



Article Detection of Xylene Using Ni(OH)₂-Enhanced Co₃O₄ Nanoplate via p–n Junctions

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Abstract: This study reports a novel Ni(OH)₂/Co₃O₄ heterostructured nanomaterial synthesized through a simple two-step hydrothermal method combined with subsequent heat treatment. The Ni(OH)₂/Co₃O₄ heterostructured nanomaterial showed excellent performance in the detection of xylene gas. XRD, SEM, and EDS characterized the crystal structure, microstructure, and composition elements of Co₃O₄ and Ni(OH)₂/Co₃O₄, and the gas sensing properties of the Co₃O₄ sensor and Ni(OH)₂/Co₃O₄ sensor were systematically tested. The test results indicate the Ni(OH)₂/Co₃O₄ sensor has an optimal operating temperature of 175 °C, which is 10 °C lower than that of the Co₃O₄ sensor; has a response of 14.1 to 100 ppm xylene, which is 7-fold higher than that of the Co₃O₄ sensor; reduces the detection limit of xylene from 2 ppm to 100 ppb; and has at least a 4-fold higher response to xylene than other gases. The Ni(OH)₂/Co₃O₄ nanocomposite exerts the excellent catalytic performance of two-dimensional nanomaterial Ni(OH)₂, solves the deficiency in the electrical conductivity of Ni(OH)₂ materials, and realizes the outstanding sensing performance of xylene, while the construction of the p–n heterojunction between Ni(OH)₂ and Co₃O₄ also improves the sensing performance of two-dimensional Ni(OH)₂ materials.

Keywords: xylene; gas sensor; Ni(OH)₂; p-n junctions

1. Introduction

Xylene, as a toxic, flammable, volatile organic substance, is extensively applied in paint, chemical, automotive, and other fields [1–3]. Xylene is flammable and explosive; long-term exposure can cause cancer, high-concentration exposure can harm the skin and eyes, and inhalation of xylene can jeopardize the human respiratory system and nervous system and cause irreversible damage [4]. The detection of xylene gas is essential. Currently, there are already available detection devices such as fiber optic sensors [5], optical waveguide sensors [6], gas chromatography analyzers [7], electrochemical sensors, etc. However, these devices have large sizes and high costs, which are not conducive to portability. Semiconductor sensors have gained much attention for their low cost, good portability, and online operation [8–10]. Many semiconductor sensors for xylene have been developed. Ka Yoon Shin et al. [11] synthesized Ag-Co₃O₄ nanomaterials with a unique core–shell structure using chemical synthesis, which lowered the optimum operating temperature and improved the response to xylene gas compared to pristine Co₃O₄. The fabricated sensors had an optimum working temperature of 250 °C, and their response to 50 ppm xylene at



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 250 °C was 2.47; this enhanced sensing performance is probably due to the high specific surface area of the Ag-Co₃O₄ nanomaterials, the catalytic effect of the Ag nanoparticles, and the formation of heterojunctions between Ag and Co₃O₄. Fengdong Qu et al. [12] synthesized Co₃O₄@NiMoO₄ core–shell nanowires using a two-step hydrothermal route to fabricate sensors for xylene detection. The fabricated sensor showed good gas-sensing properties at 255 °C, its response to 100 ppm xylene was 24.6, and it presented good selectivity for xylene. The mechanism of the increased gas-sensing performance is probably due to the formation of a heterojunction between Co₃O₄ and NiMoO₄, and the synergistic catalytic effect between them. Table 1 lists some of the reported xylene sensors and their gas-sensing performance. Although these sensors have excellent performance, their operating temperatures are generally high, which, on the one hand, is not conducive to lowering power consumption. On the other hand, excessively high temperatures can lead to the explosion of VOC gases. Lower operating temperatures mean that more efficient catalytic materials are needed, and this is significant for the low-temperature detection of xylene.

