



Article WO₃-LaFeO₃ Nanocomposites for Highly Sensitive Detection of Acetone Vapor at Low Operating Temperatures

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Abstract: The development of a rapid, highly sensitive, and dependable acetone sensor holds significant importance for human health and safety. To enhance the acetone sensing performance of LaFeO₃ nanoparticles for practical applications, commercial n-type WO₃ nanoparticles were incorporated as additives. They were directly mixed with LaFeO₃ nanoparticles produced through a sol-gel method, creating a series of WO₃-LFO nanocomposites with varying mass ratios. These nanocomposites were characterized using XRD, SEM, BET, and XPS techniques. Compared to pure LFO nanoparticles, the prepared nanocomposites exhibited larger specific surface areas with enhanced surface reactivity. The introduction of p-n heterojunctions through the mixing process improved the regulation of acetone molecules on internal carrier conduction within nanocomposites. As a result, the nanocomposites demonstrated superior acetone sensing performance in terms of optimal operating temperature, vapor response value, selectivity, and response/recovery speed. Notably, the nanocomposites with a 5wt% addition of WO₃ showed the lowest optimal operating temperature (132 °C), the fastest response/recovery speed (28/9 s), and the highest selectivity against ethanol, methanol, and EG. On the other hand, the nanocomposites with a 10wt% addition of WO3 displayed the maximum vapor response value (55.1 to 100 ppm) at an optimal operating temperature of 138 °C, along with relatively good repeatability, stability, and selectivity.

Keywords: LaFeO₃; WO₃; nanocomposites; acetone; XPS

1. Introduction

Acetone is an extremely versatile solvent with a wide range of applications. It is commonly used to dissolve various substances, such as cellulosics, dyestuffs, fats, greases, gums, resins, oils, and waxes. Furthermore, it serves as a carrier for acetylene in the production of coatings and plastics. In the chemical industry, acetone is an essential raw material for synthesizing numerous products, including bisphenol A, diacetone alcohol, hexylene glycol, isophorone, ketene, methylmethacrylate, and methyl isobutyl ketone [1]. However, it is important to be cautious when handling acetone due to its high volatility and flammability. The risk of explosions exists, especially in environments with high vapor concentrations. Prolonged inhalation of acetone vapors can cause anesthesia, irritation of the eyes, nose, throat, and headaches. Interestingly, acetone naturally occurs in human blood, but it is found in higher concentrations in individuals with diabetes. Consequently, acetone can be used as a biomarker for diabetes detection through breath analysis [2]. Given these factors, developing efficient and reliable acetone vapor sensors is of significant importance for ensuring human safety and promoting public health.

 $LaFeO_3$ (LFO) perovskite is classified as a type of p-type oxide semiconductor. When reducing gas molecules are present, the resistance of the LFO materials increases, and it



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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/). recovers when these gas molecules are removed. LFO exhibits high thermal and chemical stability, making it a promising material for chemiresistive acetone vapor sensing applications [3–9]. However, pure LFO material often exhibits low sensitivity, weak selectivity, or requires high operating temperatures due to its inherent inferior sensing properties as a p-type oxide semiconductor [10].

The gas response process of sensing materials involves the diffusion of gas molecules into the sensing matrix, the adsorption and reaction of gas molecules on the surface, and the conduction of charge carriers within the sensing materials [11]. In order to further enhance the acetone sensing performance of LFO materials to meet practical application requirements, researchers have focused on designing and preparing novel microstructures that improve the adsorption and diffusion of target gas molecules within the sensing matrix. For instance, Song et al. utilized a sorghum straw biotemplate method to prepare a biomorphic porous LFO. The resulting porous structure, large surface area, numerous surface active sites, and increased oxygen vacancies enabled biomorphic porous LFO to exhibit superior acetone sensing performance compared to bulk LFO particles [5]. Lu et al., on the other hand, synthesized yolk-shell LFO microspheres through a hydrothermal method combined with annealing and etching processes. The sensor incorporating these yolk-shell LFO microspheres demonstrated a high response (25.5–100 ppm) and good selectivity toward acetone at an operating temperature of 225 °C [6].

The highly stable crystal structure of LFO perovskite allows for efficient doping at La or Fe sites, which has led researchers to investigate the impact of different doping elements on the acetone vapor-sensing performance of LFO materials. For instance, Murade et al. utilized a sol-gel citrate method to prepare Sr-doped nanostructured LFO. The resulting nanocrystalline La_{0.7}Sr_{0.3}FeO₃ exhibited superior sensing performance toward acetone vapor at 275 °C, demonstrating a rapid response and high sensitivity compared to pure LFO [12]. Hao et al., on the other hand, prepared a series of Ni-doped porous LFO microspheres using a hydrothermal method. By introducing an appropriate amount of Ni²⁺ ions at Fe sites, the prime operating temperature of the LFO microspheres decreased by 40 °C, and the acetone vapor response increased to 82.8–100 ppm [13]. This enhancement in sensing performance was attributed to increased oxygen adsorption and active sites resulting from Ni doping.

