MOFs-Derived Porous NiFe₂O₄ Nano-Octahedrons with Hollow Interiors for an Excellent Toluene Gas Sensor

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Abstract: Toluene is extensively used in many industrial products, which needs to be effectively detected by sensitive gas sensors even at low-ppm-level concentrations. Here, NiFe₂O₄ nano-octahedrons were calcinated from NiFe-bimetallic metal-organic framework (MOFs) octahedrons synthesized by a facile refluxing method. The co-existence of p-Phthalic acid (PTA) and 3,3-diaminobenzidine (DAB) promotes the formation of smooth NiFe-bimetallic MOFs octahedrons. After subsequent thermal treatment, a big weight loss (about 85%) transformed NiFe₂O₄ nanoparticles (30 nm) into NiFe₂O₄ porous nano-octahedrons with hollow interiors. The NiFe₂O₄ nano-octahedron based sensor exhibited excellent gas sensing properties for toluene with a nice stability, fast response, and recovery time (25 s/40 s to 100 ppm toluene), and a lower detection limitation (1 ppm) at 260 °C. The excellent toluene-sensing properties can not only be derived from the hollow interiors combined with porous nano-octahedrons to favor the diffusion of gas molecules, but also from the efficient catalytic activity of NiFe₂O₄ nanoparticles.

Keywords: MOFs; NiFe₂O₄; octahedron; gas sensor; toluene

1. Introduction

Toluene is one kind of a colorless substance with a unique aromatic odor that is widely used in commercial products and industrial applications. Unfortunately, toluene is seriously harmful to human health as it strongly affects the nervous system to induce brain function disturbances and damage to the kidneys or liver [1,2]. In addition, toluene is considered as one of the important biomarkers for a diagnosis of lung cancer [3,4]. Moreover, toluene is easily flammable when the temperature is above 4.4 °C [5,6]. Due to the harmful effects of toluene, it is of great urgency to be able to effectively detect toluene. To date, various gas sensors have been developed. In particular, resistive-based gas sensors on a metal oxide base are the most attractive with respect to their cost-effective, versatile, and simple fabrication techniques. Recently, p-type oxide semiconductors have been used as sensing materials due to their good catalysts and multivalent characteristics that favor the selective oxidation of various volatile organic compounds (VOCs) [7]. Although many p-type oxide semiconductors such as NiO [8], CuO [9], Co₃O₄ [10], Cr₂O₃ [11], Mn₃O₄ [12], and so on have been reported to have potential for gas sensors, it is still far less than their counterpart, n-type oxide semiconductors.

Recently, spinel ferrites, MFe₂O₄ (M = Zn, Ni, Co, Cu, Mn, Cd, etc.), which are materials that include two types of transition metals, have stood out due to their robust catalytic activity as exhibiting significant potential applications in various fields. In particular, a few of them such as ZnFe₂O₄ [13,14],
NiFe$_2$O$_4$ [15–22], CoFe$_2$O$_4$ [23], MnFe$_2$O$_4$ [24], Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ [25], and NiCuZn ferrites [26] have been reported to be greatly promising in the electrical properties of gas sensors and humidity sensors. More interesting, NiFe$_2$O$_4$ with various microstructures have been prepared so far to effectively detect acetone [14–17], ammonia [18], NO$_2$ [19], n-propanol [20], and triethylamine [21]. However, intense efforts are expected to further enhance the sensing properties of the NiFe$_2$O$_4$ based gas sensor. Designing NiFe$_2$O$_4$ with unique microstructures is considered to be the most highly promising way. To date, templates (hard template, soft template, and bio-template) are widely used to tune the morphologies of products [27–29]. In particular, soft templates are beneficial for the synthesis of different materials to tune the morphologies under relatively mild experimental conditions. Typically, self-assembly occurs involving the soft template, precursor, and solvent molecules. Organic ligands can be used as a sufficient soft template to coordinate metal ions to obtain a unique structure. For instance, Prussian blue analogue derived porous NiFe$_2$O$_4$ nanocubes have been synthesized, which exhibit sensitivity and selectivity to acetone at low operating temperatures [16].