Recently, novel two-dimensional (2D) materials have gained more and more attention from researchers, which is attributed to their unique electronic structure and abundant specific surface area [13–15], and 2D materials have been applied in catalysis [16], solar power [17], and gas sensitization [18–20]. Two-dimensional materials such as graphene, transition metal sulfides, and carbides have received extensive and sustained attention [21–25]. In recent years, two-dimensional layered double hydroxides (LDH) [26-28] have gradually come into the limelight, and have been applied in the fields of catalysis and electrochemistry due to their unique electronic structure, high activity, and superior catalytic performance. LDH is a 2D layered ionic crystal consisting of positively charged metal layers and anions used for charge balance between the layers, which is rich in defects and active sites [29] and is a potential material for gas sensing. Flaky Ni(OH)₂ has a structure similar to hydrotalcite, which has excellent catalytic properties, but its poor electrical conductivity restricts the utilization of this material in gas sensors [30]. Utilizing the outstanding catalytic properties of Ni(OH)₂ holds the promise of solving this problem of insufficient sensitivity of the sensor to xylene due to insufficient catalytic properties, and the problem of insufficient conductivity of the Ni(OH)₂ material can be solved through constructing heterojunctions. Taking into account the conductivity issue, spinel Co_3O_4 , with good conductivity, becomes an ideal material for constructing heterojunctions [31–33]. The special flaky spinel structure of Co_3O_4 can be used as a suitable loading substrate, which can fully solve the problem of poor conductivity of Ni(OH)₂ and exert the catalytic effect of Ni(OH)₂. Although there are fewer related reports, in-depth study of the effect of $Ni(OH)_2/Co_3O_4$ nanomaterials on the detection of xylene is of great significance.

In this work, a Ni(OH)₂/Co₃O₄ heterojunction nanomaterial was synthesized through a two-step hydrothermal route. The synthesized material exploits the excellent catalytic performance of Ni(OH)₂, solves the problem of the insufficient electrical conductivity of Ni(OH)₂, and achieves excellent sensing performance for xylene, while the construction of the p–n junction between Ni(OH)₂ and Co₃O₄ also improves the sensing performance. The Ni(OH)₂/Co₃O₄ sensor has an optimal operating temperature of 175 °C, which is 10 °C lower than that of the Co₃O₄ sensor; has a response of 14.1 to 100 ppm xylene, which is 7-fold higher than that of the Co₃O₄ sensor; reduces the detection limit of xylene to 100 ppb; and has a response to xylene at least 4-fold higher than several other gases (ammonia, glacial acetic acid, dibutyl ketone, formaldehyde, benzene, toluene, styrene, and ethanol). Finally, the mechanism of the superior performance of Ni(OH)₂/Co₃O₄ as a xylene sensor was analyzed in detail. This work utilizes two-dimensional Ni(OH)₂ materials to provide a strategy for designing high-performance xylene sensors.

Materials	Concentration (ppm)	Temperature (°C)	Response (Rg/Ra)	Lower Detection Limit (ppm)	Reference
C/Co ₃ O ₄	100	183	17.62	1	[32]
W-doped NiO	200	375	8.74	15	[34]
NiCo ₂ O ₄ /WO ₃	100	300	15.69	5	[35]
CuO/WO ₃	50	260	6.36	0.3	[36]
Ag-Co ₃ O ₄	50	250	2.47	0.14	[11]
Co ₃ O ₄ @NiMoO ₄	100	255	24.6	0.42	[12]
Ni(OH) ₂ /Co ₃ O ₄	100	175	14.1	0.1	This work

Table 1. Xylene gas sensors have been reported.

2. Materials and Experimental Details

2.1. Experimental Materials Overview

The reagents used in the experiments included cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O, Mack-lin Biochemical Technology Co., Ltd., Shanghai, China), anhydrous sodium carbonate <math>(Na_2CO_3, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), nickel chloride <math>(NiCl_2 \cdot 6H_2O, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), urea <math>(CO(NH_2)_2, Xiya Chemical Technology, Shandong, China)$ and cetyltrimethyl ammonium bromide $(CTAB, C_{19}H_{42}BrN, PHYGENE, Fujian, China).$ All the reagents used in the experiments were analytically pure and could be used directly.