In addition to doping elements into the LFO lattice, researchers have discovered that constructing heterostructures with other metal oxide semiconductors and utilizing p-p or p-n heterojunction effects can enhance the regulation of internal carrier conduction, thereby improving the acetone vapor sensing performance of LFO materials. For example, Zhang et al. synthesized a mesoporous p-p heterostructure of La₂O₃/LFO using a one-step hydrothermal method. Compared to pure LFO, the La₂O₃/LFO heterostructure exhibited a higher response value (42.0–100 ppm), better selectivity, and a lower detection limit (500 ppb) for acetone at 200 °C [10]. Liu et al., on the other hand, prepared porous and hollow α -Fe₂O₃/LFO nanostructures using a microwave-assisted hydrothermal method. The gas sensor based on α -Fe₂O₃/LFO showed a high vapor response (48.3–100 ppm), short response/recovery time (16.5/2.0 s), and excellent selectivity toward acetone at 350 °C [14].

WO₃, as an n-type metal oxide semiconductor with a wide band gap, exhibits good chemical stability and high electron mobility, making it a promising host material for chemoresistive acetone sensors [15–17]. For instance, Hu et al. prepared a novel flower-like WO₃-In₂O₃ hollow heterostructure using an in situ etching method. The sensor based on this WO₃-In₂O₃ heterostructure showed a high vapor response (55.0–100 ppm) to acetone at 280 °C [15]. In another study, Zhang et al. synthesized porous MoO₃-WO₃ nanofibers through an electrospinning approach. The nanofibers with a 6% Mo/W molar ratio exhibited a high response of 26.5 toward 100 ppm acetone and a low detection limit of 19.2 ppb at 375 °C [16]. However, it is important to note that the prime working temperatures of these sensors are relatively high.

Commercially available materials are often produced on a large scale, making them more cost-effective compared to lab-synthesized materials. On the other hand, lab-synthesized

materials may possess unique characteristics or enhanced functionality that can be beneficial when combined with commercial materials. Hence, mixing lab-synthesized materials with commercial ones offers the opportunity to leverage the advantages of both types of materials, leading to improved performance and cost effectiveness. In our previous study, we found that preparing nanocomposites using commercial p-type polyaniline (PANI) powders effectively enhanced the acetone sensing performance of lab-synthesized LFO nanoparticles. This improvement was achieved by increasing the amount of oxygen adsorption on the LFO side of the LFO/PANI interface and enhancing the modulation of carrier conduction within the nanocomposite [9]. As a result, the operating temperature was reduced from 144 $^{\circ}$ C to 120 $^{\circ}$ C, and the vapor response to 100 ppm acetone increased from 11.9 to 36.6.

In the current research, LFO nanoparticles synthesized through a sol-gel method were utilized as the host material. Commercial monoclinic-phase WO₃ nanoparticles were explored as a heterostructure material due to the small difference in Fermi energy levels between WO₃ and LFO. This facilitates charge redistribution in the interfacial regions, resulting in faster equilibrium. Various WO₃-LFO nanocomposites with different mass ratios were prepared by directly mixing LFO nanoparticles with commercial WO₃ nanoparticles. XRD, SEM, BET, and XPS techniques were used to characterize the crystal structure, microstructure, pore structure, and surface state. The improved sensing performance of WO₃-LFO nanocomposites for acetone vapor was analyzed from the perspectives of gas adsorption and reaction on the surface.

2. Materials and Methods

2.1. Preparation of Sensing Materials

The LFO nanoparticles were synthesized using a sol-gel method. Analytical grade $La(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, citric acid (CA), and polyethylene glycol (PEG2000) were used as raw materials. Initially, 2.02 mmol of $La(NO_3)_3 \cdot 6H_2O$ (99.0%, Aladdin, Shanghai, China) and 2.03 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ (98.5%, Aladdin) were dissolved in ion-free water while continuously stirring to obtain a homogeneous solution. Then, 8 mmol of CA (99.5%, Aladdin) was added to the solution, serving as a chelator. Subsequently, 2 g of PEG2000 (99.5%, Aladdin) was added to the mixed solution and stirred at 80 °C to form a wet gel. The gel was then transferred to an evaporating dish and heated at 400 °C in air for 30 min to form gel pieces, which were ground into fine powders. These powders were further calcinated at 600 °C for 2 h in an oven to produce the LFO powder samples [18]. Commercial WO₃ nanoparticles (99.8%, Aladdin) were added, mixed, and ground according to mass ratios of 5%, 10%, and 15% with respect to the LFO. For convenience, the resulting nanocomposites were denoted as 5WO₃-LFO, 10WO₃-LFO, and 15WO₃-LFO, respectively.

2.2. Characterization of Sensing Materials

The crystal phase was determined using a Cu K α radiation X-ray diffractometer (Empyrean, PANalytical, Almelo, the Netherlands). The morphology and microstructure were examined using a Field Emission Scanning Electron Microscope (FE-SEM) (Gemini 300, Zeiss, Germany). Surface information was obtained through an X-ray Photoelectron Spectrometer (XPS) with monochromated Al K α radiation (Escalab 250, Thermo Electron Corporation, Waltham, MA, USA). The BET-specific surface area and porous structure were measured using a Surface Area and Porosity Analyzer (ASAP 2460, Micromeritics Instruments Corporation, Norcross, GA, USA).

