Ru-functionalized Ni-doped dual phases of α/γ-Fe₂O₃ nanosheets for an optimized acetone detection

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Abstract
Lately novel strategies to enhance the sensing properties on iron oxide have been proposed to achieve high performance gas sensors for acetone detection. In this working report, the synthesis of iron-glycerate (Fe-Gly) using glycerol to combine with Fe³⁺ is first presented. Depending on the thermal treatment, this compound can evolve into γ-Fe₂O₃, α/γ-Fe₂O₃ and α-Fe₂O₃. α/γ-Fe₂O₃ shows better sensing performance as far as acetone detection is concerned. Using the dual phases of α/γ-Fe₂O₃ as a fundamental building block, their sensing properties were further improved using Ni doping and Ru nanoparticles functionalization. The high response and selectivity to acetone detection was ascribed to the synergistic effects of unique nanosheets, mixed phases, rich oxygen vacancies and excellent catalytic activity of Ru nanoparticles.

Graphical abstract

Keywords Fe₂O₃ · Dual phases · Nanosheets · Gas sensor · Acetone detection

Introduction
Nowadays, human beings are more exposed to the environmental treats related to industrial development and resources overconsumption. For example, acetone (CH₃COCH₃) is considered one of the most popular air pollutants because
of its wide utilization as a common reagent and solvent in industries and laboratories [1, 2]. In particular, acetone inhalation may cause irreversible damage to human health. For instance, it may anaesthetize human central nervous system and, in case of a long-term exposure even to its traces, it can cause serious symptoms. Besides, acetone may cause explosions due to its intrinsic properties of having a low boiling point and a flammable nature. Moreover, there is a correlation between the acetone in exhaled breath and the diagnosis of type I diabetes: diabetic patients, in fact, present a higher concentration than 1800 ppb, while the concentration in healthy individual ranges between 300 and 900 ppb [3, 4]. Therefore, an accurate and reliable detection of acetone concentration is extremely important. Admittedly, considerable efforts have been so far devoted to the investigation of various materials for the preparation of acetone gas sensors. Novel sensing materials and new functionalization strategies have been explored to enhance acetone detection.

Over the past decades, metal-oxide semiconductor-based gas sensors have shown great potentials due to their remarkable sensing properties, low cost and easy sensing mechanism [5–8]. Iron oxide (Fe$_2$O$_3$) is one of the most promising metal-oxides, because of its superior properties, such as high sensitivity, easy synthesis, rich raw material resources, non-toxicity, and so forth. Among the four Fe$_3$O$_4$ polymorphs including alpha, beta, gamma, and epsilon, alpha-Fe$_2$O$_3$ is the most stable one and has shown effective gas sensing properties. Diverse methods have been used to prepare alpha-Fe$_2$O$_3$ for developing gas sensors for a wide range of gases [9–14]. Although gamma-Fe$_2$O$_3$ has been less studied in gas sensing, many reports can be found in recent years showing its promising characteristics. Zheng et al. fabricated nanosheets-assembled hollowed-out hierarchical gamma-Fe$_2$O$_3$ microrods using MgO as template, which exhibited a response of 125.5 to 100 ppm acetone at 220 °C [15]. Hjiri’s group has investigated into the effects of Gd doping on the sensing properties of gamma-Fe$_2$O$_3$ for acetone detection. It was found that 3% Gd-doped gamma-Fe$_2$O$_3$ showed the response of 31.2 to 20 ppm acetone, which is 30 times more than that of gamma-Fe$_2$O$_3$ [16].

In addition, the gamma-Fe$_2$O$_3$-based composites such as gamma-Fe$_2$O$_3$/rGO [17] and ZnO/gamma-Fe$_2$O$_3$ [18] have been tested for H$_2$S detection at room temperature. In general, the alpha-Fe$_2$O$_3$ and gamma-Fe$_2$O$_3$ have been studied individually because of their different crystalline structures and intrinsic properties. Only a few reports were found about the combination of alpha-Fe$_2$O$_3$ and gamma-Fe$_2$O$_3$, especially in relation to gas sensor applications. For instance, Zhao et al. prepared porous hollow biphase gamma-alpha-Fe$_2$O$_3$ nanoparticle with a CO$_2$-assisted template, which showed higher sensitivity and selectivity to ethanol than gamma-Fe$_2$O$_3$ powder [19]. Therefore, to achieve excellent sensing performance, it is desirable to prepare iron oxide with the same compositions but different crystalline structures by a certain precursor.