2.2. Synthesis of Ni(OH)₂ Nanosheets

The Ni(OH)₂ nanosheets [37,38] were synthesized through one template-free hydrothermal route with the following experimental protocol: 0.2 g of Na₂CO₃, 0.2 g of NiCl₂·6H₂O, and 0.01 g of CTAB were placed in one beaker sequentially, then, 15 mL ultrapure water was poured into the beaker. After that, a rotor of suitable size was placed in the beaker, and the beaker was placed on a magnetic stirrer to stir with 500 r/min speed. After stirring, the solution of the precursor was placed into one 40 mL volume Teflon-lined hydrothermal autoclave reactor, then stored under 180 °C over 6 h. As the hydrothermal process slowed down and the solution utterly cooled down to ambient temperature, the solution was placed into a centrifuge tube. Then, the centrifuge was used to wash the residue to remove impurity ions, and the washing steps were as follows. First of all, ultrapure water was added to the solution to flatten the centrifuge tube; it was placed into the centrifuge and centrifuged for three minutes at 8000 r/min; after the centrifugation was completed, the top layer of the liquid was poured off and the residue left at the bottom. Then, a certain amount of anhydrous ethanol was poured into the centrifuge tube, the centrifuge tube was flattened, and the solution centrifuged. This process was repeated three times to complete the washing process, and then the tube was placed in an oven at 60 °C to dry overnight. When drying was completed, the precipitate was fully ground in a mortar, placed into a ceramic boat, and spread evenly. Finally, the ceramic boat was placed in a muffle furnace to heat up to 200 °C for 190 min, and kept at 200 °C for 120 min. Finally, greenish Ni(OH)₂ was obtained.

2.3. Synthesis of Co₃O₄ Nanoplates and Ni(OH)₂/Co₃O₄ Nanomaterials

 Co_3O_4 nanoplates [39–41] and Ni(OH)₂/Co₃O₄ nanocomposites [42,43] were prepared using a simple hydrothermal route, as described below. Briefly, 0.00624 g of Ni(OH)₂ nanomaterials was measured and poured into a beaker containing 24 mL of ultrapure water for dissolution, after which the beaker was placed into an ultrasonic machine to sonicate the material for 10 min; after completion of the sonication, the beaker was placed onto a magnetic stirrer for stirring. Under continuous stirring, 1.14 g of Co(NO₃)₂·6H₂O and 0.86 g of CO(NH₂)₂ were added to the solution and stirred well. Then, the solution of the precursor was placed into a 40 mL Teflon-lined hydrothermal autoclave reactor and reacted at 180 $^{\circ}$ C over 16 h. As the hydrothermal process slowed down and the solution utterly cooled down to ambient temperature, the washing and drying process, as described above, was repeated. The dried residue was placed into a mortar, fully ground, and evenly spread into a porcelain boat. Finally, the ceramic boat was placed in a muffle furnace to heat up to 250 °C for 150 min, and kept at 250 °C for 115 min to obtain the black Ni(OH)₂/Co₃O₄ nanomaterials. The same method was used to prepare Co₃O₄ nanoplate materials, except that Ni(OH)₂ nanomaterials were not added during the fabrication process, and black Co₃O₄ nanomaterials were finally obtained.

2.4. Material Characterization Methods

The morphology and microstructure of the nanomaterials were observed using scanning electron microscopy (SEM, SSX-550, Shimadzu Corporation, Japan) attached with energy dispersive spectroscopy (EDS), the elemental composition of the materials was determined using EDS, and the crystal structure of the materials was characterized using X-ray diffractometry (XRD, XRD-7000, Shimadzu Corporation, Kyoto, Japan), using Cu Ka radiation ($\lambda = 0.15418$ nm) with a 5°/min scanning speed and a 30~80° scanning range.

2.5. Gas Sensor Fabrication and Gas Sensing Performance Test

The detailed construction of the gas sensor is given as Figure 1a. It is composed of a sensor base, a ceramic tube, and a heating resistance wire. The heating resistance wire is a Ni-Cr alloy wire with a resistance value of 30 Ω , remaining constant during the heating process. The ceramic tube is made of Al₂O₃, which has a diameter of about 1 mm and a length of about 4 mm, with two rings of gold electrodes on the surface. The width of the individual gold electrodes is about 0.6 mm, the distance of the gold electrodes to each other is approximately 2 mm, two platinum wires are led out from the individual gold electrodes, and the length of the platinum wires is 5~6 mm.