2.3. Fabrication and Measurement of Sensing Elements

The prepared LFO nanoparticles, WO_3 -LFO nanocomposites, and commercial WO_3 nanoparticles were mixed with terpineol (95.0%, Aladdin) to create a paste. The paste was then coated onto a ceramic tube with a pair of gold electrodes fixed at both ends. Each electrode was connected to two platinum wires to measure electrical signals. The sensor elements were subjected to air calcination at 200 °C for 2 h. To create an indirectly

heated gas sensor configuration, a Ni-Cr heating wire was inserted into the ceramic tube. Subsequently, the sensor underwent a stabilization process at 104 °C for 24 h [19].

The gas sensing properties of the sensors were evaluated using an Intelligent Gas Sensing Analysis System (CGS-8, Beijing Elite Tech Co., Ltd., Beijing, China) in an environment with a relative humidity of 30%. Relative humidity values were set and measured at a temperature of 25 °C. The sample vapors were prepared by vaporizing the corresponding liquid. During a typical test procedure, once the resistances of all the sensors reached a stable state, a specific volume of the target liquid was injected into the test chamber using a micro-injector. The concentration of the target gas was determined using the following formula [20]:

$$C = (22.4\rho \cdot d \cdot V_1) / (M \cdot V_2) \tag{1}$$

where *C* (ppm) represents the desired concentration of the target gas, V_2 (L) is the volume of the test chamber, ρ (g/mL), *d*, V_1 (L), and *M* (g/mol) denote the density, purity, volume, and molecular weight of the liquid, respectively. The vapor response of the sensor is defined as the ratio of the resistance in dry air (R_a) to the resistance in the target gas (R_g). The response time and recovery time refer to the duration needed for the total resistance to change by 90% during the adsorption and desorption processes, respectively [21].

3. Results and Discussion

3.1. Characterization of Sensing Materials

Figure 1 presents the X-ray diffraction (XRD) patterns of the LFO nanoparticles, WO_3 nanoparticles, and WO_3 -LFO nanocomposites. The diffraction peaks observed for pure LFO and WO_3 correspond to the orthorhombic LFO phase (PDF#37-1493) and monoclinic WO_3 phase (PDF#83-0950), respectively. In addition to the diffraction peaks associated with the orthorhombic LFO phase, the XRD patterns of the WO_3 -LFO nanocomposites also exhibit characteristic peaks (002), (020), (200), (022), (202), and (400) of monoclinic WO_3 . As the composite ratio of WO_3 to LFO increases, the intensity of these characteristic peaks of WO_3 becomes more pronounced, indicating the successful preparation of the composite sample.



Figure 1. XRD patterns of the LFO nanoparticles, WO₃ nanoparticles, and WO₃-LFO nanocomposites.

Figure 2 exhibits field emission scanning electron microscopy (FE-SEM) images of the LFO nanoparticles, WO₃ nanoparticles, and WO₃-LFO nanocomposites. The LFO sample that was prepared consists of nanoparticles with sizes ranging from 18.8 to 52.9 nm, with a concentration around 34.5 ± 0.6 nm, as shown in the particle size distribution and Gaussian fitting inset in Figure 2a. The purchased WO₃ sample comprises nanoparticles ranging from 24.5 to 124.5 nm, with particle sizes concentrated around 63.8 ± 1.8 nm (Figure 2b). In Figure 2c–e, it is evident that the agglomeration phenomenon of the WO₃-LFO nanocomposites is mitigated. The WO₃ nanoparticles, which account for a smaller proportion and have larger sizes, are enveloped by the LFO nanoparticles, which have a higher content and smaller sizes. The average particle sizes of $5WO_3$ -LFO, $10WO_3$ -LFO, and $15WO_3$ -LFO 48.3 ± 0.5 nm, 49.5 ± 0.6 nm, and 50.5 ± 0.7 nm, respectively. All particles with relatively clear outlines in the SEM images are included in the particle size statistics.



Figure 2. FE-SEM images of (**a**) LFO, (**b**) WO₃, (**c**) 5WO₃-LFO, (**d**) 10WO₃-LFO, and (**e**) 15WO₃-LFO. The insets show the corresponding particle size distribution.

Figure 3 illustrates the N₂ isothermal adsorption and desorption curves of the LFO nanoparticles, WO₃ nanoparticles, and WO₃-LFO nanocomposites. There is no distinct saturated adsorption plateau, indicating that the pore structure of all samples is irregular. The BET-specific surface areas of the LFO nanoparticles, WO₃ nanoparticles, 5WO₃-LFO, 10WO₃-LFO, and 15WO₃-LFO nanocomposites were determined to be 19.5, 11.4, 22.8, 20.8, and 21.7 m²/g, respectively. This indicates that the introduction of WO₃ increased the specific surface area of the composite material, which is beneficial for enhancing the vapor response. The pore size distribution curves in the insets reveal corresponding BJH average pore sizes of 29.1, 17.2, 25.2, 28.2, and 26.3 nm, respectively. The inclusion of WO₃ led to a slight reduction in the BJH average pore size of the composite material to varying degrees, thereby slightly lowering the Knudsen diffusion coefficient of the target gas molecules within the sensing matrix [21].