Recently, metal alkoxides by coordinating metal ions with the hydroxyl groups of alcohols have been developed to be an effective method for the fabrication metal oxides [20]. In this study, a novel Fe-Gly nanosheet has been prepared by coordinating Fe$^{3+}$ with glycerol under hydrothermal condition. Then, iron oxide with different crystalline structures, including pure gamma-Fe$_2$O$_3$, alpha-Fe$_2$O$_3$ and their mixed phases, were obtained by controlling the thermal treatment temperature. Interestingly, with regard to acetone detection, the dual phases of alpha/gamma-Fe$_2$O$_3$ nanosheets show better sensing properties than their pure counterparts. Two strategies have been used to improve alpha/gamma-Fe$_2$O$_3$ nanosheets sensing properties: doping and functionalization. Elemental doping has been widely used to tailor the lattice and electronic structure of metal oxide to tune its gas sensing properties [21]. Several elements such as Ce [22], Cu [23], and Sn [24, 25] have been incorporated into alpha-Fe$_2$O$_3$ to induce defects and increase oxygen vacancies density. The achieved results confirm that Ni doping (0.88 wt%) improves the sensing properties of alpha/gamma-Fe$_2$O$_3$ nanosheets. Moreover, the functionalization with Ru nanoparticles (0.41 wt%) further increases its sensing performances. Hence, it is clearly showed that alpha/gamma-Fe$_2$O$_3$ is a potential candidate for acetone detection.

### Experimental section

#### Materials synthesis

All the chemical reagents of analytical grade were purchased from Aladdin Industrial, Inc. (Shanghai, China), and used without any further purification. A hydrothermal route to synthesize Fe$_3$O$_4$ nanosheets is schematically illustrated in Fig. 1. At the very beginning, the Fe-Gly was synthesized by a facile hydrothermal method using hydrated ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) as iron source. A solution was prepared by mixing 10 mL of glycerol into 40 mL of isopropyl alcohol. Later, 2 mmol Fe(NO$_3$)$_3$·9H$_2$O was dissolved in the mixture for 30 min, to form a homogenous solution with constant magnetic stirring. Next, the mixture was sealed in a Teflon-lined autoclave and maintained at the temperature of 180 ℃ for 12 h. After cooling to room temperature, the precursor was collected and washed several times with deionized water and absolute ethanol, and then dried at 60 ℃. Finally, the precursor was calcined at 300 ℃, 400 ℃, and 450 ℃ (heating rate of 2 ℃/min) in air ambient conditions for 2 h to produce gamma-Fe$_2$O$_3$, alpha/gamma-Fe$_2$O$_3$, and alpha-Fe$_2$O$_3$. Ni-alpha/gamma-Fe$_2$O$_3$ was prepared following the same procedure for alpha/gamma-Fe$_2$O$_3$ except for the addition of 0.1 mmol Ni(NO$_3$)$_3$·6H$_2$O.
Synthesis of Ru/Ni-α/γ-Fe₂O₃

In a typical synthetic process, RuCl₃ was dissolved into ethanol to form 0.1 g/mL solution. After completely dispersing Ni-doped Fe-Gly precursor in 20 mL ethanol, 0.405 mL the RuCl₃ solution was added and stirred for 24 h. The product was collected and further calcined at 400 °C in air for 2 h.

Materials characterization

The samples of crystal phase were studied using an X-ray diffraction (XRD, Rigaku TTRIII) with a source of Cu Kα radiation (1.5418 Å) in the 2θ range of 10°–90° in steps of 0.02°. The field emission scanning electron microscopy (FESEM) images were taken on a FEI QUANTA 200 microscope (USA). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were generated using a JEM-2100 (Japan) with energy-dispersive X-ray spectroscopy (EDS). Thermo-gravimetric analysis (TGA) was recorded in a flow of air from room temperature to 800 °C with a heating rate of 10 °C/min. The surface and pore characterization of the α/γ-Fe₂O₃ nanosheets were examined through nitrogen adsorption–desorption measurements at 77.3 K with a Micromeritics ASAP 2010 automated sorption analyser. Before the measurement, the α/γ-Fe₂O₃ nanosheets were degassed at 300 °C. The specific surface area was calculated from the nitrogen adsorption isotherm through Brunauer–Emmett–Teller (BET) method, while the pore distribution was obtained by Barrett–Joyner–Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) investigation was operated using Al Kα (1486.6 eV) X-ray source. To correct the shift caused by the charge effect, all the binding energies were referenced to the C 1s peak at 284.6 eV from the adventitious carbon on the surface.

Gas sensor fabrication and measurement

Extensive details for the gas sensor fabrication and testing were provided in our previous work [26, 27]. To fabricate the gas sensor, a slurry was formed by mixing prepared samples and water, which was further coated onto an alumina tube (4 mm in length, 1.2 mm in external diameter and 0.8 mm in internal diameter) with two Au electrodes connected by Pt wires on both ends of the tube. A Ni–Cr alloy (99.9%) was put through the alumina tube with sensing materials coating to control the working temperature of the gas sensor by tuning the heating voltage. The final sensor unit was obtained by welding the alumina tube and the heating wire onto a pedestal. A completed gas sensor and the details structure of the gas sensor are shown in Fig. 2b, d. The gas-sensing properties were measured using a commercial WS-30 sensing system (Weisheng Instruments Co., Zhengzhou, China), as shown in Fig. 2a. Figure 2c shows the basic testing principle, where $V_h$ is the heating voltage, $R_l$ is a load resistance, $V_{out}$ is the export voltage, and $V_c$ is the working voltage (5 V). During the tests, the air was used both as dilution and reference gas and the relative humidity was maintained at 30% at 20 °C. The volatile organic compounds (VOCs) vapor was obtained by evaporating the corresponding commercial liquid reagents. As widely accepted, the response ($β$) of the sensor is described by the ratio of sensor resistance in air ($R_a$) and in target gas ($R_g$). The response/recovery time is defined as the time required for the gas sensor to reach 90% of the stable resistance when exposed to the reference air or target gas.
Results and discussion