Today, MOFs have attracted particular attention as sacrificial templates to obtain designable nanoarchitectures [30] with intriguing properties aside from their direct applications in energy storage [31], catalysis [32], electronic devices [33], drug delivery [34], adsorbents [35], separation [36], etc. Among uncountable MOFs, Fe-containing MOFs have been extensively studied thus far due to their good diversity, low toxicity, excellent stability, and easy functionality [37]. Taking the template of MIL-88-Fe, spindle like α-Fe$_2$O$_3$ with porous structures have been reported to enhance electrochemical performance [38]. In addition, the NiFe bimetallic MOFs have been synthesized by metal Ni incorporation, which is further converted to ternary oxides of NiFe$_2$O$_4$. Song et al. obtained hollow NiFe$_2$O$_4$ microspindles from NiFe bimetallic MOFs, illustrating a high sensitivity for acetone detection [14]. Zhang et al. prepared 1D α-Fe$_2$O$_3$/NiFe$_2$O$_4$ heterojunction, which showed an improved response to acetone vapors using NiFe-bimetallic MOFs [39]. Previously, we prepared 1D porous NiFe$_2$O$_4$ nanorods using 2-aminoterephthalic acid as the ligand, which showed excellent selectivity and sensitivity to toluene [40]. Nevertheless, as of now, tuning the NiFe$_2$O$_4$ microstructures on a NiFe-bimetallic MOFs template base is still developing and in the early stage.

As discussed above, we herein combined both PTA and DAB to prepare NiFe-bimetallic MOFs octahedrons. After thermal treatment, porous NiFe$_2$O$_4$ nano-octahedrons with hollow interiors were obtained by assembling a large number of nanoparticles. The gas sensor based on NiFe$_2$O$_4$ nano-octahedrons showed excellent gas sensing properties for toluene detection at low-ppm-levels with good reproducibility, a fast response and recovery time, and a lower detection limit at the optimum operating temperature. Thus, the gas sensing mechanism for the NiFe$_2$O$_4$ based sensor is understood in detail.

2. Materials and Methods

2.1. Materials Synthesis

All the starting reagents were of analytical grade (AR grade) and unpurified. Highly pure water (18 MΩ cm at 25 °C) was used throughout the experiments. First, the octahedron NiFe-bimetallic MOFs were synthesized through a refluxing method, as schematically shown in Figure 1, which were further transferred into NiFe$_2$O$_4$ with thermal treatment. Typically, 9 mmol of p-Phthalic acid (PTA) was completely dissolved in 50 mL N,N-Dimethylformamide (DMF). At the same time, 0.3 mmol 3,3-diaminobenzidine (DAB) was dissolved into 30 mL ethanol. Next, the ethanol was slowly added to form a homogenous solution. When the desirable NiCl$_2$·6H$_2$O (0.5 mmol) and FeCl$_2$·4H$_2$O (1 mmol) were dissolved into 10 mL DMF, it was dropped into the above mixture with vigorous stirring for 30 min. The whole mixture was refluxed at 120 °C by an oil bath under magnetic stirring for 3 h. Subsequently, the NiFe-bimetallic MOFs were collected after washing several times with ethanol and deionized water, and then air dried at 60 °C for 24 h. Finally, the as-prepared NiFe-precursor was
thermally treated at 350 °C for 1 h, and then at 500 °C for a further hour in air at a heating rate of 3 °C/min. Therefore, the NiFe$_2$O$_4$ nano-octahedrons were obtained.

![Figure 1. Schematic illustration of the fabrication of the NiFe$_2$O$_4$ nano-octahedrons.](image)

### 2.2. Materials Characterization

The structure of NiFe$_2$O$_4$ was characterized using a Rigaku TTRIII x-ray diffraction with Cu K$_\alpha$ radiation (1.540 Å). A FEI QUANTA 200 microscope was used to investigate the morphology of NiFe$_2$O$_4$ and the NiFe-precursor. The TEM and HRTEM images and corresponding elemental mapping images were obtained by a JEOL JEM-2100 microscope. X-ray photoelectron spectroscopy (XPS) spectra were also measured under Al K$_\alpha$ X-ray radiation at 15 kV, which were calibrated by a C 1s peak (284.6 eV). An American TA SDT-2960 thermal analyzer was used to examine the transformation from the NiFe-precursor to the final NiFe$_2$O$_4$ (heating rate of 10 °C/min). After degassing at 300 °C for 3 h under vacuum, a Micromeritics ASAP 2010 automated sorption analyzer was applied to carry out the nitrogen adsorption/desorption measurements.