Figure 4 displays the La 3*d*, Fe 2*p*, O 1*s*, and W 4*f* core level XPS of LFO and 10WO₃-LFO. All spectra were charge corrected using the C–C peak at 284.8 eV in the C 1*s* XPS as a reference. According to the work by Mullica [22] and Sunding [23], the La 3*d* core level spectra in Figure 4a were deconvoluted into three peaks. The main peak, labeled as $c4f^0$ (c indicates the presence of a core hole, $4f^0$ the absence of electrons in the 4*f* orbital), corresponds to the final state without charge transfer. The two satellite peaks, denoted as $c4f^1L$, represent the bonding and antibonding components of the final state, with an electron transfer from the ligand atom L to the 4*f* orbital [24]. Aside from the satellites, the Fe 2*p* spectra in Figure 4b consist of two doublets that correspond to Fe³⁺ and Fe⁴⁺ ions [24,25]. The O 1*s* spectra in Figure 4c were deconvoluted into three oxygen components: lattice oxygen (O_L), oxygen vacancy (O_V), and chemisorbed oxygen species (O_C) which include the O₂⁻, O⁻, O²⁻ and OH⁻) [11,26]. In the case of the W 4*f* XPS of 10WO₃-LFO,



there is a doublet from the W^{6+} ions, and the fitting of the spectrum reveals an additional doublet at lower binding energies, assigned to the W^{5+} ions [27,28].

Figure 3. N₂ isothermal adsorption and desorption curves of (**a**) LFO, (**b**) WO₃, (**c**) 5WO₃-LFO, (**d**) 10WO₃-LFO, and (**e**) 15WO₃-LFO. The insets show the corresponding pore diameter distribution.



Figure 4. (a) La 3*d*, (b) Fe 2*p*, (c) O 1*s*, and (d) W 4*f* core level XPS of LFO and 10WO₃-LFO.

Compared to pure LFO, the relative content of La $\underline{c}4f^0$ on the surface of LFO nanoparticles in the 10WO₃-LFO nanocomposites decreases from 45.81% to 39.52%. Meanwhile, the relative contents of $\underline{c}4f^1\underline{L}$ (bonding) and $\underline{c}4f^1\underline{L}$ (antibonding) increase from 28.58% and 25.61% to 30.87% and 29.62%, respectively. This indicates that the presence of WO₃ leads to a higher electron transfer from the ligand atoms to the 4*f* orbital of La ions in LFO. The increased relative content of Fe⁴⁺ ions (from 23.53% to 25.43%) and the presence of W⁵⁺ ions (11.93%) in the 10WO₃-LFO nanocomposites demonstrate electron transfer from LFO to WO₃, specifically from Fe³⁺ ions to W⁶⁺ ions. Since the O_V on the surface acts as a good reactive site for the adsorption of oxygen during the sensing process, the higher relative content of oxygen vacancies (O_V) on the surface (33.68%) in the 10WO₃-LFO nanocomposites indicates a stronger surface reactivity for oxygen adsorption.

3.2. Acetone Sensing Performance

Figure 5a illustrates the relationship between resistance and temperature for both the LFO and WO₃-LFO nanocomposite sensing elements in air. It is observed that the addition of a small amount of WO₃, such as 5wt%, lowers the resistance of the nanocomposite material. This is attributed to the formation of a heterojunction between WO₃ and LFO, which facilitates hole transfer from WO₃ nanoparticles to LFO nanoparticles, subsequently reducing the resistance of the nanocomposite material. However, the incorporation of higher amounts of WO₃, such as 10wt% and 15wt%, leads to an increase in the resistance of the nanocomposite material. This could be due to excessive WO₃ obstructing the conduction channels for the main carrier holes. By analyzing the ln [R/T] versus 1000/T relationship depicted in the internal illustration, it can be inferred that the composite resistance follows the small polaron transition model within the temperature range of 168 °C to 186 °C. According to the formula [29,30]:

$$R(T) = R_0 T \exp(E_a / k_B T)$$
⁽²⁾

the corresponding small polaron activation energy (E_a) can be obtained from the slope of the fitting line. The results show that the E_a of the composite material increases with the rise in WO₃ content. Among the different compositions, 5WO₃-LFO exhibits the lowest E_a value of 0.67 eV.

Figure 5b illustrates the relationship between the vapor response and operating temperature for LFO and WO₃-LFO nanocomposite sensing elements exposed to 100 ppm acetone. The vapor response values of all sensing elements exhibit an initial increase followed by a decrease with temperature. At the optimal operating temperature, where the vapor response value reaches its maximum, the WO₃-LFO sensing elements consistently demonstrate higher vapor response values than pure LFO. Specifically, at their respective prime operating temperatures, the vapor response of the 5WO₃-LFO (33.4@132 °C) and 10WO₃-LFO (55.1@138 °C) sensing elements to 100 ppm acetone are two and three times greater than that of the LFO (16.6@138 °C) sensing element, respectively. When compared to other pure LFO and LFO-based composite sensing materials in Table 1, our 5WO₃-LFO and 10WO₃-LFO nanocomposites exhibit higher gas response values at relatively lower optimal operating temperatures. This characteristic is advantageous in terms of energy efficiency for practical applications.

Figure 5c shows the dynamic response of LFO and WO₃-LFO nanocomposite sensing elements to 10–500 ppm acetone at 138 °C. The resistance of the sensing elements increases upon exposure to reducing gas, indicating that the nanocomposite materials exhibit p-type semiconducting properties. As the concentration of reducing acetone increases, the response values of the sensing elements also gradually increase.

