Enhanced High-Temperature (600 °C) NO₂ Response of ZnFe₂O₄ Nanoparticle-Based Exhaust Gas Sensors

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Abstract: Fabrication of gas sensors to monitor toxic exhaust gases at high working temperatures is a challenging task due to the low sensitivity and narrow long-term stability of the devices under harsh conditions. Herein, the fabrication of a chemiresistor-type gas sensor is reported for the detection of NO₂ gas at 600 °C. The sensing element consists of ZnFe₂O₄ nanoparticles prepared via a high-energy ball milling and annealed at different temperatures (600–1000 °C). The effects of annealing temperature on the crystal structure, morphology, and gas sensing properties of ZnFe₂O₄ nanoparticles are studied. A mixed spinel structure of ZnFe₂O₄ nanoparticles with a lattice parameter of 8.445 Å is revealed by X-ray diffraction analysis. The crystallite size and X-ray density of ZnFe₂O₄ nanoparticles increase with the annealing temperature, whereas the lattice parameter and volume are considerably reduced indicating lattice distortion and defects such as oxygen vacancies. ZnFe₂O₄ nanoparticles annealed at 1000 °C exhibit the highest sensitivity (0.13% ppm⁻¹), sharp response (τ_res = 195 s), recovery (τ_rec = 17 s), and linear response to 100–400 ppm NO₂ gas. The annealing temperature and oxygen vacancies play a major role in determining the sensitivity of devices. The plausible sensing mechanism is discussed. ZnFe₂O₄ nanoparticles show great potential for high-temperature exhaust gas sensing applications.

Keywords: annealing temperature; chemiresistors; gas sensors; oxygen vacancies; sensing mechanism; ZnFe₂O₄ nanoparticles

1. Introduction

Hazardous exhaust gases such as nitrogen dioxide (NO₂) and sulfur dioxide (SO₂) are the major atmospheric pollutants [1]. The European Union’s (E.U.) ambient air quality directives have set the hourly NO₂ concentration threshold as 200 µg/m³ [2]. According to the European Environment Agency (EEA) report published in 2016, NO₂ pollution was responsible for 71,000 premature deaths in the E.U. [3]. Thus, it is important to detect the emission and subsistence of NO₂ in indoor and outdoor air. The main source of NO₂ pollution is the exhaust emissions as a result of the combustion processes in motor vehicles and manufacturing industries [4]. The direct inspection of the exhaust emissions requires devices that can detect NO₂ at high temperatures, i.e., usually ≥500 °C [5]. In this regard,
metal oxide-based electronic gas sensors are the most sought-after devices for applications in harsh environments\cite{6-8}.

According to a recent review of high-temperature gas sensors, Ghosh et al.\cite{9} noted the majority of the metal oxide-based gas sensors work at moderately high temperatures only, while the sensitivity of metal oxides is substantially influenced at temperatures above 350 °C. Albeit a large number of metal oxide-based NO\textsubscript{2} gas sensors are reported \cite{10-13}, only a few work at high temperatures, i.e., ≥600 °C. For instance, Miura et al.\cite{14} reported Yt-stabilized zirconia and spinel ZnFe\textsubscript{2}O\textsubscript{4} sensing electrodes for the electrochemical detection of NO\textsubscript{2} at 600–700 °C. However, chemiresistive-type NO\textsubscript{2} gas sensors for high-temperature applications are rarely reported \cite{13,15,16}. Therefore, the fabrication of high-temperature NO\textsubscript{2} gas sensors for harsh environments is highly desired due to their widespread applications in all types of combustion systems.

