



Article Glucose-Assisted Synthesis of Porous, Urchin-like Co₃O₄ Hierarchical Structures for Low-Concentration Hydrogen Sensing Materials

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Abstract: The Co_3O_4 is a typical p-type metal oxide semiconductor (MOS) that attracted great attention for hydrogen detection. In this work, porous, urchin-like Co_3O_4 was synthesized using a hydrothermal method with the assistance of glucose and a subsequent calcination process. Urchin-like Co_3O_4 has a large specific surface area of $81.4 \text{ m}^2/\text{g}$. The response value of urchin-like Co_3O_4 to 200 ppm hydrogen at 200 °C is $36.5 (R_g/R_a)$, while the low-detection limit is as low as 100 ppb. The obtained Co_3O_4 also exhibited good reproducibility, long-term stability, and selectivity towards various gases (e.g., ammonia, hydrogen, carbon monoxide, and methane). Porous, urchin-like Co_3O_4 is expected to become a potential candidate for low-concentration hydrogen-sensing materials with the above advantages.

Keywords: Co₃O₄; urchin-like; glucose; hydrogen; gas sensing



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1. Introduction

Hydrogen, a futuristic and ideal clean energy source, is widely used in the fields of biomedicine, metal smelting, chemical production, and fuel cells [1–3]. However, the properties of hydrogen, such as its wide range of explosion concentration (4.0–74.5% in the air), low ignition energy (0.018 MJ), and high explosion index (550, 10 times of methane), limit its application [4,5]. Hydrogen sensing is an efficient way to monitor hydrogen concentration and promote hydrogen applications. Therefore, the need to develop and apply practical sensing materials to high-performance hydrogen sensors is urgent.

 Co_3O_4 , as a p-type MOS with a spinel structure, is a promising gas-sensing material due to its high stability, good humidity resistance, and high catalytic activity [6,7]. However, Co_3O_4 still suffers from having a high detection limit, low response, and poor selectivity. The regulation of morphology is an effective way to improve Co_3O_4 sensing performance, such as in nanorods [8], nanowires [9], nanodisks [10], nanotubes [11], nanoflowers [12,13], etc. For example, Qiu et al. synthesized needle-like Co₃O₄ for ethanol sensing using a hydrothermal method that has a response value of 19.6 to 100 ppm ethanol at 160 °C [14]. Fang et al. fabricated MOF-derived Co₃O₄ hollow nanotubes, which have a detective limit of 10 ppm to toluene [15]. Three Co₃O₄ samples with different morphologies were synthesized by Zhang et al. to investigate structure-dependent gas-sensing properties. The results showed that the sensing performance of rod-assembled spheres of Co₃O₄ and sheetassembled flowers of toluene outperformed cube-shaped Co_3O_4 [16]. One-dimensional nanostructures show good sensing performance due to their higher specific surface area, electron transfer efficiency, and surface energy; also, the material size reaches the Debye length [17]. However, studies of one-dimensional Co_3O_4 materials conducted for hydrogen are rare. Therefore, it is necessary to investigate further one-dimensional Co_3O_4 with a highly specific surface area and porosity for high-performance hydrogen-sensing materials. In this work, porous, urchin-like Co_3O_4 was synthesized through a hydrothermal process, with the assistance of glucose, followed by a calcination treatment. The hierarchical structure retained the advantage of a one-dimensional nanoneedle. Meanwhile, it also avoids the agglomeration of conventional nanoneedle materials and provides more active sites for gas adsorption. Thus, the gas diffusion channels were well preserved. The influence of the additive glucose dosage on the morphology of Co_3O_4 was investigated, and a possible formation mechanism of urchin-like hierarchical structure was elucidated. The hydrogen-sensing performance of urchin-like Co_3O_4 was tested, while the structure was also characterized using SEM, TEM, XRD, and XPS. The obtained results were beneficial for clarifying the sensing mechanism of Co_3O_4 and, thus, contributed to expanding hydrogen-sensing materials.

2. Experimental Section

2.1. Preparation of Porous, Urchin-like Co₃O₄ Hierarchical Structure

All chemicals were purchased from Shanghai Aladdin Reagent Co., Ltd., Shanghai, China. All chemical reagents were used directly and did not require secondary purification.

A total of 0.146 g Co(NO₃)₂·6H₂O, 0.180 g urea, and a fixed mass of glucose (the mass ratio of glucose/Co(NO₃)₂·6H₂O was 0, 0.25, 0.5, and 0.75, respectively) were added to a mixed solvent (10 mL of ethanol and 20 mL of deionized water). After magnetic stirring for 1 h, the mixed solution was transferred to a 50 mL Teflon-sealed autoclave and kept in an oven at 110 °C for 12 h. Subsequently, after being air-cooled to room temperature, a pinkish–purple precipitate (Co₃O₄ precursors) was obtained by washing several times with deionized water and ethanol and dried at 60 °C for 12 h. According to the TGA curves of the precursors (Figure S2), the calcination treatment was set to 400 °C for 2 h to obtain mixed-valent Co₃O₄ and protect the urchin-like structure from collapse. The obtained precursors are named $G_xCo_3O_4$, where x represents the mass ratio of glucose to cobalt nitrate hexahydrate: x = 0, 0.25, 0.5, and 0.75. It is accordingly named $T_{400}G_xCo_3O_4$ after calcination at 400 °C.