Figure 5d illustrates the three consecutive dynamic responses of LFO and WO₃-LFO nanocomposite sensing elements to 100 ppm acetone. All sensing elements showed good repeatability, and the average response/recovery times of the LFO, 5WO₃-LFO, 10WO₃-LFO, and 15WO₃-LFO sensing elements were 37/38 s, 28/9 s, 36/25 s, and 39/77 s, respectively. This indicates that introducing a small amount of WO₃ can accelerate the response and recovery process, while excessive WO₃ can slow it down. The 5WO₃-LFO sensing element demonstrated the fastest response and recovery speed, potentially due to its lowest E_a [31]. Compared to other pure LFO and LFO-based composite sensing materials in Table 1, our WO₃-LFO nanocomposite sensing elements showed a relatively longer response/recovery time, which can be attributed to the negative effect of operating at a lower temperature.

Figure 5e demonstrates the vapor response of LFO and WO₃-LFO nanocomposite sensing elements to 100 ppm acetone over a span of one week at 138 °C. All sensing elements exhibit a relatively stable vapor response with minimal fluctuations. Figure 5f shows the vapor response of LFO and WO₃-LFO nanocomposite sensing elements to

100 ppm different target vapors at 138 °C. All sensing elements demonstrated selective detection of acetone against ethanol, methanol, and ethylene glycol (EG). However, the introduction of WO₃ not only enhanced the vapor response of nanocomposite materials to acetone but also to ethanol, methanol, and EG. The selectivity of the gas-sensitive element toward acetone can be represented by a selectivity factor. The selectivity factor for acetone is defined as the ratio of the gas response of the gas-sensitive element to acetone to the gas response of the same gas-sensitive element to another gas at the same concentration. This parameter provides a measure of the relative sensitivity of the gas-sensitive element to acetone compared to other gases at the same concentration. Although the 10WO₃-LFO nanocomposite showed the highest vapor response to ethanol, methanol, and EG, the highest selectivity factor for acetone was obtained with the 5WO₃-LFO nanocomposite.



Figure 5. For the LFO and WO₃–LFO sensing elements, (**a**) temperature dependence of resistance in the air from 120 to 186 °C, the inset shows the corresponding $\ln[R/T]$ vs. 1000/T from 168 to 186 °C; (**b**) operating temperature dependence of vapor response to 100 ppm acetone from 120 to 186 °C; (**c**) dynamic responses to 10–500 ppm acetone at 138 °C; (**d**) three consecutive dynamic responses to 100 ppm acetone at 138 °C; (**e**) vapor responses to 100 ppm acetone at 138 °C within a week; (**f**) vapor responses to 100 ppm different target vapors at 138 °C.

Sensing Materials	Synthesis Approach	Temperature (°C)	Concentration (ppm)	Response (R _g /R _a)	$\tau_{res./rec.}$ (s).	Ref.
LFO nanocrystalline powders	Sol-gel method	260	0.5	2.1	62/107	[4]
Biomorphic porous LFO	Sorghum straw biotemplate	240	200	12.2	9/18	[5]
Yolk-shell LFO microspheres LFO porous microspheres	Hydrothermal method & annealing and etching process	225	100	25.5	5/25	[6]
	Hydrothermal method	260	100	29.0	9/17	[7]
LFO nanoparticles	Sol-gel method	138	100	16.6	37/38	This work
α-Fe ₂ O ₃ /LFO porous nano-octahedron PANI/LFO nanocomposites	Solvothermal method & annealing process	230	100	21.0	1/3	[8]
	Sol-gel method & compositing process	120	100	36.6	44/102	[9]
Mesoporous La ₂ O ₃ /LFO composites	Hydrothermal method	200	100	42.0	9/15	[10]
Hollow α-Fe ₂ O ₃ /LFO nanostructures	Microwave-assisted hydrothermal method	350	100	48.3	17/2	[14]
5WO ₃ -LFO nanocomposites	Sol-gel method &	132	100	33.4	28/9	This work
10WO ₃ -LFO nanocomposites	Sol-gel method & compositing process	138	100	55.1	36/25	This work

Table 1. Comparison of acetone vapor sensing performance of pure LFO and LFO-based composite sensing materials.

3.3. Sensing Mechanism

Both direct and indirect interactions can occur between vapor molecules and the surfaces of sensing materials. It is widely accepted that indirect interaction, assisted by adsorbed oxygen, plays a more significant role in the resistance change of metal oxides [21]. When p-type LFO is exposed to air, oxygen molecules in the air adsorb on the surface of LFO nanoparticles and transform into $O_{2(ads)}^{-}$ through the following reactions [32].

$$O_{2(gas)} \leftrightarrow O_{2(ads)}$$
 (3)

$$O_{2(ads)} + e^- \leftrightarrow O_{2(ads)}^- (T < 147 \,^\circ C) \tag{4}$$

As shown in Figure 6a, electrons transfer from LFO to the adsorbed oxygen molecules, creating a hole accumulation layer (HAL), thereby reducing the resistance of the LFO nanoparticles. When acetone molecules are introduced, they can react with adsorbed reactive oxygen ions as follows [9]:

$$CH_3COCH_{3(gas)} + 4O^-_{2(ads)} \to 3CO_2 + 3H_2O + 4e^-$$
 (5)

As illustrated in Figure 6b, electrons captured by adsorbed oxygen are reinjected into the conduction band of the LFO, narrowing the HAL and increasing the resistance of LFO nanoparticles. Hence, the higher acetone vapor response of the WO₃-LFO nanocomposites can be partially attributed to the higher surface reactivity, i.e., larger specific surface area and higher relative content of O_V on the surface, as revealed by the BET and XPS results above.