This article reports the first high-temperature thick film chemiresistive gas sensor for NO\textsubscript{2} detection at 600 °C. The sensor is based on highly stable spinel zinc ferrite (ZnFe\textsubscript{2}O\textsubscript{4}) nanoparticles prepared via a solid-state, high-energy ball-milling (HEBM) process followed by high-temperature thermal annealing at different temperatures (600, 800, and 1000 °C). ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles have been used for the detection of toxic organic vapors and gases such as acetone at 260\cite{17} and 275 °C\cite{18}, ethanol at 27\cite{19} and 220 °C\cite{20}, toluene at 300 °C\cite{21}, H\textsubscript{2}S at 85 °C\cite{22} and 135 °C\cite{23}, and O\textsubscript{2} at 180 °C\cite{24}. Recently, Runa et al.\cite{25} fabricated a chemiresistive NO\textsubscript{2} gas sensor using ZnO/ZnFe\textsubscript{2}O\textsubscript{4} composites with p-n heterostructure, which revealed excellent selectivity and high gas response toward 0.1–20 ppm NO\textsubscript{2} compared to pure ZnO. However, the gas response diminished rapidly at temperatures of ≥220 °C\cite{25}. In this work, the effects of high-temperature annealing on the crystal structure and NO\textsubscript{2} gas sensing properties are studied. The cubic spinel ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles are stable at high temperatures and demonstrate excellent NO\textsubscript{2} sensing capability at 600 °C with fast response and recovery times.

2. Materials and Methods

Iron(III) oxide (Fe\textsubscript{2}O\textsubscript{3} nanopowder) and zinc oxide (ZnO nanopowder) obtained from MilliporeSigma (Merck KGaA, Darmstadt, Germany) were used to prepare ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles. ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles were synthesized by high-energy ball milling (HEBM) process using a SPEX \textsuperscript{TM} 8000M Mixer/Mill\textsuperscript{TM} (SPEX \textsuperscript{®} SamplePrep, New Jersey, NJ, USA). The ball mill was equipped with a 500-cc stainless steel vessel containing stainless steel balls for mechanical milling of Fe\textsubscript{2}O\textsubscript{3} and ZnO. The mass ratio of steel balls and chemical powders was fixed at 50:1. HEBM was performed under ambient conditions for 2 h at 600 rpm. The product was subsequently vacuum annealed at 600, 800, and 1000 °C for 2 h, and characterized. Corresponding to the annealing temperature (600–1000 °C), the samples were abbreviated as ZnFe\textsubscript{2}O\textsubscript{4}-600, ZnFe\textsubscript{2}O\textsubscript{4}-800, and ZnFe\textsubscript{2}O\textsubscript{4}-1000, respectively.

The crystal structure of the annealed ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles was studied with a STOE STADI P X-ray diffractometer (XRD) (STOE & Cie GmbH, Darmstadt, Germany) using a Cu Kα irradiation source (λ = 1.5406 Å). The samples were scanned in the 2θ range of 10°–90° with a scan rate of 2°/min. The crystallite size (D) is determined by the Scherrer’s formula\cite{26} \((D = K\lambda/B\cos\theta)\), where K is a numerical factor referred to as the crystallite-shape factor with an approximate value of 0.89, λ is the wavelength of the X-rays, B is full-width at half-maximum of the most intense (311) diffraction peak in radians, and θ is the Bragg angle. The experimental lattice parameter (a), X-ray density (ρ\textsubscript{rod}), and the specific surface area (S\textsubscript{A}) are also calculated from the XRD data of annealed ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles, as described elsewhere\cite{27,28}.

The microstructure and surface morphology of ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles were studied with a JEOL JSM-6510 scanning electron microscope (SEM) (JEOL Ltd., Tokyo, Japan). The elemental composition of ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles was determined with the energy-dispersive X-ray spectroscopy (EDS) (JEOL Ltd., Tokyo, Japan).