Structural and morphological characterization

The $\text{Fe}_2\text{O}_3$ was obtained by decomposing the Fe-Gly precursor which was formed using polyalcohol of glycerol as a strong coordinator under hydrothermal condition. The decomposition process of Fe-Gly was examined by thermogravimetric analysis, as shown in Fig. 3. First, we can see a small weight loss of 2.23% below 180 °C, which is ascribed to the evaporation of residual water in the Fe-Gly precursor. Then, a prominent weight loss of 44.81% occurs when the temperature is further increased to 318 °C due to the decomposition of organic ligands. An exothermic peak is simultaneously observed at 304.93 °C in the DSC curve. To explore the effect of thermal treatment on the products in the final phase, different temperatures of 300 °C, 400 °C and 450 °C were selected to remove organic compounds and synthesize iron oxides. The crystal structure and the phase of the samples prepared at three different temperatures were analyzed through XRD, the results are shown in Fig. 4. The phases of the products can be identified in comparison with the Joint Committee for Powder Diffraction Standards (JCPDS) file number of 33–0664 ($\alpha$-Fe$_2$O$_3$) and 39–1346 ($\gamma$-Fe$_2$O$_3$). The pure maghemite ($\gamma$-Fe$_2$O$_3$) is formed at 300 °C. In this phase there is a spinel structure constituted with 16 $\text{Fe}^{3+}$ ions in tetrahedral sites, 8$\text{Fe}^{3+}$ ions at octahedral sites, and 32 $\text{O}^{2-}$ ions. The mixed phases of $\alpha/\gamma$-Fe$_2$O$_3$ are created at 400 °C. The rhombohedral $\alpha$-Fe$_2$O$_3$ (hematite) can be produced at 450 °C. This phase consists of iron atoms surrounded by six oxygen atoms. Apart from the phase change, the increase in diffraction intensity in Fig. 4b reveals that the crystallinity is increased at the annealing temperature. Especially, the dual phases of Fe$_2$O$_3$ are expected to exhibit better sensing properties due to their capability of modifying the electron transfer to favor the reaction of target gas molecules. We studied the effect of Ni doping in $\alpha/\gamma$-Fe$_2$O$_3$ to enhance the sensing properties towards acetone. XRD data in Fig. 4 show no noticeable change, suggesting that the annealing temperature is the key factor in determining the final phase. To further improve the sensing properties,
Ru functionalization was carried out. After converting into α/γ-Fe₂O₃, due to Ru nanoparticles low contents, no diffraction peaks were observed.

The morphology of the nanostructures was characterized by SEM and TEM analysis. Figure 5a shows the SEM image of α/γ-Fe₂O₃, revealing the nanosheets morphology with a slightly assembly feature. Figure 5b provides the low resolution TEM micrograph of α/γ-Fe₂O₃, which clearly indicates the nanosheets with a thin layer. The α/γ-Fe₂O₃ nanosheets will be greatly helpful for the dispersion of Ru nanoparticles functionalization. Moreover, it could provide a considerable amount of edge sites for gas molecules absorption [28]. The lattice-resolved TEM image indicates lattice fringes with spacing of 0.229 and 0.221 nm, which are attributed to (006) and (113) plane of α-Fe₂O₃ (Fig. 5c). Meanwhile, the interplanar spacing of 0.482 and 0.295 nm corresponding to (111) and (220) planes of γ-Fe₂O₃ (Fig. 5d) is observed. Especially, the lattice fringes of both α-Fe₂O₃ and γ-Fe₂O₃ are simultaneously detected, as shown in figure e. The (113) facet of α-Fe₂O₃ is neighbored with (310) and (220) planes of γ-Fe₂O₃, which verifies the existence of interface of α-Fe₂O₃ and γ-Fe₂O₃. The EDS elemental mapping of Ru/Ni-α/γ-Fe₂O₃ sample is shown in Fig. 4f–i. There is a uniform distribution and the coexistence of O, Fe, Ni, and Ru elements. It is worth to note the contents of 0.88 wt% Ni and 0.41 wt% Ru are detected.

