was applied to the experimental data. Figure 9b shows the experimental results of 48 measurement cycles of the investigated CuO/silica composite material (grey curves) and the result of the optimization of the model (red dashed curve).

The measurements were carried out in a sequence by toggling the temperature every 10 min between 350 and 160 °C. A single cycle comprises only the low-temperature sensing region. Therefore, the starting time was set to $t = 0$ after the regeneration phase when the temperature was switched from 350 to 160 °C. In addition, the 48 cycles have been normalized to the mean of the maximum relative change of the conductance measurements $\Sigma_m = \max_\Sigma(t) = 1.57 \cdot 10^{-5}$S.
\(\Sigma_0\) can be interpreted as the conductance of one “bond.” The measurements results show a stronger spread than the very homogeneous simulation results. However, the fit of the model (red dashed curve) matches well to the time-dependent mean value \(\langle \Sigma(t) \rangle_n\) (black curve). The strongest deviation between the mean value and the theoretical curve is close to the percolation point, which originates from the statistical distribution of \(p_c\). Figure 9a shows the distribution of the percolation times determined as the time span until the conductance of each cycle reaches \(\Sigma_0\). Unfortunately, the rate constant \(k\) is not easily accessible for the CuO/CuS system under the presented conditions and therefore \(p_c\) cannot be estimated utilizing Equation (5). But since the measurement conditions and therefore \(k\) were kept constant, it is assumed that \(t_c\) is proportional to \(p_c\), and therefore, the shape of the distributions of both values match (compare Figure 8a and Figure 9a).

As a summary of the theoretical studies, two key aspects have to be highlighted:

i) The experimental results can be explained well by the theoretical model of a finite high-aspect-ratio percolating strip-shaped lattice. The characteristic shape of the conductance (Figure 9b) with a critical exponent of \(\mu = 2\) and the statistical distribution of the percolation times (Figure 9a) can be reproduced. This is a strong indication, that the composite material indeed experiences a percolation type transition during \(\text{H}_2\text{S}\) exposure. However, since there is no known literature data for the CuO/CuS system under the presented conditions available and also \(k\) and \(p_c\) are dependent on each other (as can be seen in Equation (5)) the presented study is not sufficient to determine their absolute values. The rate constants or the behavior of the correlation length of the composite material have to be further verified in another study. Their full knowledge would also make it possible to approximate a lattice and the dimensionality of the percolation the system is undergoing and also estimate if the chemical process really follows a zeroth order behavior.

ii) The simulation showed that the aspect ratio of the electrode setup provides an additional degree of freedom to tune the switching behavior of the sensor. The electrode setup could also be used to estimate the correlation length, or the characteristic size of one “bond,” which will be interesting for the further development of the sensing system.

Figure 8. a) Distributions of \(p_c\) for several finite long strips; percolation is measured via the \(y\)-direction with 96 samples for each strip. b) Time-dependent conductance of the 12000 \(\times\) 4 \(\times\) 4 strip in \(y\)-direction with \(q = 10^{-3} \text{ts}^{-1}\) and \(r = 10^{-5} \text{ts}^{-1}\); the conductance of one bond \(\Sigma_0\) is 1; grey: 48 simulations of the strip; black: time-dependent mean of the 48 runs; red dashed: asymptotic fit with known \(k = 9 \times 10^{-5} \text{ts}^{-1}\) and set \(\mu = 2\), resulting in \(p_c^{\text{mean}} = 0.021\) and \(A = 10^{416}\).

Figure 9. a) Distribution of \(t_c = p_c/k\) of the measured data; \(t_c\) is the point where the maximum relative conductance change was measured. b) grey: time-dependent conductance of 48 measurement cycles normalized onto \(\Sigma_0\) (the average of the maximum relative conductance step of all 48 cycles); black: time-dependent mean of the 48 normalized cycles; red dashed: fit of the time-dependent mean: one possible parameter set: \(\mu = 2\) (fixed), \(A = 1.2 \times 10^{5}, k = 0.012 \text{min}^{-1}\), \(p_c^{\text{mean}} = 0.048\).
2.4. Stabilization/Influence of Pore Structure

The main objective of the complex compositional design is to establish the reproducibility of the gas induced switching, i.e., to stabilize the switching time \( t_s \) and the conductance amplitude. Therefore, the electrical response of the CuO/silica composite was tested by repeating several gas induced switching processes with the very same sample. As was already shown, regeneration at elevated temperature (350 °C) is also possible in H\(_2\)S containing atmosphere. In the following, a 20 min test cycle comprising an accumulation phase of ten minutes at a temperature of 160 °C and a ten-minute regeneration phase at 350 °C, was utilized. The cycle was repeated 30 times in a constant gas flow of 10 ppm H\(_2\)S in synthetic air with 30% relative humidity.