Thick-film chemiresistor-type gas sensors were fabricated by mixing an appropriate amount of ZnFe\textsubscript{2}O\textsubscript{4}-600, ZnFe\textsubscript{2}O\textsubscript{4}-800, and ZnFe\textsubscript{2}O\textsubscript{4}-1000 nanoparticles with absolute ethanol to make a thick
slurry, which was subsequently drop-coated onto alumina micro-hotplates with vapor-deposited platinum (Pt) contacts. The devices were placed in a vacuum oven at 80 °C for 2 h to dry and stabilize the sensing element. The chemiresistor-type devices were installed in a gas sensing chamber fitted with the electrical connections and the gas inlet and outlet. The measurements were performed with a Keithley 6517A electrometer. The sensor responses were measured simultaneously at 600 °C for 100–400 ppm of NO₂ gas. The sensor response (S) is defined as $S(\%) = (R_g - R_a) \times 100/R_a$, where $R_a$ and $R_g$ are the resistances in air and (100–400 ppm) NO₂ gas.

3. Results and Discussion

Figure 1 shows the XRD pattern of as-synthesized ball-milled ZnFe₂O₄ nanoparticles, referred to as BM-ZnFe₂O₄. The HEBM process yields crystalline BM-ZnFe₂O₄ nanoparticles with a cubic spinel lattice structure as indicated by the presence of characteristic (311) diffraction at 35.22° (2θ) position. The crystallite size ($D$) of as-synthesized BM-ZnFe₂O₄ nanoparticles is 9.30 nm. The lattice parameter ($a$) is calculated to be 8.445 Å, which is in agreement with the values reported for spinel ZnFe₂O₄ nanostructures in the literature and the standard value of bulk ZnFe₂O₄ ($a = 8.441$ Å) [29–31]. The lattice parameter of as-synthesized BM-ZnFe₂O₄ nanoparticles is slightly higher (~0.05%) than the standard value that may be inherent to the ball-milling process because an increase in the lattice parameter of ball-milled ZnFe₂O₄ samples has been reported earlier [32–34].

![Figure 1](image-url)

**Figure 1.** (a) X-ray diffraction pattern of the as-synthesized, ball-milled zinc ferrite (BM-ZnFe₂O₄) nanoparticles. (b) The characteristic (311) plane diffraction of cubic spinel BM-ZnFe₂O₄ nanoparticles.

Theoretically, the cation distribution in a perfect normal spinel ZnFe₂O₄ unit cell is $(\text{Zn}^{2+})_{\text{tet}}[\text{Fe}^{3+}]_{\text{oct}}O_4$, i.e., the tetrahedral (A) and octahedral (B) sites are solely occupied by Zn²⁺ and Fe³⁺ cations, respectively [35]. However, in nanocrystalline ZnFe₂O₄ the contrary distributions of Zn²⁺ and Fe³⁺ cations on both A and B sites are observed [36,37], which form mixed (or random) spinel structure. According to Chinnasamy et al. [32], the slight increase in the lattice parameter is attributed to the lattice expansion caused by the occupation of B sites by Zn²⁺ ions. Thus, the XRD pattern of as-synthesized BM-ZnFe₂O₄ nanoparticles indicates the formation of a mixed cubic spinel lattice. Nonetheless, BM-ZnFe₂O₄ nanoparticles are annealed at different temperatures to examine the effect of annealing on the crystal structure evolution, lattice parameter, crystallite size, and morphology of ZnFe₂O₄ nanoparticles.
High-temperature annealing is an important step in the fabrication of ZnFe$_2$O$_4$ nanoparticles, as it renders stability and improves the physical properties of ZnFe$_2$O$_4$ [38,39]. Figure 2 shows the XRD patterns of ZnFe$_2$O$_4$ nanoparticles annealed at 600, 800, and 1000 °C for 2 h. XRD patterns are refined using Match! (version 3.11.1.183) and FullProf programs for phase identification from X-ray powder diffraction. All samples exhibit a crystalline structure with the characteristic diffractions corresponding to the following miller indices: (111), (220), (311), (222), (400), (422), (511), (440), (620), and (533), which conform to the crystallography open database card number 230–0615 [40]. XRD results substantiate the formation of the cubic spinel ferrite structure with the Fd-3m space group. Also, the XRD patterns align well with the reported literature for ZnFe$_2$O$_4$ nanoparticles [30,41,42]. The absence of additional diffraction peaks corresponding to the impurities or unreacted oxides also reveals the formation of a single-phase cubic spinel lattice [40].