To determine the specific surface area and pore structure of the samples, the nitrogen adsorption–desorption isotherms for α/γ-Fe₂O₃ was performed, as shown in Fig. 6. The hysteresis loop indicates a mesoporous character. The Brunauer–Emmett–Teller (BET) surface area resulted 52.99 m²/g. In addition, the pore size distribution of α/γ-Fe₂O₃ nanosheets shows the emergence of many mesopores with the main size of 7.79 nm (inset in Fig. 6). The large surface area and pore volume are especially beneficial for gas sensing performance. This particularly applies to

![Fig. 5](image_url) a FESEM images, b TEM images of α/γ-Fe₂O₃, and c–e HRTEM images of Ru-Ni-α/γ-Fe₂O₃, f–i EDS elemental mapping of O, Fe, Ni and Ru in Ru/Ni-α/γ-Fe₂O₃ sample
mesopores. XPS spectra were measured to confirm the surface composition and the chemical state of α/γ-Fe₂O₃ and Ru/Ni-α/γ-Fe₂O₃ samples, as shown in Fig. 7. There are two main peaks with satellite peak related to the Fe 2p and no big difference can be found for the Fe 2p in α/γ-Fe₂O₃ and Ru/Ni-α/γ-Fe₂O₃, which confirms the Fe³⁺ oxidation state [29, 30]. However, the asymmetric O 1s (Fig. 7c, d) could be fitted into two peaks by a Gaussian fitting method with the Shirley background. The peak at a lower binding energy can be attributed to the lattice oxygen in the oxide. Regarding the other peak, which occurs at a relatively higher binding energy, it is ascribed to the surface adsorbed oxygen species playing an important role in the reaction with the analytic gas molecules necessary for the gas detection [31]. The ratio of surface adsorbed oxygen species versus lattice oxygen is 61.8% in Ru/Ni-α/γ-Fe₂O₃, thus higher than the 49.2% in α/γ-Fe₂O₃, confirming its higher reactivity. Moreover, Fig. 7e demonstrates that the binding energies of 855.21 eV and 872.58 eV correspond to Ni 2p₃/2 and Ni 2p₁/2 [32]. Therefore, the heteroatom of Ni was successfully doped in α/γ-Fe₂O₃ compositions. In addition, the binding energy of Ru 3d₃/2 was determined as 284.97 eV, demonstrating the presence of metallic Ru nanoparticles (Fig. 7f) [33].

In brief, the pure α-Fe₂O₃ and γ-Fe₂O₃, and their mixed phases with morphology of nanosheets can be synthesized via Fe-Gly decomposition by controlling the calcining temperature. The advantage of glycerol is that it contains three hydroxyl groups, which are significantly beneficial in combination with Fe³⁺ to form a stable Fe-Gly structure [20]. It is found that the transition-metal-based glycolates are prone to grow sheets, such as crystal nuclei, in which the metal ions are centered in the oxygen octahedral to create two dimensional sheets by sharing their edges [34]. Subsequently, these sheet-like nuclei gradually assemble into nanosheets under the hydrothermal conditions. The following thermal treatment plays a crucial role to control the oxide phase, because different precursors will go through different decomposition and phase transformation routes. Most importantly, the unique nanosheets morphology with abundant edges and two-phase combination could facilitate further modification, such as Ni doping and Ru functionalization, for the achievement of outstanding sensing performance.

### Gas sensing properties

Gas sensors based on samples annealed at different temperatures were prepared to verify the effect of the phase on their functional properties. As shown in Fig. 8b, all the materials show a bell-shaped curve indicating the response as a function of operating temperature in the range of 180–280 °C with a relative humidity value of 30% at 20 °C. The responses gradually increase to a maximum value and then decrease alongside the further increase in the working temperature. In general, a diffusion theory is used to explain this widely found phenomenon for gas sensors [35]. At low operating temperature, there is no adequate thermal energy to promote the ionization of absorbed oxygen molecules to generate a large number of oxygen species (O²⁻, O⁻ and O₂⁻). Moreover, the reaction between acetone molecules with those active oxygen species is unfavorable. As a result, the response of the gas sensor increases with the increase in operating temperature to reach a maximum value. However, the response gradually decreases when the operating temperature is beyond a critical point due to the gas adsorption barrier to hinder the adsorption of acetone molecules on the surface of sensing materials. Therefore, the presence of an optimal working temperature is the balance between the surface reaction activation energy and binding energy between gas molecules and sensing materials. α/γ-Fe₂O₃ exhibits the highest response of 150 towards 500 ppm acetone at 230 °C, which is much better than that of the pure α-Fe₂O₃ and γ-Fe₂O₃. Results obtained from both strategies (Ni doping and Ru functionalization) to improve acetone sensing show a great increase in performances together with a change in the optimal working temperature. Specifically, the response of the sensor based on Ru-functionalized Ni-doped α/γ-Fe₂O₃ reaches its maximum of 780 at 180 °C (Fig. 8a). A similar behavior is observed in the case of Ni-doped α/γ-Fe₂O₃ with the best response of 210 at 200 °C. The optimal temperature of both is lower than α/γ-Fe₂O₃. In particular, the response value of Ru/Ni-α/γ-Fe₂O₃ is more than four times greater than that of α/γ-Fe₂O₃. It is sufficient to prove