Figure 1. (a) Gas sensor structure; (b) Detailed drawing of the gas detection test system.

The sensor needs to be coated with sensitive materials and aged before the gas sensing performance test, and the specific details are as follows [44]. Firstly, 2~10 mg of gas-sensitive material was taken into a 1.5 mL EP tube. Secondly, $5 \sim 10 \ \mu$ L of anhydrous ethanol was added to the EP tube using a pipette gun. Thirdly, the EP tube was placed on an oscillator to disperse the mixture to a gelatinous state. In the fourth step, a pipette gun was used to suck the gelatinous mixture and uniformly coat it on the ceramic tube to form a sensitive layer. Finally, to enhance the sensor's stability, the well-coated sensor was placed at 180 °C for aging for 24 h.

The details of the gas sensing performance test system platform are shown in Figure 1b, composed of a gas chamber, a gas cylinder, a data acquisition device, a heating source, and

(a)

a PC terminal. The volume of the gas chamber is 1000 mL, and it has a gas injection port and a gas discharge port. The gas cylinder is filled with dry synthetic air, of which 21% and 79% are oxygen and nitrogen, respectively. A DC power supply provides the working temperature for the sensor, during the gas sensing test, the sensor is inserted into the PCB board at the bottom of the gas chamber, and the two electrodes welded together with the ends of the resistance wire on the sensor are connected to the DC power supply (the heating resistance wire is the same type of nickel-chromium alloy resistance wire, which has a certain resistance value). The temperature of the heating resistor wire is the working temperature of the sensor, and the temperature of the heating resistor wire and the power supply power have a corresponding one-to-one relationship; when the power applied to the heating resistor wire is stable, the temperature of the resistor wire is a fixed value, so that the resistor wire can be applied to the different power to regulate the sensor's operating temperature. A digital source meter collects the data from the sensor and processes it through gas-sensitive performance test software (Single channel voltage source v1.0) at the computer terminal, ultimately displaying the resistance change curve of the sensor on the software interface. The model of the DC power supply used in this experiment is RIGOL DP832A (DP832A, RIGOL, Beijing, China), and the model of the voltage source used is KEYSIGHT B2902A (B2902A, Keysight Technologies, Santa Rosa, CA, USA). In the process of the gas sensing performance test [44,45], the sensor is first inserted into the gas chamber, and then the gas chamber is closed. Then, the working temperature exerted on the sensor is regulated through the control of the DC power supply. After that, the valve on the pipeline connecting the gas cylinder and the gas chamber is opened, and then the synthetic air enters the gas chamber through the pipeline. After continuously blowing for 3 to 4 min, the synthetic air will fill the gas chamber and close the valve. The procedure for extracting a certain concentration of a known gas with a syringe is as follows. First, the volume of the target gas required to form a certain concentration of the target gas in the gas chamber is calculated using the static gas–liquid distribution method, after which the corresponding volume of saturated vapor gas is extracted from the liquid bottle of the target gas with a syringe and injected into the gas chamber through the inlet port of the gas chamber, where it rapidly diffuses into the gas of the required concentration. When the sensor resistance is stable and unchanged, a certain amount of target gas is extracted from the gas cylinder with a syringe and injected into the gas chamber from the air inlet. When the target gas diffuses into the desired concentration in the gas chamber, the interaction of the target gas molecules with the surface of the gas sensor causes the sensor resistance to change. The gas sensing performance test software records the sensor resistance change during the whole process. This paper defines the gas sensor response as S = Rg/Ra, with Ra and Rg being the sensor resistance when it reaches a steady state in the air and in the target gas, respectively. The response time (recovery time) of a gas sensor is defined as 90% of the time it takes for the resistance of the sensor to change after the adsorption (desorption) of the target gas on the surface of the sensor until the resistance value reaches a steady state.

