Enhanced gas sensing performance of perovskite YFe$_{1-x}$Mn$_x$O$_3$ by doping manganese ions

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Perovskite YFe$_{1-x}$Mn$_x$O$_3$ with a hierarchical structure were prepared by a simple hydrothermal method and used as gas sensing materials. The structure, morphology and composition of YFe$_{1-x}$Mn$_x$O$_3$ were investigated using X-ray diffraction, transmission electron microscopy, scanning electron microscopy and X-ray photoelectron spectroscopy. The gas sensing test showed that all YFe$_{1-x}$Mn$_x$O$_3$ perovskites with different Mn doping concentrations displayed fast response and recovery characteristics to multiple analytes as well as good stability and recoverability. With the increase of Mn doping concentration, the response of YFe$_{1-x}$Mn$_x$O$_3$ to four kinds of target atmospheres first increases, then decreases. The sensing performance of YFe$_{1-x}$Mn$_x$O$_3$ is best when $x = 0.05$. Compared with pure YFeO$_3$, the responses of YFe$_{0.95}$Mn$_{0.05}$O$_3$ to 1000 ppm of CH$_4$, C$_2$H$_4$O, H$_2$O$_2$ and 100% relative humidity were increased by 835%, 1462%, 812% and 801%, respectively. The theoretical detection limit of YFe$_{0.95}$Mn$_{0.05}$O$_3$ for H$_2$O$_2$ and CH$_2$O is 1.75 and 2.55 ppb, respectively. Furthermore, the possibility of building a sensor array based on YFe$_{1-x}$Mn$_x$O$_3$ with different doping concentrations was evaluated by principal component analysis and radar chart analysis. It is feasible to realize the visual and discriminative detection of the target analyte by constructing sensor arrays through radar chart analysis and database construction.

1. Introduction

Perovskites have a great effect in many domains, such as gas sensors. Recently, a variety of perovskite structures based on ABO$_3$-type composites have been used as gas sensors due to their high stability and also their characteristics of sensitivity and selectivity. Perovskite BaSnO$_3$, obtained from a simple wet chemical route was calcined at different temperatures and the gas sensing performance was studied in the presence of O$_2$, CO and NO$_2$ as a function of the temperature. The BaSnO$_3$ sensor shows a maximum sensitivity to O$_2$ and at 700 °C, to CO and NO$_2$ at 600 °C, respectively. Traversa fabricated the thick films of LaFeO$_3$ and SmFeO$_3$ by screen-printing technology on alumina substrates with comb-type Au electrodes. The effect of temperature and humidity on the gas sensing performance of LaFeO$_3$ and SmFeO$_3$ to NO$_2$ and CO were studied and the presence of humidity does not affect the detection of NO$_2$ and CO. The sensing properties of SrTiO$_3$ were regulated by the doping manganese ions SrTiO$_3$. The optimal relative resistance ($R_{\text{nitrogen}}/R_{\text{20\% oxygen}}$) value of 6.35 is obtained for the synthesized SrTiO$_3$ sample annealed at 400 °C and operating at 40 °C, which is much lower than that for the conventional metal oxide semiconducting oxygen gas sensors (300–500 °C). Later, traditional metal oxide semiconductors or noble metal nanoparticles were used to form composites with perovskite materials to improve their gas sensing performance. Ruan synthesized porous core–shell PrFeO$_3/\alpha$-Fe$_2$O$_3$ composites, realized a high gas response, low optimum operating temperature and superior selectivity to ethyl acetate gas. The response ($R_{\text{air}}/R_{\text{gas}}$) of the sensor based on PrFeO$_3/\alpha$-Fe$_2$O$_3$ is 22.85 toward 100 ppm ethyl acetate at 206 °C, about 3 times higher than that of pristine $\alpha$-Fe$_2$O$_3$ sensor. Besides, the sensor possesses a rapid response and recovery speed of 8 s and 9 s for detecting 100 ppm ethyl acetate.