![Fig. 6](image-url) Nitrogen adsorption–desorption isotherms recorded at 77 K for α/γ-Fe₂O₃.
that precious metals have a positive effect on improving its sensing performances. The gas sensing performance of the $\alpha/\gamma$-Fe$_2$O$_3$, Ni-$\alpha/\gamma$-Fe$_2$O$_3$ and Ru/Ni-$\alpha/\gamma$-Fe$_2$O$_3$-based gas sensors to 1–500 ppm acetone at their optimal working temperature was thoroughly
studied and compared. The dynamic response curves increase sharply with acetone introduction and then quickly return to the baseline when the sensors were exposed to air again (Fig. 9a), suggesting the reversibility of acetone detection with fast response and recovery times. The Ru/Ni-α/γ-Fe₂O₃-based gas sensor possesses a much higher response to acetone than the α/γ-Fe₂O₃ and Ni-α/γ-Fe₂O₃ ones. Ru/Ni-α/γ-Fe₂O₃ exhibits a detection limit of 1 ppm acetone with a response of 2.7. It is important to note that a good linear relationship between the responses ($\beta$) and the acetone concentrations ($C$) is evident in all samples, as depicted in Fig. 9b. Taking Ru/Ni-α/γ-Fe₂O₃ as an example, the linear relationship can be expressed as $1.56C - 5.40$. The relative correlation coefficient $R^2$ is 0.99846, thereby indicating a promising candidate for the practical acetone detection.

Furthermore, the sensor of Ru/Ni-α/γ-Fe₂O₃ shows a stable behavior without any clear degradation after five cycles, as shown in Fig. 9c. The results illustrate that the ability of α/γ-Fe₂O₃ nanosheets to detect acetone can be enhanced by Ni doping and greatly improved by further Ru functionalization. Meanwhile, fluctuation in response towards 500 ppm acetone in 30 days is about 7%, as shown in Fig. 9d, suggesting a good stability. In addition, when the acetone concentration is 50 ppm, the response of gas sensors based on α/γ-Fe₂O₃, Ni-α/γ-Fe₂O₃, Ru/Ni-α/γ-Fe₂O₃ are 22 s, 21 s and 16.5 s, and recovery times are 20.6 s, 19.5 s and 18 s, as illustrated in Fig. 10. In particular, the Ru/Ni-α/γ-Fe₂O₃ sensor exhibits rapid response and recovery time at a lower operating temperature, which is attributed to the formation of rich oxygen vacancies after Ni doping and the effective sensitization of noble metal Ru.

The specific gas sensor selectivity for the target gas is very important in practical applications. Therefore, the selectivity of the samples was tested at their corresponding optimal working temperature. Figure 11 shows their response to several normal VOCs at a concentration of 500 ppm. α/γ-Fe₂O₃, Ni-α/γ-Fe₂O₃ and Ru/Ni-α/γ-Fe₂O₃-based gas sensors exhibit relatively large response values to acetone even compared to the other VOCs tested, implying a good selectivity.

**Acetone sensing mechanism**

A comparison of acetone sensing performances of Fe₂O₃ prepared in this work and other recent reports in literature is summarized in Table 1. Numerous reports showed higher optimal working temperature and lower responses. The comparative assessment clearly suggests that the Ru/Ni-α/γ-Fe₂O₃ possesses superior sensing characteristics toward acetone. In general, the sensing mechanism for resistive-based gas sensors is heavily dependent on the change of resistance originated from the adsorption and desorption of gas molecules on the surface of the sensing materials between the switch of air and analyte, as schematically shown in Fig. 12a. Figure 12b shows the comparison of the resistance of α/γ-Fe₂O₃ and Ru/Ni-α/γ-Fe₂O₃ to acetone with a concentration of 50 ppm.

The gas sensing mechanism of a $n$-type metal oxide is based on resistance variation. As the oxide is exposed to air, oxygen molecules on its surface are adsorbed, producing oxygen species, such as $O^{2-}$, $O^-$ and $O_2^-$ according to the working temperature and capturing free electrons from the metal oxide, thereby leading to the formation of electron-depletion layers [41, 42]. In acetone atmosphere, adsorbed acetone is oxidized by ionosorbed oxygen, thus trapped electrons can be released back into the conducting valance to decrease the oxide resistance. These processes cause a resistance change according to its concentration, which is expressed below, as previously reported [43]:

$$O_2 + 2e^- \leftrightarrow 2O^- + 2e^- \leftrightarrow 2O^{2-}$$  \hspace{1cm} (1)

$$CH_3COCH_3 + 8O^{2-} \rightarrow 3CO_2 + 3H_2O + 16e^-.$$  \hspace{1cm} (2)