The concentration (C, ppm) of the individual target gases during the gas sensitivity test is obtained using Equation (1) [33]:

$$C = \frac{1000 \times (22.4 \times \Phi \times \rho \times V_1)}{M \times V_2}$$
(1)

In the above equation, Φ and ρ are the purity and density of the desired liquid (g/mL), V₁ and V₂ are the volume of the liquid (µL) and the volume of the gas chamber (L), respectively, and M is the molar mass of the desired liquid (g/mol).

3. Results and Discussion

3.1. Characterization of Material Structure and Morphology

Figure 2 is the SEM images of Ni(OH)₂, Co_3O_4 and Ni(OH)₂/ Co_3O_4 nanomaterials. Figure 2a presents the SEM image of Ni(OH)₂ sample, and it can be observed that Ni(OH)₂ nanosheets are composed of many ultrathin nanosheets laminated with each other, which are of different sizes. Figure 2b is the SEM image of Co_3O_4 sample. Pure Co_3O_4 is in the form of irregularly shaped plate-like structures, partially stacked together and of different sizes. Figure 2c shows the SEM image of Ni(OH)₂/Co₃O₄ composite; the doping of Ni(OH)₂ has no significant effect on the morphology of the material, but it can be seen from the figure that the average thickness of the Ni(OH)₂/Co₃O₄ composite is smaller than that of the Co₃O₄ sample. Therefore, the Ni(OH)₂/Co₃O₄ composites are able to provide more surface active sites for gas adsorption per unit volume, which is favorable for the reaction of gas on the surface of the gas-sensitive materials.



Figure 2. SEM images of (a) Ni(OH)₂; (b) Co₃O₄; (c) Ni(OH)₂/Co₃O₄; (d) EDS of Ni(OH)₂/Co₃O₄.

Typical XRD patterns of Co₃O₄, Ni(OH)₂, and Ni(OH)₂/Co₃O₄ nanomaterials are presented in Figure 3. The wide diffraction peaks of 31.3° , 36.9° , 44.88° , 59.45° , and 65.34° correspond to the (220), (311), (400), (511) and (440) diffraction planes of the original crystal structure of Co₃O₄, respectively, and the data are entirely in line with JCPDS 76-1802. The wide diffraction peaks of 33.41° , 38.61° , 52.21° , 59.60° , and 62.73° correspond to the (100), (002), (102), (003), and (111) diffraction planes of the original crystal structure of Ni(OH)₂, respectively, and the data correspond exactly to JCPDS file No.02-1112. Ni(OH)₂/Co₃O₄ composites have the same diffraction peaks as pure Co₃O₄, but the diffraction peak at 33.41° corresponds to the (100) point of Ni(OH)₂, demonstrating the presence of Ni(OH)₂ in the composites and the incorporation of Ni(OH)₂ did not disrupt the lattice structure of Co₃O₄. The average grain sizes of Ni(OH)₂ nanosheets, Ni(OH)₂/Co₃O₄ composites, and Co₃O₄ nanoplates were determined using the Debye-Scherrer formula [46], and were 10.00 nm, 9.93 nm and 9.38 nm, respectively. There were not any other diffraction peaks found in the XRD pattern, meaning that the synthesized material was high in purity.



Figure 3. XRD pattern of Ni(OH)₂, Co₃O₄, and Ni(OH)₂/Co₃O₄.