2.2. Characterization Methods

The morphology and structure of the samples were characterized using scanning electron microscopy (SEM, JEOL JSM-7900F, Tokyo, Japan) and transmission electron microscopy (TEM, JEOL2100 PLUS, Tokyo, Japan). Thermogravimetric analyzer analysis (TGA, Mettler Toleto TGA-DSC3+, Zurich, Switzerland) was conducted in an air atmosphere at a heating rate of 10 °C/min between 25 °C and 1000 °C. The crystal-phase composition and structure of the samples were characterized using X-ray diffraction (XRD, Smartlab KD2590N, Rigaku, Tokyo, Japan) with Cu K α source (λ = 0.15418). X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+, Al K α source, 1486.6 eV, Thermo Fisher Scientific, Waltham, MA, USA) was used to analyze the elemental composition and chemical state of the samples. The specific surface area of the sample was calculated using Brunauer–Emmett–Teller (BET, ASAP 3020, Micromeritics, Norcross, GA, USA), and the pore size information of the sample was calculated using the Barrett–Joyner–Helenda (BJH) method with N₂ isothermal adsorption–desorption testing at 77 K.

2.3. Measurement of Gas-Sensing Performance

A gas-sensing system (JF02, Gui Yan Jin Feng Technology Co., Ltd., Guizhou, China) was used to conduct gas-sensing testing of the materials. A simple schematic diagram of the JF02 gas-sensing system is shown in Figure S1. All gases used during testing were injected via external gas cylinders and mixed in the "Mixture Chamber". The mass flow and concentration of gases were controlled by the "Mass Flow" module, which was monitored through a flowmeter. The temperature control in the sensing process was achieved through the heating platform in the enclosed "Test Chamber". The changes in resistance signal were captured by a pair of electrode probes in the "Test Chamber", processed by the "Test Module", and transmitted into a PC. In a typical test process, the as-prepared Co_3O_4

samples (about 50 mg) were ultrasonically dispersed in ethanol (mass ratio 1:20) for 10 min to obtain a homogeneous suspension. Subsequently, 10 μ L of the suspension was dropped onto an alumina-ceramic sheet equipped with Ag electrodes using a pipette and then dried. Finally, the electrode sheet covered with a layer of the sample was placed in the test chamber of the gas-sensing system and connected to the electrodes in the chamber. The chamber was heated by a heating platform, which was surrounded by a pair of probes. The resistance of each sample was measured by the probes during testing. All gas-sensing measurements were conducted in a closed gas chamber, with a response (R) defined as R = R_g/R_a, where R_g and R_a are the resistance of the sample in the target gas and air, respectively. Additionally, the response time (τ_{res}) is defined as the time required for the sample resistance to reach 90% of its maximum value, and the recovery time (τ_{rec}) is defined as the time required for the sample resistance change. The selective coefficient is an evaluation of the selectivity of a gas sensor. It is defined as the ratio of the gas sensor's sensitivity between the target gas and other interfering gases. For a hydrogen sensor, it is calculated as S_c = S_{hydrogen}/S_{interfering gases}.

3. Results and Discussion

3.1. Morphology and Structure of Porous, Urchin-like Co₃O₄

In this work, glucose played a key role in the morphology regulation of the precursor, acting as the structural directing agent. Figure 1 illustrates the formation process of porous, urchin-like Co_3O_4 . During the hydrothermal process, urea continuously hydrolyzed and released OH⁻ and $CO_3^{2^-}$ ions, which then reacted with Co^{2^+} ions provided by $Co(NO_3)_2 \cdot 6H_2O$ in solution. This reaction formed crystal nuclei that grew longitudinally along the polysaccharide molecular chains resulting from the dehydration of glucose molecules, forming needle-like structures [18]. Subsequently, the nanoneedles self-assemble to form the Co_3O_4 precursor, as indicated by the XRD pattern (Figure S3), to be $Co_2(OH)_2CO_3 \cdot 11H_2O$ after oven drying. The porous Co_3O_4 phase formed after $Co_2(OH)_2CO_3 \cdot 11H_2O$ releases CO_2 and H_2O gas during calcination treatment in an air atmosphere. The reactions that occurred in the hydrothermal system can be presented as follows:

$$\mathrm{NH}_{2}\mathrm{CONH}_{2} + 3\mathrm{H}_{2}\mathrm{O} \xrightarrow{\mathrm{Hydrolysis}} 2\mathrm{NH}_{4}^{+} + \mathrm{HCO}_{3}^{-} + \mathrm{OH}^{-}$$
(1)

$$\mathrm{HCO}_{3}^{-} \to \mathrm{CO}_{3}^{2-} + \mathrm{H}^{+} \tag{2}$$

$$2Co^{2+} + 2OH^{-} + CO_3^{2-} \to Co_2(OH)_2CO_3$$
 (3)

$$\operatorname{Co}_{2}(\operatorname{OH})_{2}\operatorname{CO}_{3}+11\operatorname{H}_{2}\operatorname{O} \xrightarrow{\operatorname{Dry}} \operatorname{Co}_{2}(\operatorname{OH})_{2}\operatorname{CO}_{3}\cdot11\operatorname{H}_{2}\operatorname{O}$$
(4)

$$3\operatorname{Co}_{2}(\operatorname{OH})_{2}\operatorname{CO}_{3}\cdot11\operatorname{H}_{2}\operatorname{O}+\operatorname{O}_{2} \xrightarrow{400\,^{\circ}\operatorname{C}} 2\operatorname{Co}_{3}\operatorname{O}_{4}+3\operatorname{CO}_{2}+14\operatorname{H}_{2}\operatorname{O}$$
(5)