Results (Figure 10) reveal stable low (=5 × 10\(^{-8}\) S) and high conductance values (=2 × 10\(^{-2}\) S) corresponding to insulating and conducting state after the switching process, respectively. In addition, the cycles show a reproducible shape, except for some “chemical” noise in the rising slope at the accumulation phase. It is assumed, that this behavior is due to the breaking and reformation of the conducting pathways close to the percolation threshold (see also Section 2.3.). The noise is therefore of chemical origin and is in analogy to contact chatter for mechanical switches and evidences the percolating nature of the response. The switching time \( t_s \) is 167 ± 40 s and shows some deviation throughout the cycles, which is due to the gas sensing setup and flow effects, respectively.

In summary, it could be shown, that the new composite material offers major advantages in terms of long-term stability over current CuO based materials.[14,15,26,27]

To further elucidate the influence of the pore structure and the infiltrated fraction of the CuO, respectively, a solid mixture of porous KIT-6 silica with bulk CuO (62 wt%) was utilized. As expected, the so prepared reference material did show gas induced switching behavior as well. However, the increase of conductance is 1–2 orders of magnitude lower than the value for the nanocomposite, and the reproducibility is poor (see Supporting Information). Both strongly support the above-described model of pore-mediated formation of percolation pathways in case of the new composite material.

2.5. Application as Gas Sensing Layer (Long-Term Stability)

The here presented, novel CuO/silica composite can be utilized as an active material for the design of highly selective and sensitive gas sensors. As opposed to the well-known resistive type sensors, the signal generation is based on a chemical reaction of CuO to CuS rather than an unspecified surface adsorption/desorption process. However, a disadvantage of this concept is the discontinuous signal generation. The maximum measurement rate is determined by the length of accumulation and regeneration cycles and the switching time, respectively. Therefore, a new operating mode, utilizing custom-built electronics and software, has been developed to test the applicability of the new composite material for sensing. A simple algorithm (see the Supporting Information) detects the percolation threshold and determines the switching time.

With this setup, the long-term stability of the composite material was tested. To mimic more realistic surrounding conditions, i.e., diffusion controlled gas exposure, the sensor was placed in a 250 mL round-bottom flask. Utilizing the automated gas mixing equipment the flask was continuously flushed with a mixture of synthetic air with 10 ppm H\(_2\)S, with a low total gas flow of 100 mL min\(^{-1}\). After an 8-day measurement and over 900 detection and regeneration cycles, no significant drift effects indicating instabilities in the percolation effect could be observed after the addition of water at 75 h (Figure 11). The mean value of the switching time is 16.9 ± 8.2 min for the entire measurement; after the addition of water, the switching time is 20 ± 4.5 min. Outliers are due to the simple data evaluation algorithm, which is sensitive to electronic noise.

In addition to the inherent selectivity, the novel sensing concept allows in principle to increase dynamically the sensitivity of the sensor by increasing the accumulation time (maintaining the temperature at 160 °C). As mentioned before, the equilibrium of the underlying reaction (see Equation (1)) is strongly shifted toward the CuS formation; regeneration is therefore strongly suppressed, and the detection limit could be improved even further by the cost of a longer measurement time. As a proof of concept, switching times for 10 and 5 ppm H\(_2\)S exposure were compared (see Figure 12 and Figure S12.)