### 2.3. Fabrication and Measurement of the Gas Sensor

Following previous works, the gas sensor was fabricated and tested [41,42]. The slurry was formed by dispersing the NiFe$_2$O$_4$ powder in proper deionized water, which was coated on the surface of an alumina tube. In order to form a resistive-based gas sensor, a pair of Au electrodes were passed at each end of the tube, which was further connected by Pt wires. In general, the thickness of the sensing film was about 0.6–0.8 mm. After drying at 120 °C for 2 h, the sensor was annealed at 400 °C for 2 h in air. Then, a Bakelite base was connected to the Pt wires and a Ni–Cr alloy wire was inserted into the tube to perform measurements in a WS-30A system. During the test, the dry air was taken as the reference to mix with an evaporated target solution to obtain the desired concentration. As a typical p-type material, the response ($\beta$) of the sensor is generally defined as $R_g/R_a$, ($R_a$ and $R_g$ represent the resistance of the sensor in air and in the presence of target gases, respectively). Furthermore, the response and recovery time were evaluated by the time for 90% of the initial equilibrium resistance change in the adsorption and desorption processes.

### 3. Results

NiFe-bimetallic MOFs octahedrons were synthesized by a simple refluxing method, as schematically shown in Figure 1, which was used as the self-sacrificial template for NiFe$_2$O$_4$ fabrication. It is clear that uniform NiFe-MOFs octahedrons were well-defined with an average size of about 300 nm, as shown in the inset of Figure 2a. Close observation revealed that these NiFe-MOFs octahedrons were smooth on the surface. The as-prepared NiFe-MOFs octahedrons were further thermally transformed into NiFe$_2$O$_4$ nano-octahedrons in an air atmosphere at a heating rate of
3 °C/min. After thermal treatment, it can be seen that the configuration of the NiFe-MOFs octahedrons was perfectly preserved, as shown in Figure 2a,b. However, the NiFe₂O₄ nano-octahedrons were assembled by a large number of nanoparticles, leading to a rough surface. Importantly, the hollow interiors were strongly confirmed by a broken NiFe₂O₄ nano-octahedron in the inset of Figure 2b.

![Figure 2. FESEM images of NiFe₂O₄ nano-octahedrons in low (a) and high magnification (b), and NiFe₂O₄ synthesized without DAB (c), or PTA (d). Insets show the FESEM images of NiFe-bimetallic MOFs (a) and the hollow interior of NiFe₂O₄ (b).](image)

The crystal structure of the NiFe₂O₄ nano-octahedrons was studied by XRD measurements, as shown in Figure 3. Compared with the JCPDS: 54-0964, as indicated by the Bragg position at the bottom of the figure, a pure specimen was identified with a cubic NiFe₂O₄ structure (space-group: Fd3m). The appearance of no other diffraction peaks confirmed the high phase purity. The structural parameters were further analyzed by Rietveld refinement based on the Maud program [43]. The difference curve was not greatly fluctuated, which is a sign that the calculated pattern had good consistence with the experimental data in the whole recorded angles from 10–70°. The lattice parameters of a = 8.341092 Å were obtained. Moreover, the crystallite size of around 25.56 nm was estimated. These strong and narrow diffraction XRD peaks are persuasive evidence that an individual NiFe₂O₄ phase was completely crystallized by the above thermal treatment of NiFe-bimetallic MOFs.