The SEM images of the Co₃O₄ precursor are shown in Figure 2. The precursor exhibits a nanorod-shaped structure with no glucose (x = 0) in the fabrication process (Figure 2a). When the glucose amount is kept at x = 0.25, an ordered urchin-like Co₃O₄ precursor (Figure 2b) consisting of basic nanoneedle structures is formed under the guidance of the glucose molecular chain. From the high-magnification SEM images of the urchin-like structure precursor shown in the inset of Figure 2b, the ordered nanoneedle arrays can be seen, which is beneficial for gas molecule adsorption in the sensing process. With the increase in the amount of glucose (x = 0.5), the density of the urchin-like Co₃O₄ increases due to the agglomeration of nanoneedles (Figure 2c). The spines of the "urchin" transform from nanoneedle to rough rod-shaped structures. When the glucose amount further increases to x = 0.75, the urchin-like Co₃O₄ exhibits a nearly block-like structure (Figure 2d), which is not conducive to obtaining a high specific surface area. The main reason for agglomeration is the curling, aggregation, and branching of polysaccharide molecular chains, reducing the linear growth space of transient crystal nuclei. The results show that the optimal mass of glucose to fabricate the urchin-like Co₃O₄ precursor is 0.037 g (x = 0.25).



Figure 1. Schematic illustrations of the growth mechanism of porous, urchin-like Co₃O₄.



Figure 2. SEM images of Co_3O_4 precursors synthesized with different glucose amounts: (a) $G_0Co_3O_4$; (b) $G_{0.25}Co_3O_4$; (c) $G_{0.5}Co_3O_4$; (d) $G_{0.75}Co_3O_4$.

Figure 3a shows the SEM images of porous, urchin-like $T_{400}G_{0.25}Co_3O_4$, which was calcinated at 400 °C for 2 h. The porous structure forms because the OH⁻ and CO₃²⁻ ions and residual glucose molecules are converted into H₂O and CO₂ gas molecules during the calcination process and then escape [19]. Ultimately, a porous, urchin-like Co₃O₄ hierarchical structure is self-assembled with nanoneedles, and the nanoneedles are shaped from nanoparticles. Other $T_{400}G_xCo_3O_4$ samples are shown in Figure S4. After the calcinating process, rod-shaped $G_0Co_3O_4$ seriously aggregates into blocks with a diameter of about 1 µm, and $T_{400}G_0Co_3O_4$ is tightly composed of nanoparticles with a few stacked

pores (Figure S4a). A partial thick nanoneedle structure (about 160 nm) is retained in $T_{400}G_{0.5}Co_3O_4$ (Figure S4b). It exhibits a disorderly stacked structure, which reduces the gas adsorption and dissociation area in the gas-sensing process. $T_{400}G_{0.75}Co_3O_4$ illustrates the structure of a near-solid microsphere with a diameter of about 18 µm (Figure S4c). The structure of $T_{400}G_{0.25}Co_3O_4$ tends to obtain a high specific surface area, but others are contrary to that.



Figure 3. Porous, urchin-like T₄₀₀G_{0.25}Co₃O₄: (**a**) SEM image; (**b**) XRD pattern; (**c**) TEM image; (**d**) HRTEM image and SAED image (inset).

Figure 3b shows the XRD pattern of $T_{400}G_{0.25}Co_3O_4$ with sharp diffraction peaks, indicating high crystallinity. The characteristic peaks at $2\theta = 22.1$, 36.4, 43.1, 52.5, 70.2, and 77.5° correspond to the (111), (220), (311), (400), (511), and (440) crystal planes of the spinel Co_3O_4 (PDF#45-1467), respectively. The $Co_2(OH)_2CO_3 \cdot 11H_2O$ has completely transformed into a spinel Co_3O_4 single-phase after the calcination process at 400 °C for 2 h.

The morphology and crystal structure of the obtained porous, urchin-like Co_3O_4 were further tested by TEM. The basic nanoneedle structure is composed of nanoparticles (Figure 3c), and the nanoneedle diameter of $T_{400}G_{0.25}Co_3O_4$ is about 60 nm, which is smaller than others. The smaller size of nanomaterials provides advantages for gas-sensing, especially the 1D nanomaterials that have reached Debye length [18]. From the HRTEM image (Figure 3d), lattice fringes of 0.28 nm and 0.46 nm correspond to the (220) and (111) crystal planes of spinel Co_3O_4 after Fourier transform. The lack of clarity in the lattice fringes of 0.28 nm is probably due to the thickness of the sample. Research has shown that exposure of (111) crystal planes of Co_3O_4 is beneficial for oxygen adsorption, leading to a wider hole accumulation layer (HAL) [20]. The concentric rings presented in the SAED (inset of Figure 3d) indicate the polycrystalline structure of porous, urchin-like Co_3O_4 .

The XPS spectra are shown in Figure 4a–c, which was conducted to further clarify the elemental composition and valence state of urchin-like Co_3O_4 . According to the XPS survey spectrum (Figure 4a), the peaks located at 284.8, 530.8, 780.8, and 795.8 eV correspond to C 1s, O 1s, Co $2p_{3/2}$, and Co $2p_{1/2}$, respectively. The Co $2p_{3/2}$ peak can be divided into two peaks with binding energies of 779.8 eV and 781.5 eV, representing $Co^{3+} 2p_{3/2}$ and Co^{2+}

 $2p_{3/2}$ (Figure 4b). The Co $2p_{1/2}$ can be divided into two peaks at 794.8 eV and 797.6 eV, representing Co³⁺ $2p_{1/2}$ and Co²⁺ $2p_{1/2}$ [21]. The results certify the coexistence of Co²⁺ and Co³⁺ chemical states on the material surface. The asymmetric O 1s peak (Figure 4c) can be fitted and differentiated into three peaks, corresponding to lattice oxygen (529.8 eV), oxygen vacancies (530.2 eV), and chemically adsorbed oxygen (531.3 eV) [22]. The proportion of oxygen vacancies was calculated to be 24.7%, which is beneficial for oxygen adsorption and dissociation on the material surface [23].