![Figure 10. Conductance of the CuO/KIT-6 silica composite material in H\(_2\)S containing atmosphere (10 ppm H\(_2\)S in air) under cyclic operation conditions: accumulation of H\(_2\)S at 160 °C (blue); regeneration of CuS to CuO at 350 °C (red).[22]](image-url)
(Supporting Information). Mean values indicate, that half the concentration leads to nearly twice the switching time, i.e., $11.9 \pm 0.9$ min for 10 ppm H$_2$S and $27.8 \pm 3.8$ min for 5 ppm H$_2$S, which is consistent with the idea of an accumulation type sensor mechanism.

Future work will focus on reduction of the switching time, which will be mandatory for applications beyond dosimeters. Because of to the accumulating type sensing effect this can be achieved by optimization of the electrode structure (aspect ratio, see Section 2.3) and significant reduction of the deposited amount of material on each sensing element (miniaturization). The influence of the latter can already be seen comparing the different presented sensing measurements, which show some deviations in switching time for 10 ppm H$_2$S exposure.

3. Conclusions

A gas responsive switching material was successfully synthesized. The ordered mesoporous CuO/KIT-6 silica composites show H$_2$S induced electrical switching behavior, which can be described by percolation theory.

In addition, the impact of mechanical stress due to the volume expansion after the CuO $\rightleftharpoons$ CuS reaction could significantly be reduced, resulting in high cycling stability. Even after 8-day continuous cycling, corresponding to $\approx$900 reaction and regeneration cycles, no significant change of the switching threshold and the low and high conductance values could be observed. This was achieved by introducing void volume into the CuO nanoparticle network by utilization of ordered mesoporous KIT-6 silica as porous but rigid support. As an additional effect, this void volume led to change of conductance of at least 2 orders of magnitude larger at the switching point as it would be expected by the difference of specific conductance of CuO and CuS. This is attributed to a second percolation mechanism, the formation of physical contacts due to volume expansion, superimposing the CuO–CuS transition. The accumulating nature of the sensing mechanism was shown to be capable to tune the sensitivity of the gas sensitive switch by increasing the integration time. The size and shape of the electrode setup as a degree of freedom to tune the integration time was proposed by simulations.

The presented nanocomposite material can be utilized for a new type of chemical sensor, which offers a material encoded detection threshold value. By a combination of a series of these devices, a digital signal can be generated without the need for complex data evaluation. This will open up a new application field for this sensor class.

4. Experimental Section

Two Solvents Method: The porous solid was dispersed in dry n-hexane, which is nonpolar and therefore poorly miscible with water. For impregnation of a porous solid with a hydrophilic surface, a hydrophobic solvent and a polar solution were needed. The porous solid was dispersed in dry hexane and stirred for some time for the pores to be filled. The saturated solution of a metal salt in water was added dropwise. This polar solution replaced the nonpolar hexane inside the pores.[24]

Filtration, drying, and thermal conversion yielded the composite material. Each impregnation method was applied several times in order to vary the amount of introduced metal compound in the pores of the structure matrix.

Synthesis: In a typical synthesis of KIT-6, 16 g pluronic P-123 were dissolved in 480 g of water with 48 mL conc. HCl and stirred in a with Parafilm sealed beaker at 35 °C for 24 h. Subsequently, 19.8 mL n-butanol were added and stirred for 1 h prior to the addition of 34 mL tetraethylorthosilicate (TEOS) to the solution, which was stirred for another 24 h. For the synthesis of SBA-15, no n-butanol was added. After the hydrothermal treatment at 140 °C for 24 h the silica was washed with deionized water, dried at 60–120 °C for 48 h, and calcined in a tube furnace at 550 °C with a heating ramp of 0.5 °C min$^{-1}$ for 6 h in air.

Copper nitrate was introduced into the pores of the silica by the “two solvents” impregnation method. Typically, 2 g of silica were suspended in 40 mL n-hexane and stirred for 1 h. A saturated copper nitrate solution was added dropwise to the suspension. The volume of the saturated copper nitrate solution corresponded to the pore volume of the used silica. After stirring overnight, the n-hexane was removed by
vacuum filtration and evaporation in the fume hood. Drying at 60–80 °C for 48 h and converting the copper salt to copper oxide in a tube furnace at 500 °C for 4 h with a heating ramp of 5 °C min⁻¹ in air leads to the desired copper oxide silica composite material. This procedure was repeated several times in order to vary the amount of copper oxide in the composite material (see Figure 3).