In addition, the vapor response of sensing materials is influenced by the internal conduction of the charge carrier. The work functions of WO₃ and LFO are approximately 5.24 eV [33] and 4.93 eV [34], respectively. When LFO and WO₃ are in contact, electrons are transferred from LFO to WO₃, as confirmed by the XPS results, while holes are transferred

from WO₃ to LFO to balance the Fermi energy level. Additionally, both WO₃ and LFO react with adsorbed oxygen in the air. Figure 6c illustrates that this interaction leads to the formation of a wider HAL on the LFO side and a narrower electron depletion region (EDL) on the WO₃ side. When acetone molecules are introduced, as shown in Figure 6d, electrons captured by adsorbed oxygen are reinjected into the conduction bands of WO₃ and LFO, respectively. The redistribution of carriers caused by changes in carrier concentration at the heterojunction interface further narrows the EDL of WO₃ and the HAL of LFO. As a result, it significantly increases the resistance change of LFO nanoparticles, thereby improving the vapor response of WO₃-LFO nanocomposites.



Figure 6. Energy band structure of (**a**) LFO nanoparticles in air; (**b**) LFO nanoparticles in acetone; (**c**) WO₃-LFO nanocomposites in air; and (**d**) WO₃-LFO nanocomposites in acetone.

For ethanol (C₂H₆O), methanol (CH₄O), and EG (C₂H₆O₂) vapor molecules, the indirect surface interactions assisted by $O_{2(ads)}^{-}$ are as below: [21]:

$$C_2H_5OH_{(gas)} + 3O^-_{2(ads)} \rightarrow 2CO_2 + 3H_2O + 3e^-$$
 (6)

$$HOC_2H_4OH_{(gas)} + 2.5O_{2(ads)}^- \rightarrow 2CO_2 + 3H_2O + 2.5e^-$$
 (7)

$$CH_3OH_{(gas)} + 2O_{2(ads)}^- \rightarrow CO_2 + 2H_2O + 2e^-$$
 (8)

Compared to ethanol, methanol, and EG, acetone molecule have a longer carbon chain and fewer oxygen ions. This allows one acetone molecule to consume more $O_{2(ads)}^-$ and generate a higher number of transferred electrons [21]. Additionally, the bond dissociation energy of CH₃-COCH₃ (352 kJ/mol) is smaller than that of CH₃O-H, C₂H₅O-H, and HOC₂H₄O-H (462 kJ/mol) [35,36]. As a result, the higher response to acetone could be attributed to its longer carbon chain with fewer oxygen ions, as well as the smaller bond dissociation energy of its C-C bond. These factors enable acetone to react more easily with oxygen species and release a larger number of electrons compared to other vapors. However, due to the similar nature of ethanol to acetone, it is challenging to develop a highly selective acetone sensor based on metal oxides [37].

4. Conclusions

The WO₃-LFO nanocomposites were prepared by directly mixing commercial n-type WO₃ nanoparticles with p-type LFO nanoparticles synthesized using the sol-gel method. The nature of the nanocomposite was confirmed through XRD, which showed independent phases of monoclinic WO₃ and orthorhombic LFO, and SEM analysis, which revealed the nanoscale size of both WO₃ and LFO particles. Compared to pure LFO nanoparticles, sensing elements based on WO₃-LFO nanocomposites exhibited improved performance for detecting acetone. This included a lower prime operating temperature, higher vapor response value, faster response/recovery speed, and higher selectivity, all of which depended on the phase composition of the nanocomposites. The BET and XPS results, in combination with the enhanced acetone sensing performance, indicated that the superior performance of the WO₃-LFO nanocomposites can be attributed to the larger specific area and higher relative content of oxygen vacancies, leading to higher surface reactivity. Additionally, the p-n heterostructure formed by WO₃-LFO further enhanced the modulation of the charge carrier's internal conductivity. This research demonstrates that creating p-n heterostructured nanocomposites using suitable commercially available n-type nanoparticles is a convenient and effective approach to enhance the acetone sensing capability of p-type LFO nanoparticles.

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References

- Howard, W.L. Acetone. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2000; pp. 1–15.
- Righettoni, M.; Amann, A.; Pratsinis, S.E. Breath analysis by nanostructured metal oxides as chemo-resistive gas sensors. *Mater. Today* 2015, 18, 163–171. [CrossRef]
- Liu, H.; Chen, Y.; Cao, Y.; Liu, W.; Miao, T.; Cheng, B.; Qin, H.; Hu, J. High performance of p-p heterojunction LaFeO₃/YFeO₃ planar electrode sensor for volatile organic compounds under multi-wavelength light illumination. *Mater. Sci. Semicond. Process.* 2023, 162, 107500. [CrossRef]
- 4. Chen, Y.; Qin, H.; Wang, X.; Li, L.; Hu, J. Acetone sensing properties and mechanism of nano-LaFeO₃ thick-films. *Sens. Actuators B* **2016**, 235, 56–66. [CrossRef]
- 5. Song, P.; Zhang, H.; Han, D.; Li, J.; Yang, Z.; Wang, Q. Preparation of biomorphic porous LaFeO₃ by sorghum straw biotemplate method and its acetone sensing properties. *Sens. Actuators B* **2014**, *196*, 140–146. [CrossRef]
- Wang, B.; Yu, Q.; Zhang, S.; Wang, T.; Sun, P.; Chuai, X.; Lu, G. Gas sensing with yolk-shell LaFeO₃ microspheres prepared by facile hydrothermal synthesis. *Sens. Actuators B* 2018, 258, 1215–1222. [CrossRef]
- Xiao, H.; Xue, C.; Song, P.; Li, J.; Wang, Q. Preparation of porous LaFeO₃ microspheres and their gas-sensing property. *Appl. Surf. Sci.* 2015, 337, 65–71. [CrossRef]