Figure 4. T₄₀₀G_{0.25}Co₃O₄: (**a**) XPS survey spectrum; (**b**) High-resolution XPS spectrum of Co 2p; (**c**) High-resolution XPS spectrum of O 1s; (**d**) Nitrogen adsorption–desorption isotherms and BJH pore size distribution curve (insert).

 N_2 adsorption–desorption isotherms were tested to investigate the specific surface area and pore structure of the obtained Co₃O₄. The results are summarized in Table 1. The porous, urchin-like T₄₀₀G_{0.25}Co₃O₄ has the largest specific surface area of 81.4 m²/g, approximately twice that of the rod-shaped T₄₀₀G₀Co₃O₄. The specific surface area of the obtained material was inversely proportional to the glucose content (when x = 0.25, 0.5, and 0.75). It displayed a typical type IV adsorption isotherm with an H3-type hysteresis loop (Figure 4d), indicating a mesoporous structure [24]. T₄₀₀G_{0.25}Co₃O₄ has the smallest pore size and highest porosity, which benefits the diffusion and dissociation of H₂ (small molecule) on the material surface, improving the transmission efficiency of the H atom [25].

Sample	Specific Surface Areas (m ² /g)	Average Pore Size (nm)	Pore Volume (cm ³ /g)	
$T_{400}G_0Co_3O_4$	42.7	32.7	0.285	
T ₄₀₀ G _{0.25} Co ₃ O ₄	81.4	11.0	0.449	
T ₄₀₀ G _{0.5} Co ₃ O ₄	57.5	20.3	0.379	
T ₄₀₀ G _{0.75} Co ₃ O ₄	55.3	22.6	0.407	

Table 1. Specific surface area and pore size of T₄₀₀G_xCo₃O₄.

3.2. Hydrogen-Sensing Performance of Porous, Urchin-like Co₃O₄

The operating temperature significantly impacts gas-sensing response due to the kinetics and mechanics of gas adsorption and desorption [21,26]. Figure 5a shows the response values of $T_{400}G_xCo_3O_4$ to 200 ppm H₂ over a temperature range of 100–350 °C. With increasing operating temperature, the response values of $T_{400}G_xCo_3O_4$ (x = 0, 0.25, 0.5, and 0.75) initially increase and then decrease. The optimal operating temperature is found to be 200 °C. This can be attributed to weak reaction kinetics between H₂ and $T_{400}G_xCo_3O_4$ at lower temperatures, while desorption of H_2 on the $T_{400}G_xCo_3O_4$ surface dominates at higher temperatures, leading to a reduction in the response value. Furthermore, $T_{400}G_{0.25}Co_3O_4$ exhibits the highest response value ($R_g/R_a = 36.5$), which decreases with increasing glucose content. This is attributed to the largest specific surface area and the smallest nanoneedle diameter of $T_{400}G_{0.25}Co_3O_4$, providing more active sites for gas adsorption and dissociation, facilitating easier reaction between H₂ and the oxygen anion on the material surface. The dynamic response–recovery curve at 200 °C (Figure 5b) shows a fast recovery time of 9.1 s. However, the porous structure and multi-layer adsorption mechanism, as presented by the type IV nitrogen adsorption-desorption isotherms curve (Figure 4d) of the material, results in a relatively long response time (178 s). This occurs because H₂ molecules take more time to reach the surface of the inner layer of the material for adsorption and reaction. The above indicates that the porous, urchin-like Co_3O_4 is much more sensitive to H₂. Based on the above, subsequent gas-sensing performance tests, such as response to different H₂ concentrations, selectivity, and repeatability, have been conducted at the optimal operating temperature (200 °C).



Figure 5. $T_{400}G_xCo_3O_4$ material: (a) Response to 200 ppm H₂ at different operating temperatures; (b) The dynamic response–recovery curve for 200 ppm H₂ at 200 °C.

The response curves of $T_{400}G_xCo_3O_4$ materials towards 0.1–200 ppm H₂ at 200 °C were further investigated (Figure 6). The insufficient response to low-concentration hydrogen remains one of the urgent challenges for current MOS hydrogen-sensing materials. Figure 6a shows that $T_{400}G_{0.25}Co_3O_4$ exhibits a higher response than others at various H₂ concentrations, indicating the optimal ratio of glucose is $m_G/m_{Co} = 0.25$. Moreover,

the dynamic response curve of $T_{400}G_{0.25}Co_3O_4$ (Figure 6b) shows a high response value (8.5) at extremely low H₂ concentrations (100 ppb) and returns to the initial state after introducing air. The unique nanoneedle arrays of the "urchin" structure provide ordered pore channels for H₂ molecule transmission, resulting in sufficient gas response even at low H₂ concentrations.



Figure 6. (a) Response to different concentrations of H_2 at 200 °C; (b) Dynamic response–recovery curve of $T_{400}G_{0.25}Co_3O_4$ to different concentrations of H_2 at 200 °C.

The responses of T₄₀₀G_xCo₃O₄ to various reducing gases (ammonia, hydrogen, carbon monoxide, and methane) at 200 °C were tested to further investigate the selectivity of $T_{400}G_xCo_3O_4$. The results are shown in Figure 7a. The selectivity coefficients of $T_{400}G_{0.25}Co_3O_4$ to NH₃, CO, and CH₄ have been calculated to be 2.42, 6.19, and 4.68, respectively. Others are also shown in Table 2. A larger selectivity coefficient indicates better selectivity. It is generally considered to have excellent selectivity when the selectivity coefficient of the gas sensor is greater than 3. It exhibits more excellent sensitivity to H_2 than other counterparts at the same concentration, mainly due to the porous structure of the material acting as a molecular sieve for gas molecules with different sizes. The narrow pore channel allows small size molecules of H₂ to transit and collide with the material surface, leading to a stronger gas reaction. Repeatability refers to the degree to which the sensor deviates from the measurement result after repeated use in the case of a certain gas concentration. The response values and dynamic curves of $T_{400}G_xCo_3O_4$ to 200 ppm H₂ at $200 \,^{\circ}\text{C}$ after 9 reversible cycles are shown in Figures 7b and S6. The response value of the materials only presents a decrease of 1.9-2.6 after 9 reversible cycles, indicating an excellent repeatability of the materials.