In order to gain further insight into the structural details on NiFe₂O₄ nano-octahedrons, TEM and HRTEM measurements were carried out. The TEM observations in Figure 4a demonstrate that a large number of ultrafine nanoparticles (an average diameter of about 30 nm) were homogeneously distributed within the interconnected walls of the hollow octahedrons. From a featured octahedron in Figure 4b, the hollow interior was clearly distinguished by the dark boundary, indicating that the hollow interior was formed by porous walls of around 50 nm in thickness. The lattice fringes of 0.48 nm in the HRTEM image (Figure 4c) could be assigned to the (111) interplane spacing of NiFe₂O₄. Moreover, the porous structure and the specific surface area of NiFe₂O₄ was investigated using the nitrogen adsorption–desorption isotherms, as shown in Figure 5. Clearly, the sample showed an obvious H3 hysteresis loop, which can be described as a type IV isotherm, implying the presence...
of a mesoporous and hollow structure. The pore size distribution of the NiFe$_2$O$_4$ nano-octahedrons calculated using the BJH method was centered at 31.78 nm, as shown in the inset of Figure 5. A BET surface area of 43.89 m$^2$/g was obtained. This should offer our NiFe$_2$O$_4$ a sufficient interface and porous structure to facilitate the gas sensing properties. Furthermore, EDS elemental mapping images of individual NiFe$_2$O$_4$ nano-octahedrons (Figure 4d–g) demonstrate the homogeneous coexistence of Ni, Fe, and O elements.

**Figure 3.** XRD patterns for the experimental and Rietveld refinement data for the NiFe$_2$O$_4$ nano-octahedrons.

**Figure 4.** TEM (a,b) and HRTEM (c) images of the NiFe$_2$O$_4$ nano-octahedrons and elemental mapping images of Ni (e), Fe (f), and O (g) for an individual NiFe$_2$O$_4$ nano-octahedron (d).
Figure 5. Nitrogen adsorption–desorption isotherm along with the pore size distribution of the NiFe₂O₄ nano-octahedrons.

Thermogravimetric measurements were performed to explore the transformation from NiFe-bimetallic MOFs to NiFe₂O₄. From the TG curve shown in Figure 6, it can be seen that about 6.55% weight loss was observed in the temperature blow 120 °C, which originated from the loss of absorbed water in the precursor. By further increasing the temperature to 350 °C, around 45.60% weight loss occurred due to the decomposition of organic ligands in the NiFe-bimetallic MOFs. Up to 425 °C, 15% weight was maintained. Accordingly, a clear exothermal peak at 412.66 °C in the DSC curve was observed, suggesting the transformation of NiFe-bimetallic MOFs to NiFe₂O₄. It is noteworthy that the large weight loss can be reasonably explained by the large numbers of organic ligands in the NiFe-bimetallic MOFs synthesized by coupling DAB with PTA in a mixed solution of DMF and ethanol.

Figure 6. TGA–DSC curves of transformation from NiFe-bimetallic MOFs to NiFe₂O₄.

Taken together, the porous NiFe₂O₄ nano-octahedrons were thermally obtained from NiFe-bimetallic MOFs synthesized by a facile refluxing route, which was assembled by a large number of nanoparticles. The existence of abundant organic ligands was revealed by the large weight loss in TG measurements due to the cooperative effects of PTA and DAB in the mixture of DMF and ethanol. It has been reported that Schiff-base polymer spheres have been obtained using certain amounts of PTA and DAB in ethanol at 80 °C under stirring-reflux, which can be further transformed
into N-doped porous carbons [44]. To understand the growth mechanism, contrast experiments were conducted only dependent on PTA or DAB following the same experimental process, respectively. Without DAB, the NiFe₂O₄ nanoparticles were observed with some sheets, as shown in Figure 2c. In the presence of DAB, the NiFe₂O₄ nanoparticles seemed to be more uniform (Figure 2d). Therefore, the combination of PTA and DAB plays a critical role in coordinating with the metal ions to produce octahedral NiFe-bimetallic MOFs through the refluxing approach.

To evaluate the potential practicality and reliability of the gas sensor based on NiFe₂O₄ nano-octahedrons, the fundamental properties of a gas sensor were thoroughly studied. The responses of our NiFe₂O₄ based sensor to 100 ppm toluene at various operating temperatures from 220–300 °C are shown in Figure 7a. Clearly, the responses kept increasing to reach a maximum at 260 °C and then started to decrease with further increased temperatures. At lower temperatures, the slow diffusion of the tested gas molecules and the insufficient thermal energy to accelerate the reaction between the gas molecules and adsorbed oxygen species is believed to result in a relatively low response. The existence of oxygen species will be given in the XPS analysis below. Although enough thermal energy is available at higher temperatures, it could reduce the gas adsorption capacity from the sensing materials, leading to a decreased response [45,46]. Hence, the gas sensing measurements in the following were performed at 260 °C.