3.2. Xylene Gas-Sensing Properties

The main detected gas is xylene. In the practical application of gas sensors, the optimum working temperature is an essential index to evaluate the sensing performance of gas sensors. Therefore, the sensors were tested over a temperature range of 100 °C to 250 °C to find the optimum working temperature of the synthesized Co₃O₄-based gas sensors. The working concentration of the sensing response was chosen to be 100 ppm, and Figure 4a presents the sensor responses of Co_3O_4 and $Ni(OH)_2/Co_3O_4$ gas sensors for 100 ppm xylene gas of 100~250 °C. The response curve of Ni(OH)₂ is not shown, because pure $Ni(OH)_2$ has almost no response to xylene. From the figure, it can be observed that the response curves of both sensors show a similar trend with the increase in the working temperature, that is, the response of the sensor gradually increases to a peak value as the working temperature increases, and the response of the sensor decreases gradually as the working temperature is further increased. The Co_3O_4 gas sensor showed the largest response to xylene at 185 °C, with a response value of 2.08; the Ni(OH)₂/Co₃O₄ gas sensor showed the largest response to xylene at 175 °C, with a response value of 14.1. The Ni(OH)₂ nanomaterials by themselves did not have a response to xylene, and the response was enhanced by about seven times after $Ni(OH)_2$ decorated Co_3O_4 , meaning the addition of $Ni(OH)_2$ enhances the reaction of Co_3O_4 nanomaterials to xylene gas. The mechanism of the sensor response changes with temperature can be explained below. When at a lower temperature, the response of the sensor becomes larger as the working temperature increases, which may be attributed to two factors: firstly, as the operating temperature increases, the type of adsorbed oxygen on the surface of the material is changed from O₂⁻ to O^- . The oxidizing ability of O^- is higher than that of O_2^- . Therefore, as the temperature increases, the material becomes increasingly sensitive to the presence of xylene, a reducing gas, contributing to an increased response [47,48]. Secondly, with the increase in working temperature, the thermal energy of xylene gas molecules increases steadily, and more and more xylene gas molecules are able to surpass the activation energy barrier and react in redox reactions with the chemically adsorbed oxygen of the gas-sensitive material, causing an increase in response [49]. As the temperature rises to $175 \,^{\circ}$ C, the maximum response is reached, and then the response decreases as the temperature continues to increase, which

may be due to the desorption process of the previously adsorbed oxygen ions, causing a decrease in the amount of adsorption active sites for xylene gas molecules. Another possibility is that at high temperatures, xylene gas molecules have a smaller adsorption capacity than desorption capacity, and gas molecules adsorbed on sensitive materials tend to escape before charge transfer, reducing the utilization of the sensitive material and resulting in a reduced response [36].



Figure 4. (a) Response of Co_3O_4 sensor and $Ni(OH)_2/Co_3O_4$ sensor xylene at 100 ppm under various working temperatures; (b) Response of the Co_3O_4 sensor and $Ni(OH)_2/Co_3O_4$ sensor to various gases at 100 ppm under 185 °C and 175 °C, respectively.

In order to further examine the selectivity of Co_3O_4 and $Ni(OH)_2/Co_3O_4$ nanomaterials for different gases, which refers to the immunity of the sensor to other gases, the response of Co_3O_4 and $Ni(OH)_2/Co_3O_4$ sensors to 100 ppm concentration of ammonia, glacial acetic acid, xylene, dibutyl ketone, formaldehyde, benzene, toluene, styrene, and ethanol at their best working temperature is presented in Figure 4b. The $Ni(OH)_2/Co_3O_4$ sensors showed a significant increase in response to all target gases, with the most significant increase in response to xylene, and the response values for xylene were significantly higher than those for the other gases. The $Ni(OH)_2/Co_3O_4$ composite-based sensors showed better selectivity to xylene gas.

Figure 5a,b represent the response recovery curves of Co_3O_4 and $Ni(OH)_2/Co_3O_4$ sensors at different xylene concentrations from 100 ppm to 100 ppb at their best operating temperature, respectively. As can be observed, the response of both the Co_3O_4 sensor and the $Ni(OH)_2/Co_3O_4$ sensor showed a gradual decrease in the detected gas concentration. The responses of Co₃O₄ were 2.28 (100 ppm), 1.67 (50 ppm), 1.25 (20 ppm), 1.18 (10 ppm), 1.14 (5 ppm), and 1.1 (2 ppm), and the responses of $Ni(OH)_2/Co_3O_4$ were 13.1 (100 ppm), 9.7 (50 ppm), 4.2 (20 ppm), 2.6 (10 ppm), 2.3 (5 ppm), 2 (2 ppm), 1.82 (500 ppb), 1.58 (200 ppb), 1.4 (100 ppb), respectively. From the above results, the improved sensor response is increased, the lower limit of detection is reduced, and the minimum concentration of detectable xylene is reduced from 2 ppm to 100 ppb, which means that ppb-level detection of xylene is accomplished. Ni(OH)₂/Co₃O₄-based gas sensors can recognize the early warning of the presence of xylene gas at low concentrations. Figure 5c presents the curve of linear fitting with the average response value of $Ni(OH)_2/Co_3O_4$ sensor at different xylene concentrations. The curve shows a good linear correlation relationship of xylene gas concentration with the sensor sensitivity, which indicates that the stability of the sensor is good and the detection range is enormous.