Figure 7. $T_{400}G_xCo_3O_4$ material at 200 °C: (**a**) Response values to different reducing gases; (**b**) Response value after 9 hydrogen cycles.

Sample	NH ₃	СО	CH ₄
$T_{400}G_0Co_3O_4$	2.13	4.98	4.74
T ₄₀₀ G _{0.25} Co ₃ O ₄	2.42	6.19	4.68
$T_{400}G_{0.5}Co_3O_4$	4.37	5.53	2.77
$T_{400}G_{0.75}Co_3O_4$	3.82	4.94	2.60

Table 2. The selectivity coefficients of $T_{400}G_xCo_3O_4$.

3.3. Hydrogen-Sensing Mechanism and Performance Analysis of Porous, Urchin-like Co₃O₄
3.3.1. Hydrogen-Sensing Mechanism of Co₃O₄

The sensing mechanism of MOS-type hydrogen-sensing materials is based on the resistance variation mediated by surface chemistry [27–29]. Therefore, the specific surface area is one critical factor affecting the gas-sensing properties [30]. As a p-type MOS, the main charge carrier of Co_3O_4 is holes. When Co_3O_4 is exposed to air (Figure 8a), O_2 absorbs on the surface of the material and then dissociates into oxygen anions (O_2^- , O^- , O^{2-}) by seizing electrons from the conduction band of the material. Different oxygen anions are formed at different temperatures, as shown in Equations (6)–(9) since chemisorption is an energy-activated process [31]. As shown in Figure 8a, O_2 dissociates to O^- at 200 °C (the optimal operation temperature in this work) on the Co_3O_4 surface. Meanwhile, the energy band bends upwards, forming a hole accumulation layer (HAL), which leads to a decrease in resistance [32]. When Co_3O_4 is exposed to H₂ (Figure 8b), the subsequent hydrogensensing process occurs through a chemical reaction between O^- and H₂ (Equation (10)). This process releases the electrons back to the HAL and narrows them, increasing material resistance.

$$O_{2(g)} \to O_{2(ads)} \tag{6}$$

$$O_{2(ads)} + e^{-} \rightarrow O_{2(ads)}^{-} (T < 150 \ ^{\circ}C)$$
 (7)

$$O_2^{-}_{(ads)} + e^- \rightarrow 2O^-_{(ads)} (150 \ ^\circ\text{C} < \text{T} < 400 \ ^\circ\text{C})$$
(8)

$$O^{-}_{(ads)} + e^{-} \to O^{2-}_{(ads)} (T > 400 \ ^{\circ}C)$$
 (9)

$$H_2 + O^-_{(ads)} \to H_2 O_{(gas)} + e^-$$
 (10)



Figure 8. Schematic diagram of gas-sensing mechanism and energy-band changes in Co₃O₄ material: (a) in air; (b) in hydrogen.

3.3.2. Analysis of Hydrogen-Sensing Performance of Porous, Urchin-like Co₃O₄

The response value and detection limit of the obtained material to H_2 are comparable to other competing sensing materials in Table 3. MOS gas-sensing materials of different

structures were listed in the table and compared regarding the optimal working temperature, response at a certain concentration, and detection limit to this work. To ensure the comparability of data from references, the different response calculation methods of these references have been unified and provided as annotations under the table. The sensing material obtained in this work shows great advantages in terms of sensitivity and detection limits that have reached the ppb level. Considering the hydrogen-sensing mechanism of Co_3O_4 , the performance of the porous, urchin-like Co_3O_4 was enhanced by excellent structure regulation. According to the results of the structure analysis, the $T_{400}G_{0.25}Co_3O_4$ material had an ultra-high specific surface area of $81.4 \text{ m}^2/\text{g}$ and a high porosity of 0.449 cm³/g. It provided sufficient active sites for adsorption and dissociation of H₂ on the material surface, which, combined with high O⁻ coverage, further promoted the redox reaction during the sensing process [33].

Table 3. Comp.	arison of M	OS-sensing 1	naterials for H ₂
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Materials	Structure	Working Temperature (°C)	Concentration (ppm)	Response	Detection Limit (ppm)	Ref.
Pd-SnO ₂ /Co ₃ O ₄ NiO	nanoparticle	300	100	57.9	10	[34]
	nanofilm	250	200	35.7 *	50	[35]
1 at.% Pt-ZnO	pencil-like microrods	150	100	2.8 *	10	[27]
$Pt-Fe_2(MoO_4)_3$	nanoflower	300	10	3.1 *	1	[36]
In ₂ O ₃	octahedra	260	500	14	4	[37]
V_2O_5	hollow structure	25	200	2.9	10	[38]
MnCo ₂ O ₄ /r-GO	flower	160	250	1.1	100	[39]
T ₄₀₀ G _{0.25} Co ₃ O ₄	urchin-like	200	200	36.5	0.1	This work

* All the response values calculated by S% = $\frac{|R_a - R_g|}{R_g} \times \%$ were converted to R_a/R_g (n-type MOS) or R_g/R_a (p-type MOS).