Figure 2. X-ray diffraction patterns of ZnFe$_2$O$_4$ nanoparticles annealed at different temperatures: (a) 600, (b) 800, and (c) 1000 °C.

Figure 3a–c shows the most intense diffractions of the characteristic (311) plane in ZnFe$_2$O$_4$ nanoparticles annealed at different temperatures. The XRD data were used to calculate the crystallite size (D), lattice parameter (a), interplanar distance (d$_{311}$), volume (V), X-ray density ($\rho_{xrd}$), and specific surface area (S) of the annealed ZnFe$_2$O$_4$ nanoparticles. Table 1 presents these structural parameters for different samples. The effect of annealing is obvious because of the changes in position and breadth of (311) diffraction peak as a function of the annealing temperature, which reveal variations in the crystallite size and lattice parameter. The position of (311) shifts to a higher 2θ value as the annealing temperature increases.
While annealing at 800 °C, the lattice parameter (from 8.448 to 8.427 Å) was caused by the redistribution of cations within the nanocrystalline ZnFe$_2$O$_4$, it is believed that Zn$^{2+}$ ions due to their volatile nature escape from the nanoparticles as a function of annealing temperature.

On the other hand, the lattice parameter decreases with the increase in annealing temperature, as shown in Figure 3e. Although this is contrary to the findings reported earlier that demonstrate an increase in the lattice parameter upon high-temperature annealing [47–49], the lattice parameter and crystal structure essentially depend on the processing method and conditions. As discussed above, in the starting sample, as-synthesized BM-ZnFe$_2$O$_4$ nanoparticles exhibit a random spinel structure with a certain degree of inversion that is inherently observed for the ball-milled ZnFe$_2$O$_4$ nanoparticles [32,33]. The reduction in the lattice parameter of annealed ZnFe$_2$O$_4$ nanoparticles can be explained by the redistribution of cations and crystal defects (oxygen vacancies).

During the high-temperature annealing process, both Zn$^{2+}$ and Fe$^{3+}$ cations may alter positions that influence the crystal structure. For instance, Lemine et al. [50] demonstrated that a decrease in the lattice parameter (from 8.448 to 8.427 Å) was caused by the redistribution of cations within the interstitial sites. However, this can also be attributed to the crystal defects [39,51]. It is a well-known fact that high-temperature annealing induces lattice defects and distortions. Furthermore, in the case of nanomaterials, the temperature, the greater is the crystallite size [43–45]. The annealing at 600 °C doubles the crystallite size of ZnFe$_2$O$_4$@600 nanoparticles compared to as-synthesized BM-ZnFe$_2$O$_4$ nanoparticles. While annealing at 800 °C results in a further increase in the crystallite size, the crystallite sizes of ZnFe$_2$O$_4$@800 and ZnFe$_2$O$_4$@1000 nanoparticles are comparable. Thus, the little difference in the crystallites sizes of samples treated at 800 and 1000 °C means the rate or degree of annealing decreases with the increasing crystallite size [46].

As shown in Figure 3d, the crystallite size of ZnFe$_2$O$_4$ nanoparticles increases with the annealing time, which is certainly comprehensible because annealing results in grain growth, and the higher the temperature, the greater is the crystallite size [43–45]. The annealing at 600 °C doubles the crystallite size of ZnFe$_2$O$_4$@600 nanoparticles compared to as-synthesized BM-ZnFe$_2$O$_4$ nanoparticles. While annealing at 800 °C results in a further increase in the crystallite size, the crystallite sizes of ZnFe$_2$O$_4$@800 and ZnFe$_2$O$_4$@1000 nanoparticles are comparable. Thus, the little difference in the crystallites sizes of samples treated at 800 and 1000 °C means the rate or degree of annealing decreases with the increasing crystallite size [46].