Response recovery characteristic is another vital parameter of gas sensors, and in practical applications, the sensors are required to have good response and recovery characteristics. Figure 6a,b presents the response recovery curves of 100 ppm xylene for Co_3O_4 nanomaterials and Ni(OH)₂/Co₃O₄ composites at 185 °C and 175 °C, respectively. Since the sensors are in a 100 ppm xylene atmosphere, the response and recovery times are 100 s and 40 s for the Co_3O_4 sensor and 90 s and 75 s for the Ni(OH)₂/Co₃O₄ sensor, respectively. Compared with the Co_3O_4 sensor, the Ni(OH)₂/Co₃O₄ sensor's response time is reduced by 10 s, and the recovery time is increased by 35 s. The longer recovery time of the Ni(OH)₂/Co₃O₄ sensor is probably due to its lower operating temperature, making it harder for the xylene molecules to desorb from the surface of the material, leading to a longer recovery time. For practical applications, the response recovery characteristic of the sensor is still unsatisfactory, so in the future, this may be improved by adding noble metals or other substances.



Figure 6. (a) Co_3O_4 (b) $Ni(OH)_2/Co_3O_4$ response recovery curve at the best operating temperature with 100 ppm xylene; (c) Comparison of sensor response to 100 ppm xylene gas in dry air (0% RH) and humid air (95% RH).

In order to investigate the interference of humidity in the sensor, the sensor was exposed to 95% humid air. Figure 6c compares the response of the Ni(OH)₂/Co₃O₄ sensor to 100 ppm xylene in dry air (0% RH) versus humid air (40% RH) at 175 °C. The response of the sensor to xylene decreased by 84.4% compared to dry air, and the humid atmosphere reduced the response of the sensor due to the fact that H₂O molecules can occupy the adsorption sites on the surface of the sensitive material, reducing the available sites for xylene gas molecules to be adsorbed, and ultimately exhibiting a lower response in humid air, as confirmed by previous studies [50,51].

4. Xylene Sensing Mechanism

Ni(OH)₂ is an n-type semiconductor, and Co_3O_4 is a typical p-type semiconductor. From the above results, the Ni(OH)₂/Co₃O₄ sensor resistance increases after exposure to xylene gas, which indicates that it exhibits typical p-type semiconductor characteristics. The widely accepted gas-sensing mechanism of metal oxide semiconductor gas sensors is the surface-adsorbed oxygen model [19,47,48]. Specifically, when the target gas enters the gas chamber, the target gas molecules will react with chemically adsorbed oxygen present on the gas-sensitive material to cause charge transfer, which in turn will cause a change in the resistance of the sensor. As a typical p-type semiconductor, most of the carriers in Co_3O_4 are holes. When the sensor is placed in the air, the oxygen molecules attach to the surface of Co_3O_4 to form chemisorbed oxygen, and in the process, Co_3O_4 loses electrons to form a hole accumulation layer (HAL), which reduces the sensor resistance. The type of chemisorbed oxygen ions is dependent on the sensor working temperature, and the adsorbed oxygen exists in the form of O_2^- [36,49], as the working temperature is below 100 °C.

$$O_2(gas) \rightarrow O_2(ads)$$
 (2)

$$O_2(ads) + e^- \rightarrow O_2^-(ads) \tag{3}$$

When the operating temperature is in the range of 100~300 °C, the adsorbed oxygen is converted from O_2^- to O^- .

$$O_2^{-}(ads) + e^- \rightarrow 2O^-(ads) \tag{4}$$

When the operating temperature is greater than 300 °C, the adsorbed oxygen is converted into O^{2-} .

$$O^{-}(ads) + e^{-} \rightarrow O^{2-}(ads)$$
(5)

Because the working temperature of the sensor is at 100~300 $^{\circ}$ C, chemisorbed oxygen exists mainly in the form of O⁻.