Perovskite LaCoO$_3$ was synthesized by sol–gel method and functionalized by Ag nanoparticles. An improved sensitivity and selectivity to H$_2$S was observed for Ag/LaCoO$_3$ composites, compared with pure LaCoO$_3$ sensor. The role of Ag nanoparticles in the selective sensitivity of Ag/LaCoO$_3$ composites to H$_2$S gas were unveiled using in situ infrared spectroscopy. Mandayo prepared BaTiO$_3$–CuO films and annealed at different temperatures in order to test their electrical behavior by means of impedance measurements under different CO$_2$ concentrations (0–2000 ppm). Pt and Ag are tested as electrode materials and the influence of Ag as surface and multilayer additive for sensing response enhancement is also studied.
Compared with the composite method of improving the sensing performance of the perovskites, doping may be a simpler and more effective way to regulate the sensing properties of perovskites, which can be done synchronously in the process of synthesizing materials. The cubic ABO₃ unit cell of perovskites contain a large 12-coordinated A cation centered between the corner-sharing BO₆ octahedra. The ABO₃ structure is favorable for cation substitution in either A, or B positions, which influences the electrophysical and chemical properties of the perovskite oxides. This means that the controlled doping of ABO₃ structure can effectively control the gas sensing properties of perovskites. Rothschild explored the sensing performances of SrTi₁₋ₓFeO₃₋₄ as oxygen sensors in lean burn engines and found that with the change of the molar ratio of Ti/Fe, the bandgap energy and gas sensing performance of the SrTi₁₋ₓFe₂O₅₋₄ material changed synchronously. Among these perovskites, yttrium orthoferrite (YFeO₃) has attracted the attention of researchers due to their excellent magnetic, magneto-optical, physical and chemical properties originated by their ionic and electronic defects as well as structure distortions. In our work, the hierarchical YFe₁₋ₓMnO₃ was prepared by hydrothermal method and the substitution of Mn ions at Fe site was achieved, because of the close ionic radius of Mn³⁺ (0.58 Å), Mn²⁺ (0.67 Å) and Fe³⁺ (0.64 Å). The effect of Mn doping on the gas sensing performances of YFe₁₋ₓMnO₃ to CH₂O, C₂H₆O and H₂O₂ has been studied. Furthermore, the possibility of building sensor array based on YFe₁₋ₓMnO₃ with different doping concentration was evaluated by principal component analysis (PCA) and radar chart analysis.

2. Experimental section

2.1 Material preparation

Yttrium nitrate hexahydrate [Y(NO₃)₃·6H₂O], iron(III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O], manganese(II) chloride (MnCl₂·4H₂O), and potassium hydroxide (KOH) are analytical reagents, purchased from Sinopharm Chemical Reagent Co., Ltd. YFe₁₋ₓMnO₃ (x = 0, 0.025, 0.05, 0.075 and 0.1) nanopowders were prepared by hydro-thermal method. First, 0.01 mol of Y(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O, and a certain amount of MnCl₂·4H₂O were weighed and dissolved in 30 ml of distilled water with stirring. Second, 0.75 mol of KOH as mineralizing agent was directly added into the above solution, the mixtures were then transferred to Teflon-lined stainless steel autoclave and heated at 230 °C for 72 h. Third, the dark products were filtered and washed several times with distilled water to obtain crystals that are then dried in air.

2.2 Device fabrication and testing

The fabrication and testing of sensors are the same as the previous reports. Specifically, sensors based on YFe₁₋ₓMnₓO₃ (x = 0, 0.025, 0.05, 0.075 and 0.1) were fabricated by coating the paste of YFe₁₋ₓMnₓO₃ on a ceramic substrate by a thin brush to form a sensing film on which silver interdigitated electrodes with both finger-width and inter finger spacing of about 200 μm was previously printed. The sensors based on YFe₁₋ₓMnₓO₃ (x = 0, 0.025, 0.05, 0.075 and 0.1) were defined as S1, S2, S3, S4 and S5, respectively. The sensor were dried at 25 °C about 24 h and then aged at 3 V in air for about 48 h to ensure the good stability. Gas sensing performance was measured by an electrochemical workstation (CIMPS-2, ZAHER ENNIUM) in a 25 °C test room controlled by air conditioning system. For the target vapor of different concentrations is prepared according to formula (1):

\[ Q = \frac{1}{22.4 \times 10^3} \times \frac{V \times C \times M}{d \times \rho} \times \frac{273 + T_R}{273 + T_R} \]

where: Q and V is the volume of the liquid to be taken and the volume of the test bottle, respectively; M is the molecular weight of the substance; d is the purity of the liquid; C is the concentration of the gas to be prepared; p is the density of the liquid; T_R and T_R is the test ambient temperature and the temperature in the test bottle. During the preparation of the target vapors by heating, the containers were sealed. After a certain concentration of vapors were generated, the sealed containers were placed at 25 ± 1 °C for about 2 h to reduce the temperature of the target vapors to 25 ± 1 °C. A constant potential of 3 V was applied across the sensor and the relative change of electric current when switching from air to the target gases was recorded by electrochemical workstation at room temperature. The response was defined as the ratio \( \Delta I/I_0 = (I_R - I_0)/I_0 \), where \( I_R \) and \( I_0 \) were electric current in the reference gas and the target gas, respectively. The response and recovery time was defined as the interval between when response reached 90% of its maximum and dropped to 10% of its maximum.