- Zhang, N.; Ruan, S.; Yin, Y.; Li, F.; Wen, S.; Chen, Y. Self-sacrificial template-driven LaFeO₃/α-Fe₂O₃ porous nano-octahedrons for acetone sensing. ACS Appl. Nano Mater. 2018, 1, 4671–4681. [CrossRef]
- Zhang, Y.; Sun, L.; Yu, Z.; Nie, Z.; Cao, E. Constructing p-p heterojunction with PANI to improve the acetone sensing performance of LaFeO₃ nanoparticles. *Appl. Phys. A* 2022, *128*, 355. [CrossRef]
- Wu, H.; Meng, F.; Gong, X.; Tao, W.; Zhao, L.; Wang, T.; Liu, F.; Yan, X.; Sun, P.; Lu, G. A solution to boost acetone sensing performance of perovskite oxides chemiresistors: In-situ derived p-p heterostructures. *Sens. Actuators B* 2023, 378, 133092. [CrossRef]
- 11. Jing, R.; Ibni Khursheed, A.; Song, J.; Sun, L.; Yu, Z.; Nie, Z.; Cao, E. A comparative study on the acetone sensing properties of ZnO disk pairs, flowers, and walnuts prepared by hydrothermal method. *Appl. Surf. Sci.* 2022, 591, 153218. [CrossRef]
- 12. Murade, P.A.; Sangawar, V.S.; Chaudhari, G.N.; Kapse, V.D.; Bajpeyee, A.U. Acetone gas-sensing performance of Sr-doped nanostructured LaFeO₃ semiconductor prepared by citrate sol-gel route. *Curr. Appl. Phys.* **2011**, *11*, 451–456. [CrossRef]
- Hao, P.; Lin, Z.; Song, P.; Yang, Z.; Wang, Q. Hydrothermal preparation and acetone-sensing properties of Ni-doped porous LaFeO₃ microspheres. J. Mater. Sci. Mater. Electron. 2020, 31, 6679–6689. [CrossRef]
- Zhang, D.; Chen, M.; Zou, H.; Zhang, Y.; Hu, J.; Wang, H.; Zi, B.; Zhang, J.; Zhu, Z.; Duan, L.; et al. Microwave-assisted synthesis of porous and hollow α-Fe₂O₃/LaFeO₃ nanostructures for acetone gas sensing as well as photocatalytic degradation of methylene blue. *Nanotechnology* 2020, *31*, 215601. [CrossRef] [PubMed]
- 15. Hu, J.; Xiong, X.; Guan, W.; Long, H.; Zhang, L.; Wang, H. Self-templated flower-like WO₃-In₂O₃ hollow microspheres for conductometric acetone sensors. *Sens. Actuators B* **2022**, *361*, 131705. [CrossRef]
- 16. Zhang, J.; Lu, H.; Lu, H.; Li, G.; Gao, J.; Yang, Z.; Tian, Y.; Zhang, M.; Wang, C.; He, Z. Porous bimetallic Mo-W oxide nanofibers fabricated by electrospinning with enhanced acetone sensing performances. *J. Alloys Compd.* **2019**, *779*, 531–542. [CrossRef]
- 17. Zhang, J.; Lu, H.; Yan, C.; Yang, Z.; Zhu, G.; Gao, J.; Yin, F.; Wang, C. Fabrication of conductive graphene oxide-WO₃ composite nanofibers by electrospinning and their enhanced acetone gas sensing properties. *Sens. Actuators B* **2018**, *264*, 128–138. [CrossRef]
- 18. Cao, E.; Qin, Y.; Cui, T.; Sun, L.; Hao, W.; Zhang, Y. Influence of Na doping on the magnetic properties of LaFeO₃ powders and dielectric properties of LaFeO₃ ceramics prepared by citric sol-gel method. *Ceram. Int.* **2017**, *43*, 7922–7928. [CrossRef]
- Cao, K.; Cao, E.; Zhang, Y.; Hao, W.; Sun, L.; Peng, H. The influence of nonstoichiometry on electrical transport and ethanol sensing characteristics for nanocrystalline LaFe_xO_{3-δ} sensors. *Sens. Actuators B* 2016, 230, 592–599. [CrossRef]
- Zhang, S.; Song, P.; Wang, Q. Enhanced acetone sensing performance of an α-Fe₂O₃-In₂O₃ heterostructure nanocomposite sensor. *J. Phys. Chem. Solids* **2018**, 120, 261–270. [CrossRef]
- 21. Cao, E.; Wu, L.; Zhang, Y.; Sun, L.; Yu, Z.; Nie, Z. Hydrothermal synthesis of cubic-rhombohedral-In₂O₃ microspheres with superior acetone sensing performance. *Appl. Surf. Sci.* 2023, *613*, 156045. [CrossRef]
- 22. Mullica, D.F.; Lok, C.K.C.; Perkins, H.O.; Young, V. X-ray Photoelectron Final-state Screening in La(OH)₃: A multiplet Structural Analysis. *Phys. Rev. B* **1985**, *31*, 4039–4042. [CrossRef]