Figure 7. Polar graphs shows the gas responses of gas sensors based on NiFe₂O₄ nano-octahedrons as 30, 50, and 100 ppm toluene vs. operating temperatures from 220–300 °C (a). Dynamic sensing plot of sensors based on NiFe₂O₄ nano-octahedrons upon exposure to toluene (b). Concentration dependent response curve vs. the toluene concentrations (1–200 ppm) (c). Response/recovery graph to 100 ppm toluene (d), and reproducibility of sensor upon exposure (five cycles) to 100 ppm toluene at 260 °C (e). Long-term stability (30 days) of sensor to 100 ppm toluene (f).

Figure 7b shows the dynamic responses of the NiFe₂O₄ nano-octahedrons to 1–200 ppm toluene. It can be seen that a stepwise distribution of the curves appeared by switching dry air and a certain
concentration of the target gas. With increasing toluene concentrations, the responses of the sensor rapidly increased. Specifically, the sensor showed approximately responses of 1.24, 2.10, 2.76, 4.50, 5.52, 6.01, 6.57, and 7.13 to 1, 5, 10, 30, 50, 70, 100, and 200 ppm of toluene, respectively, as shown in Figure 7b. It is noteworthy that the responses sharply increased at lower toluene concentrations because the coverage of the gas molecules was low on the surface of the sensing material (Figure 7c). In our case, the sensor was capable of detecting 1 ppm toluene. With the further increase in the toluene concentration, the material surface was gradually covered completely. Thus, the rising trend of responses gradually slowed down, indicating the saturation of the sensor to some extent [47].

Taking 100 ppm toluene as an example, the sensor exhibited fast response/recovery times of 25 s/40 s (Figure 7d). In addition, the responses were almost maintained for the five cyclic toluene exposures, as displayed in Figure 7e, which showed good repeatability within a fluctuation of 2.2%. Furthermore, the long-term stability of the gas sensor was evaluated. The continuous tests were carried out over 30 days with a one day interval while exposing the sensor to 100 ppm toluene. As shown in Figure 7f, the sensor exhibited small deviations (6.2%) during the test over 30 days, demonstrating the good stability of the NiFe$_2$O$_4$. Importantly, our NiFe$_2$O$_4$ based gas sensor showed a comparable sensing performance with typical p-type nanomaterials, as summarized in Table 1.

### Table 1. Comparison of toluene sensing performance among the gas sensors based on typical p-type materials.

| Materials          | Microstructures     | Concentration (ppm) | T (°C) | Response | Limit of Detection | Ref. |
|--------------------|---------------------|---------------------|--------|----------|--------------------|------|
| NiO                | Flower-like         | 5                   | 250    | 2.63     | 0.5 ppm            | [48] |
| NiO                | Nanoparticle        | 200                 | 210    | 1.6      | 100 ppm            | [49] |
| CuO                | Flower              | 500                 | 260    | 2.5      | 10 ppm             | [50] |
| Co$_3$O$_4$        | Nanorod             | 200                 | 200    | 35       | 10 ppm             | [51] |
| Co$_3$O$_4$        | Nanosheet           | 100                 | 150    | 6.08     | 1 ppm              | [52] |
| Co$_3$O$_4$        | Microsphere         | 100                 | 180    | 2.2      |                    | [53] |
| Cr$_2$O$_3$        | Microsphere         | 100                 | 170    | 33.64    | 1 ppm              | [54] |
| Ag-LaFeO$_3$       | Nanoparticle        | 5                   | 215    | 24       | 5 ppm              | [55] |
| NiGa$_2$O$_4$-NiO  | Nanosphere Ordered  | 100                 | 230    | 12.7     | 0.5 ppm            | [56] |
| NiFe$_2$O$_4$      | Ordered mesoporous  | 1                   | 230    | 77.3     | 2 ppb              | [57] |
| NiFe$_2$O$_4$      | Hexagonal biyramid  | 200                 | 140    | 5.73     | 5 ppm              | [20] |
| NiFe$_2$O$_4$      | Nano-octahedron     | 100                 | 260    | 6.41     | 1 ppm              | This work |