Table 1. The structural properties of ZnFe$_2$O$_4$ nanoparticles, annealed at different temperatures (T).

| Sample          | T (°C) | D (nm) | a (Å)   | V (Å$^3$) | d$_{311}$ (Å) | $\rho_{xrd}$ (g/cm$^3$) | S (m$^2$/g) |
|-----------------|-------|-------|---------|----------|---------------|-------------------------|-------------|
| BM-ZnFe$_2$O$_4$|       | 9.30  | 8.445   | 602.3    | 2.546         | 5.321                   | 121.24      |
| ZnFe$_2$O$_4$@600| 600   | 18.71 | 8.430   | 599.0    | 2.542         | 5.350                   | 59.94       |
| ZnFe$_2$O$_4$@800| 800   | 23.03 | 8.424   | 597.8    | 2.540         | 5.361                   | 48.59       |
| ZnFe$_2$O$_4$@1000| 1000  | 23.25 | 8.420   | 597.0    | 2.539         | 5.368                   | 48.07       |

Figure 3. The characteristic (311) plane diffractions of cubic spinel ZnFe$_2$O$_4$ nanoparticles annealed at (a) 600, (b) 800, and (c) 1000 °C. (d) The crystallite size, and (e) lattice parameter of ZnFe$_2$O$_4$ nanoparticles as a function of annealing temperature.
of nanocrystalline ZnFe$_2$O$_4$, it is believed that Zn$^{2+}$ ions due to their volatile nature escape from the lattice during thermal treatment that successively results in oxygen vacancies [39,52]. Thus, a decrease in the lattice parameter (from 8.445 Å for BM-ZnFe$_2$O$_4$ to 8.420 Å for ZnFe$_2$O$_4$@1000) is attributed to the cationic redistribution (distortion) and lattice compression caused by escaping Zn$^{2+}$ ions and oxygen vacancies.

Consequently, the interplanar distance and the volume of the annealed ZnFe$_2$O$_4$ nanoparticles are reduced as a function of the annealing temperature. On the other hand, the X-ray density increases (from 5.321 g cm$^{-3}$ for BM-ZnFe$_2$O$_4$ to 5.368 g cm$^{-3}$ for ZnFe$_2$O$_4$@1000) with the increase in annealing temperature. However, as shown in Table 1, the specific surface area is reduced to 48 m$^2$ g$^{-1}$ due to an increase in the crystallite size of the annealed ZnFe$_2$O$_4$ nanoparticles. These results demonstrate that ZnFe$_2$O$_4$@1000 and ZnFe$_2$O$_4$@800 nanoparticles have bigger crystallite size and smaller specific surface area, but the greatest number of defect sites (as oxygen vacancies) and a geometrically frustrated [53] or distorted cubic spinel crystal structure compared to as-synthesized BM-ZnFe$_2$O$_4$ nanoparticles.

Figure 4a–c shows the SEM images of ZnFe$_2$O$_4$ nanoparticles annealed at different temperatures. An increase in the annealing temperature (to 1000 °C) results in a more compact surface, as shown in Figure 4c: the micrograph of ZnFe$_2$O$_4$@1000 nanoparticles. On the other hand, ZnFe$_2$O$_4$@600 nanoparticles annealed at 600 °C (Figure 4a) show less compact surface morphology with smaller particle size and relatively less aggregation of nanoparticles into clusters. The ZnFe$_2$O$_4$@800 nanoparticles demonstrate a similar surface morphology with slightly larger aggregates of nanoparticles, as shown in Figure 4b.

![Figure 4](image-url)

**Figure 4.** Scanning electron microscopy images of ZnFe$_2$O$_4$ nanoparticles annealed at (a) 600, (b) 800, and (c) 1000 °C. The respective histograms are given in the inset. (d) Energy-dispersive X-ray spectrum of ZnFe$_2$O$_4$ nanoparticles annealed at 1000 °C.
As the annealing temperature increases, the relative percentage of Fe increases while the proportions of Zn and O decrease. A decrease in the oxygen content with increasing temperature is attributed to theoretically calculated values (wt.% or at.%). Annealed ZnFe₂O₄ nanoparticles exhibit variations. The increase in the Fe/Zn ratio as a function of annealing temperature may be attributed to the volatile nature of Zn²⁺ ions [39], as discussed earlier. Thus, the results are consistent and exhibit the microstructure evolution in the annealed ZnFe₂O₄ nanoparticles as a function of annealing temperature.