Moreover, the $T_{400}G_{0.25}Co_3O_4$ had the optimal pore size of 11 nm, which provides an effective diffusion channel for H₂. At this pore size, it was conducive to the diffusion of small hydrogen molecules and played a screening role in large molecule gases [40]. The diffusion of gas molecules in pores is related to the relationship between the mean free path and pore size of gas molecules, which is derived from three types of diffusion process: volume diffusion, Knudsen diffusion, and transition diffusion [41]. The diffusion way of H₂ in the $T_{400}G_{0.25}Co_3O_4$, which has an 11 nm porous size, belongs to Knudsen diffusion. In this way, the H₂ molecule can smoothly pass through the pore channel and collide with the material surface, promoting the adsorption and dissociation of H₂ on the $T_{400}G_{0.25}Co_3O_4$ surface. Meanwhile, large molecule gas tends to undergo transition diffusion and volume diffusion. Therefore, the porous structure of $T_{400}G_{0.25}Co_3O_4$ resulted in high sensitivity at low hydrogen concentrations and further increased the hydrogen selectivity of the material.

In addition, the high-resolution spectrum of Co 2p in the XPS (Figure 4b) illustrated the coexisting chemical states of Co^{2+} and Co^{3+} of the material. The conversion of two types of ions can create additional active sites and induce redox reactions, which improve the sensitivity of the material to different concentrations of H₂ [42–44].

4. Conclusions

In summary, porous, urchin-like Co_3O_4 was controllably synthesized through a hydrothermal method followed by a calcination process for hydrogen detection. The Co_3O_4 exhibited excellent hydrogen detection performance, with a response value (8.5) to 100 ppb hydrogen that is superior to other morphology Co_3O_4 samples. The ratio of glucose to cobalt salt greatly affected the structure of Co_3O_4 , and porous, urchin-like $T_{400}G_{0.25}Co_3O_4$ material can be obtained while the m_G/m_{Co} ratio is 0.25. It exhibits optimum hydrogen

sensing performance, which can be attributed to (1) the ultra-large specific surface area, providing more active sites, (2) the high porosity and appropriate pore size corresponding to Knudsen diffusion, and (3) the conversion between Co^{2+} and Co^{3+} of Co_3O_4 , which enhances catalytic activity and promotes sensing performance.

Supplementary Materials: The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/ma17061364/s1, Figure S1: Schematic diagram of JF02 system; Figure S2: TGA curves of Co_3O_4 precursors; Figure S3: XRD pattern of $G_{0.25}Co_3O_4$; Figure S4: SEM images of $T_{400}G_xCo_3O_4$: (a) $T_{400}G_0Co_3O_4$; (b) $T_{400}G_{0.5}Co_3O_4$; (c) $T_{400}G_{0.75}Co_3O_4$; Figure S5: Response to different concentrations of H₂ at 200 °C: (a) $T_{400}G_0Co_3O_4$; (b) $T_{400}G_0Co_3O_4$; (c) $T_{400}G_{0.25}Co_3O_4$; (c) $T_{400}G_{0.5}Co_3O_4$; (c) $T_{40}G_{0.5}Co_3O_4$; (c) $T_{40}G_{0.5}Co$

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References

- 1. Staffell, I.; Scamman, D.; Velazquez Abad, A.; Balcombe, P.; Dodds, P.E.; Ekins, P.; Shah, N.; Ward, K.R. The role of hydrogen and fuel cells in the global energy system. *Energy Environ. Sci.* **2019**, *12*, 463–491. [CrossRef]
- Abe, J.O.; Popoola, A.P.I.; Ajenifuja, E.; Popoola, O.M. Hydrogen energy, economy and storage: Review and recommendation. *Int. J. Hydrog. Energy* 2019, 44, 15072–15086. [CrossRef]
- Rasul, M.G.; Hazrat, M.A.; Sattar, M.A.; Jahirul, M.I.; Shearer, M.J. The future of hydrogen: Challenges on production, storage and applications. *Energy Convers. Manag.* 2022, 272, 116326. [CrossRef]
- 4. Hübert, T.; Boon-Brett, L.; Black, G.; Banach, U. Hydrogen sensors—A review. Sens. Actuators B Chem. 2011, 157, 329–352. [CrossRef]
- Dawood, F.; Anda, M.; Shafiullah, G.M. Hydrogen production for energy: An overview. Int. J. Hydrogen Energy 2020, 45, 3847–3869. [CrossRef]
- Kruefu, V.; Inpan, U.; Leangtanom, P.; Arkarvipath, C.; Kongpark, P.; Phokharatkul, D.; Wisitsoraat, A.; Tuantranont, A.; Phanichphant, S. Enhanced Gas-Sensing Performances of Ru-Loaded p-Type Co₃O₄ Nanoparticles. *Physica Status Solidi (a)* 2018, 215, 1701015. [CrossRef]
- Ahmad, M.H.; Akhond, M.R.; Islam, M.J.; Rahaman, M.; Alam, R.B.; Ul-hamid, A.; Islam, M.R. A combined experimental and theoretical study on the structural, optical and electronic properties of hetero interface-functionalized MoS₂/Co₃O₄ nanocomposite. *Surf. Interfaces* 2023, *37*, 102750. [CrossRef]
- Makole, R.; Tshabalala, Z.P.; Swart, H.C.; Coetsee-Hugo, L.; Leshabane, N.; Motaung, D.E. Fabrication of one-dimensional porous p-type Co₃O₄ rods-based sensors for ultra-high sensitivity and selectivity towards benzene vapour. *Mater. Today Commun.* 2024, 38, 108426. [CrossRef]
- 9. Kumarage, G.W.C.; Zappa, D.; Mihalcea, C.G.; Maraloiu, V.-A.; Stefan, M.; Comini, E. Revolutionizing n-type Co₃O₄ Nanowire for Hydrogen Gas Sensing. *Adv. Energy Sustain. Res.* **2023**, *4*, 2300067. [CrossRef]
- 10. Bhalerao, K.D.; Khan, M.; Nakate, Y.T.; Kadam, R.M.; Manzoor, S.; Masrat, S.; Mishra, P.; Nakate, U.T.; Ahmad, R. Co₃O₄ hexagonal nanodisks: Synthesis and efficient ethanol gas sensing application. *Surf. Interfaces* **2023**, *42*, 103350. [CrossRef]
- 11. Hu, J.; Xiong, X.; Guan, W.; Long, H. Controllable fabrication of hierarchical bubble-like Co₃O₄ tubes with enhanced trimethylamine sensing performance. *Sens. Actuators B Chem.* **2023**, *389*, 133886. [CrossRef]