The selectivity generally demonstrated the capability that the gas sensor had to distinguish the target gas without any interference, which is also important for practical applications. Figure 8 compares the sensing response of the NiFe$_2$O$_4$ nano-octahedron based sensor to 100 ppm toluene, acetone, ethanol, methanol, isopropanol, n-butyl alcohol, formaldehyde, ammonia, and toluene at the same operating temperature of 260 °C. Against the interferences, the gas sensor showed a relatively selective and sensitive detection toward toluene. One plausible explanation for the selective detection of toluene could be ascribed to the excellent catalytic nature of p-type NiFe$_2$O$_4$ to toluene, leading to more released electrons back to the NiFe$_2$O$_4$ materials after the reactions of target molecules on the surface [58,59]. Moreover, the optimum operating temperature of 260 °C could provide suitable active energy to promote the reactions of toluene on the NiFe$_2$O$_4$ surface. Thus, a big change of resistance for the sensor occurred, which exhibits excellent sensing performances.
As defined above, the sensing response of a semiconductor is dependent on the variation of resistance, which is highly related to both the surface compositions and valance states of the elements in the sensing materials. Therefore, the XPS investigation was conducted, as shown in Figure 9. The high resolution XPS analysis of the Ni 2p spectra in Figure 9a displays the specific peaks of Ni 2p$_{1/2}$ and Ni 2p$_{3/2}$ at the binding energies of 8723.18 eV and 854.61 eV with two apparent satellite peaks at 878.46 eV and 860.94 eV, respectively. Meanwhile, the Fe-related fitting peaks with binding energy values of 723.92 eV and 710.24 eV, corresponded well with Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$, respectively (Figure 9b). The XPS results verify the Ni(II) and Fe(III) in the NiFe$_2$O$_4$ [39]. In particular, the O 1s XPS spectrum, as shown in Figure 9c, could be resolved by two peaks located at 529.69 eV and 530.97 eV, implying various oxygen contributions. Specifically, the peak at the low binding energy of 529.69 eV is typically assigned to that of lattice oxygen (O$_{\text{lattice}}$), which is unreactive with target gases. In contrast, the well-resolved peak at a higher binding energy of 530.97 eV was assigned to surface adsorbed oxygen species, which evolved into O$_2^-$, O$^-$, and O$^{2-}$. These oxygen species are believed to play a critical role in reacting with the target gas to determine the gas sensing properties [60]. As is well known, O$_2$ has a stronger electron affinity, making it adsorbed on the surface of NiFe$_2$O$_4$ even at room temperature though a physical process.

When the operating temperature rose to 260 °C, a more stable adsorbed oxygen species can be formed. Thus, the mechanism governing the sensing properties of NiFe$_2$O$_4$ nano-octahedrons can be systematically discussed by the following process. As a typical p-type semiconductor, holes are the charge carriers in NiFe$_2$O$_4$. The evolution of absorbed oxygen into oxygen species, as confirmed by the above XPS analysis, will reduce the electrons in the sensing materials (Figure 9d). Therefore, the rich existence of holes generates a hole accumulation layer on the very surface of NiFe$_2$O$_4$, leading to a highly conductive state in the air. After exposure to a reductive gas atmosphere such as toluene, the reaction between these oxygen species and target gas molecules can release the trapped electrons back (Figure 9e), which results in the conductivity of the NiFe$_2$O$_4$ based sensor decreasing greatly. Thus, a high resistance state can obviously appear. For instance, a real resistance of about 82 kΩ was measured in the air for the NiFe$_2$O$_4$ based sensor, as shown in Figure 9f. After exposure to even 1 ppm toluene, the resistance dramatically increased to approximately 98 kΩ. When the NiFe$_2$O$_4$ based sensor was switched to air again, sufficient oxygen molecules alternatively adsorbed on the NiFe$_2$O$_4$ surface. As a result, the resistance restored its initial status, leading to the achievement of a whole response–recovery period. In contrast with the electrical conductivity seen in previous reports [61,62], our nano-octahedron NiFe$_2$O$_4$ exhibited good electrical conductivity with low resistivity. The variation