Ru/Ni-α/γ-Fe₂O₃ superior sensing performances and high selectivity for acetone may be attributed to several factors, such as the unique nanosheet morphology, the coexistence of two phases, oxygen vacancies density, Ni doping, and the catalytic activity of Ru nanoparticles. The nanosheet morphology can maximize the surface area and edge, thus providing a large number of active sites for gas molecules absorption. More
the formation of oxygen vacancies to provide more active sites\cite{25, 47}. In addition, the Ni\textsuperscript{2+} ions may be easily oxidized to a higher state of Ni\textsuperscript{3+} ions, which can serve as catalytic centers to favor the reactions between acetone molecules with active oxygen species\cite{48}. The reasons of enhanced gas sensing performances after Ru functionalization can be explained by a chemical sensitization mechanism of noble metal nanoparticles\cite{49, 50}. The high catalytic properties of Ru nanoparticles can activate the absorbed oxygen molecules to form oxygen species. Furthermore, it will catalyze the reaction between target gas of acetone molecules on the surface of Ru-Ni/α/γ-Fe\textsubscript{2}O\textsubscript{3} to reduce the active energy. Thus, the catalytic activity of the Ru nanoparticles together with doped Ni\textsuperscript{2+} centers results in a lower optimal working temperature, higher response and the excellent selectivity for acetone detection.

Defects are present on these edges, favoring its reaction with acetone molecules. Moreover, the presence of phase boundaries may cause a more efficient modification in the electron depletion layer\cite{44}. Similar phenomena were investigated to enhance the sensing performance in the mixed hexagonal and cubic phases of In\textsubscript{2}O\textsubscript{3}\cite{45} as well as the coexistence of tetragonal and orthorhombic phases of SnO\textsubscript{2}\cite{46}. Moreover, as revealed by the EPR spectra in Fig. 12c, with the peak of oxygen vacancies at $g = 2.004$, the α/γ-Fe\textsubscript{2}O\textsubscript{3} is rich in oxygen vacancies which is slightly increased following Ni doping and Ru functionalization. The oxygen vacancies are generally electron donors. Increasing the amount of oxygen species on the surface should promote the reaction with adsorbed oxygen molecules, inducing a higher response. The lattice distortion originating from the Ni\textsuperscript{2+} substitution for Fe\textsuperscript{3+} could produce the formation of oxygen vacancies to provide more active sites\cite{25, 47}. In addition, the Ni\textsuperscript{2+} ions may be easily oxidized to a higher state of Ni\textsuperscript{3+} ions, which can serve as catalytic centers to favor the reactions between acetone molecules with active oxygen species\cite{48}. The reasons of enhanced gas sensing performances after Ru functionalization can be explained by a chemical sensitization mechanism of noble metal nanoparticles\cite{49, 50}. The high catalytic properties of Ru nanoparticles can activate the absorbed oxygen molecules to form oxygen species. Furthermore, it will catalyze the reaction between target gas of acetone molecules on the surface of Ru-Ni/α/γ-Fe\textsubscript{2}O\textsubscript{3} to reduce the active energy. Thus, the catalytic activity of the Ru nanoparticles together with doped Ni\textsuperscript{2+} centers results in a lower optimal working temperature, higher response and the excellent selectivity for acetone detection.
Conclusion

The dual phases of $\alpha/\gamma$-$\text{Fe}_2\text{O}_3$ nanosheets and their counterparts were achieved with a reliable and controllable synthesis method by conversing Fe-Gly at a different calcining temperature. The Fe-Gly precursor was hydrothermal synthesized using coordinator of glycerol. This reveals that the mixed phases of $\alpha/\gamma$-$\text{Fe}_2\text{O}_3$ exhibit the best gas sensing properties to acetone. Based on these findings, $\alpha/\gamma$-$\text{Fe}_2\text{O}_3$ is proposed as a unique building sensing material, and Ni doping and Ru modification were further investigated as strategies to improve its sensing performances. The results show that Ru/Ni-$\alpha/\gamma$-$\text{Fe}_2\text{O}_3$ has a lower optimal temperature (180 °C), a high response value (780 to 500 ppm acetone), a fast response/recovery time (16.5 s/18.0 s (50 ppm)) and good selectivity against potential interfering compounds. In addition, the response calibration curves towards acetone concentration are linear in a wide range. Hence, $\alpha/\gamma$-$\text{Fe}_2\text{O}_3$ is a potential candidate for acetone sensors; moreover, Ni doping and Ru functionalization are effective strategies for the improvement of sensing performance.