Table 2 presents the elemental composition of the annealed ZnFe₂O₄ nanoparticles. Compared to theoretically calculated values (wt.% or at.%), annealed ZnFe₂O₄ nanoparticles exhibit variations. The increase in the Fe/Zn ratio as a function of annealing temperature may be attributed to the volatile nature of Zn²⁺ ions [39], as discussed earlier. Thus, the results are consistent and exhibit the microstructure evolution in the annealed ZnFe₂O₄ nanoparticles as a function of annealing temperature.

Figure 5 shows three-dimensional surface micrographs and topographic profiles of the sensing layers composed of ZnFe₂O₄ nanoparticles annealed at different temperatures. ZnFe₂O₄@600 surface exhibits a relatively smooth profile and roughness (Figure 5a). On the other hand, ZnFe₂O₄@800 (Figure 5b) and ZnFe₂O₄@1000 (Figure 5c) nanoparticles demonstrate higher roughness, greater particle size, and cluster formation. Thus, both X-ray diffraction and microscopic results indicate that ZnFe₂O₄ nanoparticles annealed at 800 and 1000 °C exhibit bigger crystallite size and a compact surface microstructure compared to those annealed at 600 °C.

Table 2. The chemical composition of ZnFe₂O₄ nanoparticles annealed at different temperatures.

| Sample               | Zn (%) | Fe (%) | O (%) |
|----------------------|--------|--------|-------|
| ZnFe₂O₄@600          | 26.61  | 14.08  | 47.15 | 29.17 | 26.24 | 56.75 |
| ZnFe₂O₄@800          | 25.60  | 13.51  | 48.04 | 29.64 | 26.36 | 56.85 |
| ZnFe₂O₄@1000         | 25.65  | 13.68  | 48.67 | 30.34 | 25.69 | 55.98 |
Figure 6 demonstrates the NO$_2$ gas response of ZnFe$_2$O$_4$ nanoparticles annealed at different temperatures. The sensor measurements are performed at 600 °C. The as-synthesized BM-ZnFe$_2$O$_4$ nanoparticles based chemiresistive devices are not stable at 600 °C and do not show a measurable response to NO$_2$ gas. On the other hand, all the annealed ZnFe$_2$O$_4$ samples show a significant measurable response to 100–400 ppm NO$_2$, as shown in Figure 6. The sensor responses are generally saturated after ~4 min of exposure to the different concentrations of NO$_2$ gas. ZnFe$_2$O$_4$@1000 nanoparticles exhibit the highest NO$_2$ gas response, which is attributed to their greater stability at elevated temperatures and the presence of a large number of lattice defects. ZnFe$_2$O$_4$@600 and ZnFe$_2$O$_4$@800 nanoparticles also exhibit significant gas response at 600 °C. Peng et al. [55] recently demonstrated that the gas sensing properties of ZnFe$_2$O$_4$ nanoparticles could be enhanced by controlling the oxygen vacancies and that ZnFe$_2$O$_4$ nanoparticles with more oxygen vacancies revealed superior gas (acetone vapors) sensing performance at 280 °C. Thus, the higher NO$_2$ response of ZnFe$_2$O$_4$@1000 nanoparticles may be attributed to the oxygen vacancies resulting from high-temperature annealing of nanoparticles.