- Su, C.; Zhang, L.; Han, Y.; Chen, X.; Wang, S.; Zeng, M.; Hu, N.; Su, Y.; Zhou, Z.; Wei, H.; et al. Glucose-assisted synthesis of hierarchical flower-like Co₃O₄ nanostructures assembled by porous nanosheets for enhanced acetone sensing. *Sens. Actuators B Chem.* 2019, 288, 699–706. [CrossRef]
- 13. Yusof, N.M.; Rozali, S.; Ibrahim, S.; Siddick, S.Z. Synthesis of hybridized fireworks-like go-Co₃O₄ nanorods for acetone gas sensing applications. *Mater. Today Commun.* **2023**, *35*, 105516. [CrossRef]
- 14. Qiu, Y.; Wang, Y. Controllable synthesis of porous Co₃O₄ nanorods and their ethanol-sensing performance. *Ceram. Int.* **2022**, *48*, 29659–29668. [CrossRef]
- 15. Fang, B.; Yao, H.; Xiao, X.; Zhang, Q.; Zhang, X.; Yang, W. Metal-organic frameworks-derived hollow Co₃O₄ nanotubes for efficient detection of toluene vapor. *J. Alloys Compd.* **2023**, 937, 168535. [CrossRef]
- Zhang, R.; Gao, S.; Zhou, T.; Tu, J.; Zhang, T. Facile preparation of hierarchical structure based on p-type Co₃O₄ as toluene detecting sensor. *Appl. Surf. Sci.* 2020, 503, 144167. [CrossRef]
- 17. Yang, B.; Myung, N.V.; Tran, T. 1D Metal Oxide Semiconductor Materials for Chemiresistive Gas Sensors: A Review. *Adv. Electron. Mater.* **2021**, *7*, 2100271. [CrossRef]
- 18. Chang, B.; Gu, Z.; Guo, Y.; Li, Z.; Yang, B. Glucose-assisted synthesis of Co₃O₄ nanostructure with controllable morphologies from nanosheets to nanowires. *J. Alloys Compd.* **2016**, *676*, 26–36. [CrossRef]
- 19. Xu, J.M.; Zhang, J.; Wang, B.B.; Liu, F. Shape-regulated synthesis of cobalt oxide and its gas-sensing property. *J. Alloys Compd.* **2015**, *619*, 361–367. [CrossRef]
- 20. Liu, D.; Pervaiz, E.; Adimi, S.; Thomas, T.; Qu, F.; Huang, C.; Wang, R.; Jiang, H.; Yang, M. Theoretical study on W-Co₃O₄ (111) surface: Acetone adsorption and sensing mechanism. *Appl. Surf. Sci.* **2021**, *566*, 150642. [CrossRef]
- Ullah, M.; Bai, X.; Chen, J.; Lv, H.; Liu, Z.; Zhang, Y.; Wang, J.; Sun, B.; Li, L.; Shi, K. Metal-organic framework material derived Co₃O₄ coupled with graphitic carbon nitride as highly sensitive NO₂ gas sensor at room temperature. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *612*, 125972. [CrossRef]
- 22. Kishore, K.R.; Teddu, L.B.; Balamurugan, D.; Gopalakrishnan, J.B. Electrospun Co₃O₄ nanoparticles and its methanol detection property. *Appl. Nanosci.* **2021**, *11*, 637–655. [CrossRef]
- Manoharan, M.; Govindharaj, K.; Muthumalai, K.; Kumaravel, S.; Haldorai, Y.; Rajendra Kumar, R.T. Interface Oxygen Vacancy-Enhanced Co₃O₄/WO₃ Nanorod Heterojunction for Sub-ppm Level Detection of NO_x. *Adv. Eng. Mater.* 2023, 25, 2300727. [CrossRef]
- Jiao, Q.; Fu, M.; You, C.; Zhao, Y.; Li, H. Preparation of Hollow Co₃O₄ Microspheres and Their Ethanol Sensing Properties. *Inorg. Chem.* 2012, *51*, 11513–11520. [CrossRef] [PubMed]
- 25. Pham, T.K.N.; Brown, J.J. Hydrogen sensors using 2-dimensional materials: A review. Chem. Sel. 2020, 5, 7277–7297. [CrossRef]
- 26. Krishna, K.G.; Parne, S.; Pothukanuri, N.; Kathirvelu, V.; Gandi, S.; Joshi, D. Nanostructured metal oxide semiconductor-based gas sensors: A comprehensive review. *Sens. Actuators A Phys.* **2022**, *341*, 113578. [CrossRef]
- Kumar, S.; Lawaniya, S.D.; Agarwal, S.; Yu, Y.T.; Nelamarri, S.R.; Kumar, M.; Mishra, Y.K.; Awasthi, K. Optimization of Pt nanoparticles loading in ZnO for highly selective and stable hydrogen gas sensor at reduced working temperature. *Sens. Actuators B Chem.* 2023, 375, 132943. [CrossRef]
- 28. Raju, P.; Li, Q. Review—Semiconductor Materials and Devices for Gas Sensors. J. Electrochem. Soc. 2022, 169, 057518. [CrossRef]
- Lee, J.H.; Kim, J.Y.; Kim, J.H.; Mirzaei, A.; Kim, H.W.; Kim, S.S. Co₃O₄-loaded ZnO nanofibers for excellent hydrogen sensing. *Int. J. Hydrog. Energy* 2019, 44, 27499–27510. [CrossRef]
- Makole, R.; Tshabalala, Z.P.; Jozela, M.; Cummings, F.R.; Swart, H.C.; Motaung, D.E. Facile synthesis of high surface area of p-n Co₃O₄-In₂O₃ heterostructure-based sensor for improved xylene detection at low temperature. *Inorg. Chem. Commun.* 2023, 158, 111652. [CrossRef]
- Kumarage, G.W.C.; Comini, E. Low-Dimensional Nanostructures Based on Cobalt Oxide (Co₃O₄) in Chemical-Gas Sensing. Chemosensors 2021, 9, 197. [CrossRef]
- 32. Kim, H.-J.; Lee, J.-H. Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview. *Sens. Actuators B Chem.* **2014**, *192*, 607–627. [CrossRef]
- Doan, T.L.H.; Kim, J.Y.; Lee, J.H.; Nguyen, L.H.T.; Dang, Y.T.; Bui, K.B.T.; Pham, A.T.T.; Mirzaei, A.; Phan, T.B.; Kim, S.S. Preparation of n-ZnO/p-Co₃O₄ heterojunctions from zeolitic imidazolate frameworks (ZIF-8/ZIF-67) for sensing low ethanol concentrations. *Sens. Actuators B Chem.* 2021, 348, 130684. [CrossRef]
- 34. Yin, X.T.; Yang, Z.Y.; Dastan, D.; Liu, Y.; Tan, X.-M.; Gao, X.C.; Zhou, Y.-W.; Li, J.; Ma, X.-G. Sensitivity and selectivity Pt loaded SnO₂–Co₃O₄ gas sensor for hydrogen detection. *Ceram. Int.* **2023**, *49*, 38717–38725. [CrossRef]
- Pai, S.H.S.; Mondal, A.; Barathy, T.R.; Ajitha, B.; Samuel, E.J.J.; Reddy, Y.A.K. Effect of calcination temperature on NiO for hydrogen gas sensor performance. *Int. J. Hydrog. Energy* 2024, 50, 928–941. [CrossRef]
- Ai, T.; Zhang, J.; Li, J.; Zhang, Y.; Yin, Y.; Lu, J. Ultrafast response of Pt functionalized Fe₂(MoO₄)₃ nanoflower gas sensors for ultra-low ppm level H2 gas detection. J. Alloys Compd. 2024, 970, 172567. [CrossRef]
- 37. Roso, S.; Bittencourt, C.; Umek, P.; González, O.; Güell, F.; Urakawa, A.; Llobet, E. Synthesis of single crystalline In₂O₃ octahedra for the selective detection of NO₂ and H₂ at trace levels. *J. Mater. Chem. C* **2016**, *4*, 9418–9427. [CrossRef]
- Wang, Y.T.; Whang, W.T.; Chen, C.-H. Hollow V₂O₅ Nanoassemblies for High-Performance Room-Temperature Hydrogen Sensors. ACS Appl. Mater. Interfaces 2015, 7, 8480–8487. [CrossRef] [PubMed]