![Fig. 10 Response and recovery time of $\alpha/\gamma$-$\text{Fe}_2\text{O}_3$, Ni-$\alpha/\gamma$-$\text{Fe}_2\text{O}_3$, Ru/Ni-$\alpha/\gamma$-$\text{Fe}_2\text{O}_3$ to 50 ppm acetone](image)

![Fig. 11 Gas response of $\alpha/\gamma$-$\text{Fe}_2\text{O}_3$, Ni-$\alpha/\gamma$-$\text{Fe}_2\text{O}_3$ and Ru/Ni-$\alpha/\gamma$-$\text{Fe}_2\text{O}_3$-based sensors toward different gases with a concentration of 500 ppm](image)

| Table 1 | Comparison of acetone sensing performance of gas sensors based on typical Fe$_2$O$_3$ with various microstructures |
|---------|----------------------------------------------------------------------------------------------------------------------------------|
| Materials | $C$ (ppm) | $T$ (°C) | Response ($\beta$) | $t_{\text{rec}}/t_{\text{rec}}$ (s) | LOD | Refs. |
| Ce-$\alpha$-Fe$_2$O$_3$ nanosphere | 100 | 220 | 26.3 | 7/80 | 5 ppm | [22] |
| Pt-loaded Fe$_2$O$_3$ nanocubes | 100 | 139 | 25.7 | 3/22 | 0.2 ppm | [36] |
| TiO$_2$/α-Fe$_2$O$_3$ nanocomposites | 100 | 225 | 21.9 | 13/10 | 5 ppm | [37] |
| Au NP modified α-Fe$_2$O$_3$ nanodisk | 100 | 275 | 19.5 | 4/7 | 50 ppb | [38] |
| Hierarchical hollow SnO$_2$/α-Fe$_2$O$_3$ microcubes | 200 | 270 | 9.3 | 6/7 | 5 ppm | [39] |
| Flower-like α-Fe$_2$O$_3$/MWCNTs nanocomposites | 50 | 220 | 20.32 | 2.3/10.6 | 5 ppm | [40] |
| Gd/γ-Fe$_2$O$_3$ nanopowders | 20 | 200 | 31.2 | 50/- | – | [16] |
| Hollowed-out hierarchical γ-Fe$_2$O$_3$ microrods | 100 | 220 | 125.5 | 0.9/15 | – | [15] |
| Ru/Ni-α/γ-Fe$_2$O$_3$ sheets | 50 | 180 | 65 | 16.6/18 | 1 ppm | This work |
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Fig. 12 a Schematic diagram of the sensing mechanism, b diagram of resistance of α/γ-Fe₂O₃ and Ru/Ni-α/γ-Fe₂O₃ to acetone with a concentration of 50 ppm, c EPR spectra of α/γ-Fe₂O₃ and Ru/Ni-α/γ-Fe₂O₃.
References