![Figure 8. Selectivity of NiFe$_2$O$_4$ nano-octahedrons to 100 ppm of various gases at 260 °C.](image-url)
ratio of resistance is heavily determined by the sensing materials and the concentrations of the target gas. The possible reactions are clarified in the following [1,63]

\[
\begin{align*}
\text{O}_2 (\text{gas}) & \rightarrow \text{O}_2 (\text{adsorbed}) \quad (1) \\
\text{O}_2 (\text{adsorbed}) + e^- & \rightarrow \text{O}_2^- \quad (2) \\
\text{O}_2^- + e^- & \rightarrow 2\text{O}^- \quad (3) \\
\text{O}^- + e^- & \rightarrow \text{O}^{2-} \quad (4) \\
\text{C}_7\text{H}_8 + 9\text{O}^- & \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O} + 9e^- \quad (5) \\
\text{C}_7\text{H}_8 + 9\text{O}^{2-} & \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O} + 18e^- \quad (6)
\end{align*}
\]

Figure 9. High-resolution XPS spectra for Ni 2p (a), Fe 2p (b), and O 1s (c), and a schematic illustration of the sensing mechanism of the NiFe$_2$O$_4$ nano-octahedrons in air (d), and in toluene (e) with the obverse real resistance change in air and 1 ppm toluene (f).

In short, the unique assembly of NiFe$_2$O$_4$ nanoparticles into porous nano-octahedrons with hollow interiors can provide enough specific surface areas and space and rich active sites to catalyze toluene. The native features of NiFe$_2$O$_4$ may be suitable for the toluene catalyst at an optimum operating temperature due to the reversible redox reaction of Ni$^{2+} \leftrightarrow$ Ni$^{3+}$, Fe$^{2+} \leftrightarrow$ Fe$^{3+}$ [39]. Specifically, the as-prepared mesopore nano-octahedrons with hollow interiors easily facilitate the fast diffusion of gas molecules in reaching and departing from the sensing surface. In addition, a large number of NiFe$_2$O$_4$ may offer more active sites to boost the reaction between the target gas molecules and oxygen species. Thus, the as-synthesized NiFe$_2$O$_4$ nano-octahedrons show excellent sensing properties to low-ppm-level toluene. The response and selectivity could be further enhanced by proper doping, or appropriately coupling with other nanomaterials or functionalizing with noble metal nanoparticles. For instance, the Ni$_{0.33}$Co$_{0.67}$Fe$_2$O$_4$ microspheres showed the highest gas-sensing sensitivity to toluene due to their rich oxygen vacancies and large specific surface area [64]. Compared with individual $\alpha$-Fe$_2$O$_3$ and NiFe$_2$O$_4$, the 1D $\alpha$-Fe$_2$O$_3$/NiFe$_2$O$_4$ heterojunction showed better gas-sensing properties for acetone detection due to the enhanced charge separation and carrier$^4$ depletion layer at the interface [39].
4. Conclusions

In summary, porous NiFe$_2$O$_4$ nano-octahedrons were successfully synthesized using a facile refluxing route via a simple and direct pyrolysis of NiFe-bimetallic MOFs. The cooperative effects of PTA and DAB play a critical role in the formation of octahedral NiFe-bimetallic MOFs precursors. The gas sensing performance of the NiFe$_2$O$_4$ based sensor was studied for toluene detection. As a result, the gas sensor exhibited the advantages of long-term stability (30 days), excellent repeatability, short response (25 s) and recovery (40 s) time, and a lower detection limitation (1 ppm). These resulting sensing properties may stem from the decent specific surface area (43.89) with a porous structure, hollow interiors, small size (30 nm), and the catalytic nature of NiFe$_2$O$_4$. More importantly, the easy fabrication strategy can be properly extended for the preparation of other well-defined micro-/nano-structures using both PTA and DAB as coordinated ligands.

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