- Maji, B.; Barik, B.; Sahoo, S.J.; Achary, L.S.K.; Kumar Sahoo, K.; Kar, J.P.; Dash, P. Shape selective comprehensive gas sensing study of different morphological manganese-cobalt oxide based nanocomposite as potential room temperature hydrogen gas sensor. *Sens. Actuators B Chem.* 2023, 380, 133348. [CrossRef]
- 40. Zhou, T.; Sang, Y.; Wang, X.; Wu, C.; Zeng, D.; Xie, C. Pore size dependent gas-sensing selectivity based on ZnO@ZIF nanorod arrays. *Sens. Actuators B Chem.* **2018**, 258, 1099–1106. [CrossRef]
- 41. Ambardekar, V.; Bandyopadhyay, P.P.; Majumder, S.B. Atmospheric plasma sprayed SnO₂ coating for ethanol detection. *J. Alloys Compd.* **2018**, 752, 440–447. [CrossRef]
- 42. Kong, D.; Zhou, W.; Han, J.; Gao, Y.; Gao, Y.; Zhao, L.; Sun, P.; Lu, G. Mesoporous Co₃O₄ nanosheets with exposed Co²⁺-rich crystal facets for improved toluene detection. *Appl. Surf. Sci.* **2023**, *619*, 156714. [CrossRef]
- 43. Qin, C.; Wang, B.; Wu, N.; Han, C.; Wu, C.; Zhang, X.; Tian, Q.; Shen, S.; Li, P.; Wang, Y. Metal-organic frameworks derived porous Co₃O₄ dodecahedeons with abundant active Co³⁺ for ppb-level CO gas sensing. *Appl. Surf. Sci.* **2020**, *506*, 144900. [CrossRef]
- 44. Giri, S.; Anantharamaiah, P.N.; Sahoo, B. Sensing of oxidizing and reducing gases by sensors prepared using nanoscale Co₃O₄ powders: A study through Cu substitution. *Adv. Powder Technol.* **2022**, *33*, 103529. [CrossRef]

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