Sensor Preparation: The sensors with an interdigitated electrode structure and a built-in Pt10 heater were bought from UST GmbH. The copper oxide silica composite material was suspended in deionized water (25 mg in 1 mL) by ultrasonication. A 2 µL drop was placed on top of the interdigitated electrodes and dried at room temperature. Prior to using, the sensors were heated to 350 °C for 48 h.

Characterization Methods: Nitrogen physisorption was performed at 77 K on a Quantachrome Autosorb 6. Prior to measurement, the samples were degassed at 120 °C for 12 h. Pore size distributions were calculated by Barret–Joyner–Halenda (BJH) model²⁹ from the desorption branch of the isotherms. The BET surface areas³⁰ were calculated in a pressure range of 0.1 ≤ p/p₀ ≤ 0.3. Total pore volumes were derived from the second-to-last data point in the adsorption isotherm (p/p₀ = 0.99).

X-ray diffraction was carried out on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (40 kV, 40 mA) with a step size of 0.0075° and a counting time of 3 s per step for low-angle measurements. For wide-angle measurements, the step size was 2θ = 0.02°. The morphology of the layers was characterized by scanning electron microscopy (SEM, Neon 40, Zeiss). For TEM a Philips CM30-ST microscope was utilized.

Theoretical Modeling: The composite material was assumed to form an electrical conductor–insulator mixture. The CuO spots which were spread inside the silica pore matrix were forming some unconnected lattice of sites. Under H₂S exposure, the CuO transformed to CuS and expanded, as shown in Figure 6. The nontouching and therefore unconnected CuO spots were represented by an unconnected lattice. While the touching and CuS sites formed a lattice with bonds connecting the sites.

A finite 3D matrix M in Matlab was chosen to represent the spread of CuO spots in the silica. From each element in the matrix, the nearest neighbors in a simple cubic manner were known. Therefore, a Matlab graph G could be created, where a random amount of sites were connected, when N bonds were present. The graph then only needed two fix points a and b connected to two opposing sides of the matrix M to serve as theoretical electrodes. Then the conductance Σ of the finite sample could be calculated via the maximum flow between the points a and b.

The occupation p of the bond lattice was the number of present bonds N versus the maximum possible number of bonds N max. A time-dependent behavior could be modeled via a time step function which was switching (adding and removing) bonds of the graph G. Therefore, it is possible to study Σ(p), p(t), as well as Σ(t) of a finite percolating system. This setup could be adapted to different lattices with different aspect ratios, sizes, and dimensionalities. It could also be adopted to partially occupied grids and simulate combinations of bond and site percolation.

Gas Sensing Tests: Gas sensing tests were carried out with custom-built gas mixing equipment, using mass flow controllers (MFC’s, Brooks Instrument). By adjusting the flow rates synthetic air (79.5% N₂, 20.5% O₂) with 10 ppm H₂S was offered to the samples (r.H. 30%) with a total gas flow of 300 mL min⁻¹, if not stated otherwise. The sensor substrates (UST GmbH, Art No. VGS1-9991151100) were placed in a polytetrafluorethylene (PTFE) chamber with a tight gas in- and out-let. The temperature of the sensors was controlled by applying a voltage to a Pt-10 heater, integrated in the sensor substrate. The conductance was measured with a Keithley 2601 A multimeter by applying 1 V measuring voltage. Table 4 summarizes the various conditions and parameters used for the measurements shown in this manuscript.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
chemical H₂S sensor, copper oxide, mesoporous, percolation, steric stabilization

Table 4. Parameters for the various gas measurements.

| Measurement | Measurement Chamber | H₂S Concentration [ppm] | Total Gas Flow [mL min⁻¹] | Temperature Switching | Relative Humidity [%] |
|-------------|----------------------|--------------------------|---------------------------|-----------------------|-----------------------|
| 1st (Figure 5) | PTFE Block | 10 | 300 | every 10 min | 30 |
| 2nd (Figure 9) | PTFE Block | 10 | 300 | every 10 min | 30 |
| 3rd (Figure 10) | Flask | 10 | 100 | algorithm | 0–100 |
| 4th (Figure 11) | PTFE Block | 10 and 5 | 300 | algorithm | 30 |

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