![Figure 6. Time-dependent sensor response of the annealed ZnFe$_2$O$_4$ nanoparticles toward 100–400 ppm NO$_2$ gas at 600 °C.](image-url)
Figure 7 shows the calibration curves obtained by plotting the maximum gas response of the annealed ZnFe$_2$O$_4$ nanoparticles as a function of gas concentration. All ZnFe$_2$O$_4$ samples exhibit a linear response in the concentration range of 100–400 ppm as demonstrated by the straight lines in Figure 7. The sensitivity of ZnFe$_2$O$_4$-based chemiresistive devices can be calculated from the slope of a straight line. The sensitivity of NO$_2$ sensors follows the order: ZnFe$_2$O$_4$@1000 > ZnFe$_2$O$_4$@800 > ZnFe$_2$O$_4$@600, which describes the effect of annealing temperature on sensor performance. An increase in annealing temperature improves the NO$_2$ sensing properties of ZnFe$_2$O$_4$ nanoparticles. Therefore, ZnFe$_2$O$_4$@1000 nanoparticles exhibit 2.0-fold and 3.2-fold high sensitivity compared to ZnFe$_2$O$_4$@800 and ZnFe$_2$O$_4$@600 nanoparticles, respectively.

![Figure 7](image_url)

**Figure 7.** The calibration curves for different ZnFe$_2$O$_4$ samples showing NO$_2$ sensitivity of the chemiresistive devices.

Figure 8 shows the kinetics of ZnFe$_2$O$_4$-based chemiresistive gas sensors. The response ($\tau_{\text{res}}$) and recovery ($\tau_{\text{rec}}$) times of the annealed ZnFe$_2$O$_4$ nanoparticles are estimated from their response to 300 ppm NO$_2$ gas. All samples show fast response and recovery times. The response times are in the range of 145–195 s and follow the order: ZnFe$_2$O$_4$@800 > ZnFe$_2$O$_4$@600 > ZnFe$_2$O$_4$@1000. Thus, ZnFe$_2$O$_4$@1000 nanoparticles exhibit slightly longer response ($\tau_{\text{res}}$) times compared to ZnFe$_2$O$_4$@600 and ZnFe$_2$O$_4$@800 nanoparticles. The recovery times are sharp (i.e., ≤20 s) for all samples and all sensors exhibit 100% recovery to their original state. At elevated temperatures, the recovery times are generally faster [10]. Overall, ZnFe$_2$O$_4$@1000 nanoparticles exhibit excellent NO$_2$ gas sensing properties such as high sensitivity, good response kinetics, and linear response in the tested concentration range.

![Figure 8](image_url)

**Figure 8.** The response and recovery times of ZnFe$_2$O$_4$ nanoparticles annealed at (a) 600, (b) 800, and (c) 1000 °C calculated from their respective responses to 300 ppm NO$_2$.

The chemiresistive gas sensors function on the principles of changes in resistance of the sensing element when test gas molecules interact with the semiconductor surface [9]. Figure 9 demonstrates
the gas sensing mechanism of ZnFe$_2$O$_4$ nanoparticles. ZnFe$_2$O$_4$ is an $n$-type semiconductor [56]. In principle, when the ZnFe$_2$O$_4$-based chemiresistive device is exposed to air at elevated temperatures, active oxygen species are adsorbed on the surface of ZnFe$_2$O$_4$ nanoparticles. As shown in Figure 9a, O$_2$ molecules are physisorbed (O$_2^-$) at low temperatures (<200 °C) and subsequently chemisorbed (O$^-$ and O$^{2-}$) at elevated temperatures (>200 °C) by capturing mobile electrons (e$^-$) from the surface. This leads to the formation of a charge depletion layer on the surface of ZnFe$_2$O$_4$ nanoparticles. Afterward, the surface is exposed to different concentrations of NO$_2$ gas and NO$_2$ being an electron-withdrawing molecule [57] further extracts mobile e$^-$ from the surface or interacts with the chemisorbed oxygen species, as shown in Figure 9b. Consequently, the density of major charge carriers (e$^-$) decreases, and the thickness of the depletion region increases, which increases the resistance of the device. The redox reactions taking place on the surface of ZnFe$_2$O$_4$ nanoparticles are depicted in Figure 9.