- Sunding, M.F.; Hadidi, K.; Diplas, S.; Løvvik, O.M.; Norby, T.E.; Gunnæs, A.E. XPS characterisation of in situ treated lanthanum oxide and hydroxide using tailored charge referencing and peak fitting procedures. *J. Electron. Spectrosc. Relat. Phenom.* 2011, 184, 399–409. [CrossRef]
- 24. Cao, E.; Wu, A.; Wang, H.; Zhang, Y.; Hao, W.; Sun, L. Enhanced ethanol sensing performance of Au and Cl comodified LaFeO₃ nanoparticles. *ACS Appl. Nano Mater.* **2019**, *2*, 1541–1551. [CrossRef]
- Cao, E.; Yang, Y.; Cui, T.; Zhang, Y.; Hao, W.; Sun, L.; Peng, H.; Deng, X. Effect of synthesis route on electrical and ethanol sensing characteristics for LaFeO_{3-δ} nanoparticles by citric sol-gel method. *Appl. Surf. Sci.* 2017, 393, 134–143. [CrossRef]
- 26. Wu, L.; Cao, E.; Zhang, Y.; Sun, L.; Sun, B.; Yu, Z. La and Fe co-doped walnut-like cubic-rhombohedral-In₂O₃ for highly sensitive and selective detection of acetone vapor. *Mater. Lett.* **2023**, *336*, 133869. [CrossRef]
- Angelis, B.A.D.; Schiavello, M. X-ray photoelectron spectroscopy study of nonstoichiometric tungsten oxides. J. Solid State Chem. 1977, 21, 67–72. [CrossRef]
- Wang, X.G.; Jang, Y.S.; Yang, N.H.; Yuan, L.; Pang, S.J. XPS and XRD study of the electrochromic mechanism of WO_x films. *Surf. Coat. Technol.* 1998, 99, 82–86. [CrossRef]
- 29. Teresa, J.M.D.; Dorr, K.; Muller, K.H.; Schultz, L. Strong influence of the Mn³⁺ content on the binding energy of the lattice polarons in manganese perovskites. *Phys. Rev. B* **1998**, *58*, R5928–R5931. [CrossRef]
- Zhou, X.D.; Cai, Q.; Yang, J.; Kim, M.; Yelon, W.B.; James, W.J.; Shin, Y.W.; Scarfino, B.J.; Anderson, H.U. Coupled electrical and magnetic properties in (La,Sr)FeO_{3-δ}. J. Appl. Phys. 2005, 97, 10C314. [CrossRef]
- 31. Cao, E.; Chu, Z.; Wang, H.; Hao, W.; Sun, L.; Zhang, Y. Effect of film thickness on the electrical and ethanol sensing characteristics of LaFeO₃ nanoparticle-based thick film sensors. *Ceram. Int.* **2018**, *44*, 7180–7185. [CrossRef]
- Nemufulwi, M.I.; Swart, H.C.; Shingange, K.; Mhlongo, G.H. ZnO/ZnFe₂O₄ heterostructure for conductometric acetone gas sensors. Sens. Actuators B 2023, 377, 133027. [CrossRef]
- Li, F.; Gao, X.; Wang, R.; Zhang, T. Design of WO₃-SnO₂ core-shell nanofibers and their enhanced gas sensing performance based on different work function. *Appl. Surf. Sci.* 2018, 442, 30–37. [CrossRef]
- Han, B.; Zhu, P.; Liu, Y.; Qiu, Q.; Li, J.; Liang, T.; Xie, T. Enhanced photocatalytic degradation activity via a stable perovskite-type LaFeO₃/In₂S₃ Z-scheme heterostructured photocatalyst: Unobstructed photoexcited charge behavior of Z-scheme photocatalytic system exploration. J. Alloys Compd. 2022, 901, 163628. [CrossRef]

- 35. Morán-Lázaro, J.P.; López-Urías, F.; Muñoz-Sandoval, E.; Courel-Piedrahita, M.; Carreon-Alvarez, A.; Rodríguez-Betancourtt, V.M.; Zamudio-Torres, I.; Guillén-López, E.S.; Palafox-Corona, A. Evaluation of MgCo₂O₄ Nanoparticles as a Gas Sensor for the Detection of Acetone in the Diabetic and Non-Diabetic Range. *Electron. Mater. Lett.* **2022**, *19*, 66–75. [CrossRef]
- 36. Luo, Y.-R. Handbook of Bond Dissociation Energies in Organic Compounds; CRC Press: Boca Raton, FL, USA, 2003.
- 37. Amiri, V.; Roshan, H.; Mirzaei, A.; Neri, G.; Ayesh, A.I. Nanostructured Metal Oxide-Based Acetone Gas Sensors: A Review. *Sensors* 2020, 20, 3096. [CrossRef] [PubMed]

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