1. Amiri, V., Roshan, H., Mirzaei, A., et al.: Nanostructured metal oxide-based acetonitrile gas sensors: a review. Sensors 20, 3096 (2020)
2. Baharuddin, A.A., Ang, B.C., Haseeb, A., et al.: Advances in chemiresistive sensors for acetonitrile gas detection. Mater. Sci. Semicond. Process. 103, 104616 (2019)
3. Broza, Y.Y., Rotem, V., Orna, B., et al.: Synergy between nanomaterials and volatile organic compounds for non-invasive medical evaluation. Chem. Soc. Rev. 47, 4781–4859 (2018)
4. Zhou, X., Xue, Z., Chen, X., et al.: Nanomaterial-based gas sensors used for breath diagnosis. J. Mater. Chem. B 8, 3231–3248 (2020)
5. Li, Z., Li, H., Wu, Z., et al.: Advances in designs and mechanisms of semiconducting metal oxide nanostructures for high-precision gas sensors operated at room temperature. Mater. Horiz. 6, 470–506 (2019)
6. Walker, J.M., Akbar, S.A., Morris, P.A.: Synergistic effects in gas sensing semiconducting oxide nano-heterostructures: a review. Sens. Actuators B Chem. 286, 624–640 (2019)
7. Yang, H., Bai, X., Hao, P., et al.: A simple gas sensor based on zinc ferrite hollow spheres: highly sensitive, excellent selectivity and long-term stability. Sens. Actuators B Chem. 280, 34–40 (2018)
8. Xiong, Y., Liu, W., Qiao, X., et al.: Confined synthesis of 2D ultrathin ZnO/Co3O4 nanomeshes heterostructure for superior triethanolamine detection at low temperature. Sens. Actuators B Chem. 346, 130486 (2021)
9. Siebert, L., Wolff, N., Ababii, N., et al.: Facile fabrication of semiconducting oxide nanostructures by direct ink writing of readily available metal microparticles and their application as low power acetonitrile gas sensors. Nano Energy 70, 104420 (2020)
10. Xue, Y., Wang, Y.: A review of the α-Fe2O3 (hematite) nanotube structure: recent advances in synthesis, characterization, and applications. Nanoscale 12, 10912–10932 (2020)
11. Song, H., Yan, S., Yao, Y., et al.: 3D α-Fe2O3 nanorods arrays/graphene oxide nanosheets as sensing materials for improved gas sensitivity. Chem. Eng. J. 370, 1331–1340 (2019)
12. Wu, Z., Li, Z., Li, H., et al.: Ultrastable response/recovery and high selectivity of the H2S gas sensor based on α-Fe2O3 nano-ellipsoids from one-step hydrothermal synthesis. ACS Appl. Mater. Interfaces 11, 12761–12769 (2019)
13. Wang, P., Zheng, Z., Cheng, X., et al.: Ionic liquid-assisted synthesis of α-Fe2O3 mesoporous nanorod arrays and their excellent trimethylamine gas-sensing properties for monitoring fish freshness. J. Mater. Chem. A 5, 19846–19856 (2017)
14. Teng, Y., Zhang, X.-F., Xu, T.-T., et al.: A spendable gas sensor with higher sensitivity and lowest detection limit towards H2S: porous α-Fe2O3 hierarchical tubule derived from poplar branch. Chem. Eng. J. 392, 123679 (2020)
15. Song, Z., Chen, H., Bao, S., et al.: Nanosheet-assembled, hollow-out hierarchical γ-Fe2O3 microrods for high-performance gas sensing. J. Mater. Chem. A 8, 3754–3762 (2020)
16. Zahmouli, N., Hjiri, M., Leonardi, S.G., et al.: High performance Gd-doped γ-Fe2O3 based acetone sensor. Mater. Sci. Semicond. Process. 116, 105154 (2020)
17. Zhang, C., Zhang, S., Yang, Y., et al.: Highly sensitive H2S sensors based on metal-organic framework driven γ-Fe2O3 on reduced graphene oxide composites at room temperature. Sens. Actuators B Chem. 325, 128804 (2020)
18. Ghosh, S., Adak, D., Bhattacharyya, R., et al.: ZnO/γ-Fe2O3 charge transfer interface toward highly selective H2S sensing at a low operating temperature of 30 °C. ACS Sens. 2, 1831–1838 (2017)
structures for highly sensitive acetone detection. New J. Chem. 44, 16174–16184 (2020).
39. Yang, J., Liu, J., Xu, Y., et al.: Enhanced selective acetone-sensing performance of hierarchical hollow SnO$_2$/$\alpha$-Fe$_2$O$_3$ microcubes. J. Mater. Chem. C 7, 11984–11990 (2019).
40. Jia, X., Cheng, C., Yu, S., et al.: Preparation and enhanced acetone sensing properties of flower-like $\alpha$-Fe$_2$O$_3$/multi-walled carbon nanotube nanocomposites. Sens. Actuators B Chem. 300, 127012 (2019).
41. Kim, H.-J., Lee, J.-H.: Highly sensitive and selective gas sensors using p-type oxide semiconductors: overview. Sens. Actuators B Chem. 192, 607–627 (2014).
42. Hübner, M., Simion, C.E., Tomescu-Stănoiu, A., et al.: Influence of humidity on CO sensing with p-type CuO thick film gas sensors. Sens. Actuators B Chem. 153, 347–353 (2011).
43. Ge, W., Jiao, S., Chang, Z., et al.: Ultrafast response and high selectivity toward acetone vapor using hierarchical structured TiO$_2$ nanosheets. ACS Appl. Mater. Interfaces 12, 13200–13207 (2020).
44. Peng, S., Ma, M., Yang, W., et al.: Acetone sensing with parts-per-billion limit of detection using a BiFeO$_3$-based solid solution sensor at the morphotropic phase boundary. Sens. Actuators B Chem. 313, 128060 (2020).
45. Zhang, W., Zhang, W., Chen, B., et al.: Controllable biomolecule-assisted synthesis and gas sensing properties of In$_2$O$_3$ micro/nanostructures with double phases. Sens. Actuators B Chem. 239, 270–278 (2017).
46. Hu, D., Han, B., Deng, S., et al.: Novel mixed phase SnO$_2$ nanorods assembled with SnO$_2$ nanocrystals for enhancing gas-sensing performance toward isopropanol gas. J. Phys. Chem. C 118, 9832–9840 (2014).
47. Lin, Z., Li, N., Chen, Z., et al.: The effect of Ni doping concentration on the gas sensing properties of Ni doped SnO$_2$. Sens. Actuators B Chem. 239, 501–510 (2017).
48. Bai, J., Wang, Q., Wang, Y., et al.: Role of nickel dopant on gas response and selectivity of electrospun indium oxide nanotubes. J. Colloid Interface Sci. 560, 447–457 (2020).
49. Li, Y., Hua, Z., Wu, Y., et al.: Modified impregnation synthesis of Ru-loaded WO$_3$ nanoparticles for acetone sensing. Sens. Actuators B Chem. 265, 249–256 (2018).
50. Wang, J., Su, J., Chen, H., et al.: Oxygen vacancy-rich, Ru-doped In$_2$O$_3$ ultrathin nanosheets for efficient detection of xylene at low temperature. J. Mater. Chem. C 6, 4156–4162 (2018).

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