![Figure 9](image_url)

**Figure 9.** The gas sensing mechanism of ZnFe$_2$O$_4$ nanoparticles-based chemiresistive gas sensors.

Considering the mechanism described above, it is important to understand the behavior of ZnFe$_2$O$_4$ nanoparticles annealed at different temperatures. It is believed that semiconducting metal oxides with more oxygen vacancies adsorb a large number of active oxygen species, which in turn facilitates the surface redox reactions with the target gas molecules and improves the gas response [55]. Thus, oxygen vacancies and lattice defects play a major role in determining the gas response of ZnFe$_2$O$_4$ nanoparticles. Therefore, ZnFe$_2$O$_4$@1000 nanoparticles exhibit the best NO$_2$ gas sensing properties despite their slightly bigger crystallite size and smaller specific surface area. Table 3 shows a comparison of ferrite-based chemiresistive NO$_2$ sensors. The results demonstrate the potential of stable ZnFe$_2$O$_4$@1000 nanoparticles for high-temperature gas sensing applications.
Table 3. A comparison of the sensing properties of chemiresistive-type NO\(_2\) gas sensors.

| Material                  | Fabrication Method | Temperature (°C) | Detection Range (ppm) | Response \(^{†}\) (S) | Response Time (s) | Recovery Time (s) | Reference |
|---------------------------|--------------------|------------------|-----------------------|------------------------|-------------------|-------------------|-----------|
| CuFe\(_2\)O\(_4\)         | Coprecipitation    | 27               | 20–240                | 72%                    | 8                 | 5                 | [58]      |
| ZnFe\(_2\)O\(_4\)         | Hydrothermal       | 125              | 1–10                  | 248 \(^{†}\)          | 6.5               | 11                | [59]      |
| Pd-doped BiFeO\(_3\)      | Sol-gel           | 140              | 50–3500               | 93%                    | 60                | 100               | [60]      |
| CoFe\(_2\)O\(_4\)         | Spray pyrolysis    | 150              | 20–80                 | 248 \^{‡}             | 5                 | 114               |           |
| ZnO/ZnFe\(_2\)O\(_4\)     | Wet chemical       | 200              | 0.1–20                | 300 \^{‡}             | 7                 | 15                | [25]      |
| Cu-doped α-Fe\(_2\)O\(_3\)| Electrospinning    | 300              | 5–50                  | 2 \^{†}               | 118               | 258               | [62]      |
| ZnFe\(_2\)O\(_4\)         | Ball-milling       | 600              | 100–400               | 11%                    | 195               | 17                | This work |
| Zn\(_2\)SnO\(_4\)         | Sputtering         | 600              | 50–300                | ~4 \^{‡}              | -                 | -                 | [63]      |

\(^{†}\) The response (S) is reported for the highest tested concentration of NO\(_2\) gas: \(S(%) = \frac{(R_g - R_a)}{R_a} \times 100\). \(^{‡}\) If not reported as S(%), the response is measured as: \(S = \frac{R_g}{R_a}\).

4. Conclusions

In summary, this study presents the effects of annealing temperature on the microstructure evolution and gas sensing properties of ZnFe\(_2\)O\(_4\) nanoparticles. A high-energy ball-milling procedure is used to prepare pure ZnFe\(_2\)O\(_4\) nanoparticles that are annealed at different temperatures (600–1000 °C). ZnFe\(_2\)O\(_4\) nanoparticles exhibit a random spinel lattice structure that is distorted during high-temperature annealing. The XRD results show an increase in the crystallite size, but a reduction in the lattice parameter and volume that is attributed to the presence of lattice defects as oxygen vacancies. The oxygen vacancies play a major role in controlling the sensitivity of ZnFe\(_2\)O\(_4\) nanoparticles. Thus, ZnFe\(_2\)O\(_4\)@1000 nanoparticles (annealed at 1000 °C) reveal the superior gas sensing properties with the highest sensitivity, good response kinetics, and linear response toward 100–400 ppm NO\(_2\) gas. This is the first example of a ZnFe\(_2\)O\(_4\)@1000-based chemiresistive device showing significant gas response and stable sensor performance at 600 °C.

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