When the sensor lies in a xylene atmosphere, the adsorbed oxygen reacts with the xylene gas molecules in a redox reaction, and the electrons captured by the adsorbed oxygen return to the conduction band of the material, which gradually narrows the hole accumulation layer and leads to a larger resistance of the sensor. The chemical reaction between adsorbed oxygen ions and the xylene molecules occurs as follows [32,33]:

$$C_8H_{10}(ads) + 210^- \rightarrow 8CO_2(gas) + 5H_2O(gas) + 21e^-$$
 (6)

In addition, another essential factor for the sensor performance enhancement is the formed p–n heterojunction between Ni(OH)₂ and Co_3O_4 [52,53]. The energy band diagram of the Ni(OH)_{2/}Co₃O₄ xylene gas sensor in air and in xylene is shown in Figure 7. The work function of Co_3O_4 is 6.03 eV, and of $Ni(OH)_2$ is 3.7 eV, and there is a Fermi energy level difference between the two, so that when $Ni(OH)_2$ is in contact with Co_3O_4 , the electrons of Ni(OH)₂ migrate toward Co_3O_4 , and the holes flow from Co_3O_4 to Ni(OH)₂ until they form the same Fermi energy level. At this point, a self-constructed electric field is created at the interface between the two. As the electrons of $Ni(OH)_2$ complex with the holes of Co_3O_4 , a depletion layer is formed at the Ni(OH)₂/Co₃O₄ p–n junction interface, resulting in a bending of the energy bands. As electrons migrate toward Co_3O_4 , more electrons are trapped by $O^{-}(ads)$, causing an increased adsorbed oxygen on the surface of the gassensitive material, causing a large depletion of holes in Co₃O₄ and leading to the increased resistance of the sensor. When the sensor is placed in a xylene atmosphere, the xylene molecules adsorb on the surface of the Co_3O_4 and react with the oxygen ions present on the Co_3O_4 in a redox reaction, at which time the electrons captured by the chemisorbed oxygen are returned to the conduction band of the material. As the electrons are compounded with the holes, the concentration of holes in Co_3O_4 decreases, the concentration of electrons in $Ni(OH)_2$ increases, the conduction electrons from $Ni(OH)_2$ enhance the depletion layer, and the potential barrier of the p-n junction increases, which causes composite resistance increases. The decrease in the number of Co_3O_4 holes and the broadening of the depletion layer at the $Ni(OH)_2/Co_3O_4$ interface result in a larger resistivity and greater sensitivity.



Figure 7. Energy band diagram of the Ni(OH)₂/Co₃O₄ xylene gas sensor (**a**) in air and (**b**) in xylene.

5. Conclusions

In this paper, Ni(OH)₂/Co₃O₄ nanomaterials were prepared through a two-step hydrothermal route. The materials were characterized using SEM, XRD, and EDS, and the gas-sensing properties of the Ni(OH)₂/Co₃O₄ nanomaterials to xylene gas were explored in detail. In comparison to the original Co₃O₄ sensor, the Ni(OH)₂/Co₃O₄ sensor has a reduced optimal working temperature (175 °C), superior response (Rg/Ra = 14.1), faster response time (35 s), lower limit of detection (500 ppb), and better gas selectivity. The mechanism of enhanced sensing performance can be summarized as the change in electrical resistance due to the reaction between xylene molecules and the chemisorbed oxygen ions of the material; in addition, the p–n heterojunction formed by the composite of Ni(OH)₂ and Co₃O₄ widens the bandwidth of the electron depletion layer, resulting in an increase in the sensor response to xylene. The incorporation of Ni(OH)₂ nanosheets caused a remarkable enhancement of the gas-sensing properties of the origin Co₃O₄ nanomaterials, which demonstrated that the two-dimensional Ni(OH)₂ material is an effective catalyst, thereby providing a strategy for designing high-performance xylene sensors.

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