2.3 Characterization

X-ray powder diffraction (XRD) measurement was carried out using powder XRD (Bruker D8 Advance, with Cu-Kα radiation operating at 40 kV and 40 mA). Field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) was used to investigate the surface morphology of YFe₁₋ₓMnₓO₃ (x = 0.000, 0.025, 0.050, 0.075 and 0.100). Transmission Electron Microscopy (TEM, FEI Tecnai G2 F20 S-TWIN) was used to characterize the morphology of YFe₁₋ₓMnₓO₃ (x = 0.050) sample. The surface elements and chemical states of the samples were examined using X-ray photoelectron spectroscopy (XPS, PHI 5000Versa Probe). The content of each element in the materials was measured by energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma emission spectrometer (ICP).
3. Results and discussion

3.1 Morphology and structural properties

The surface morphologies of $YFe_{1-x}Mn_xO_3$ ($x = 0.000, 0.025, 0.050, 0.075$ and $0.100$) investigated by SEM are given in Fig. 1. On the macro level, all the micron particles of $YFe_{1-x}Mn_xO_3$ are basically composed of a square sheet and two sides of the square sheet symmetrically growing hierarchical structures (Fig. 1a, d, g, j, m). At the micro level, the hierarchical structure on both sides of the square sheet is like a maze of long building units (Fig. 1b, e, h, k, n), and their morphology does not change with the increase of Mn doping. More detailed observation shows that the basic unit is a quadrangular prism with width of several hundred nanometers, length of several microns or even more than ten microns. One-dimensional structure of $YFe_{1-x}Mn_xO_3$ facilitates the rapid transport and transfer of charges between one-dimensional quadrangle and target gas.$^{30,31}$ Moreover, there are some nanoparticles growing on the surface of the prism (Fig. 1c, f, i, l, o). This may provide a large surface area and active sites for the adsorption of the target gas, which
is conducive to improving the gas sensing performance of the material.\textsuperscript{22} In addition, it should be noted that when the doping amount of manganese ion reaches 10\%, the hierarchical structure becomes less fine and the basic unit becomes wider, changing slightly the morphology of the $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ materials.

XRD patterns of five $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ doped with different amount of Mn are shown in Fig. 2a. The XRD investigation suggests that all these samples give rise to well-established peaks of orthorhombic perovskite structure with lattice constant $a = 5.5957$ Å, $b = 7.6046$ Å and $c = 5.2819$ Å (JCPDS no. 89-2609).\textsuperscript{28,33,34} As shown in Fig. 2a, the typical diffraction peaks at 25.99, 31.98, 33.17, 33.94, 39.54, 47.31, 47.87, 48.91, 53.45, 57.73, 58.75, 60.24 and 76.017 can be ascribed to the (111), (200), (121), (002), (112), (202), (040), (212), (311), (321), (240) and (123) faces of orthorhombic $\text{YFeO}_3$, which are comparable to those reported in literature.\textsuperscript{28,33,34} In the concentration range of 10\%, with the increase of Mn doping concentration, the structure and crystal phase of $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ materials have almost no change, and the pure $\text{YFeO}_3$ structure is still maintained. It should be pointed out that the intensity of the diffraction peak gradually weakens with the increase of Mn ions in $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$, especially when the doping amount of Mn ions reaches 10\% (S5). This is due to the structural disorder caused by the difference of radius between Mn and Fe ions. The lattice parameters according to the XRD are plotted against Mn concentration ($x$) as shown in Fig. S1.\textsuperscript{†} The parameter $a$ increases whereas $b$ and $c$ parameters decrease with the increase of Mn concentration, which is consistent with those reported in literatures.\textsuperscript{28,29} The increase in the parameter $a$ with the increase of Mn concentration ($x$) indicates the presence of Jahn–Teller distortion associated with Mn\textsuperscript{3+} ions.

To further explore the structure of $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$, HRTEM study was carried out, as presented in Fig. 2b. The (200), (022) and (221) planes of $\text{YFeO}_3$ is observed, which show the indistinct lattice fringe of 0.264, 0.224 and 0.186 nm space, respectively. The content of Mn element in $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ was determined by energy dispersive spectroscopy (EDS) and increased significantly with the increase of the ratio of Mn/Fe in the precursor, achieving 3.26\%, 5.95\%, 12.60\% and 14.10\% (Fig. 2c) for the S2, S3, S4 and S5, respectively. It is worth pointing out that the experimental values of Mn content are higher than the theoretical values, which may be caused by the tendency of Mn doping to migrate to the surface of the material. In addition, EDS mappings of the $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ showed strong and uniform signals of Mn, Fe, Y and O, as seen in Fig. 2d, and the original SEM image selected for the EDS mapping was shown in Fig. S2.\textsuperscript{†} This shows that Mn ions are evenly distributed on the surface of $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$.

Fig. S3a\textsuperscript{†} shows the UV-vis spectra of the $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ materials. It is interesting to observe that the UV reflection intensity of $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ from 250 nm to 400 nm decreased gradually with the increase of Mn doping, which means that their absorption of ultraviolet region is gradually strengthened. The UV absorption band can be primarily ascribed to electrons promotion of $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ from the valence band to the conduction band.\textsuperscript{35} In contrast to the pure $\text{YFeO}_3$ powder, the absorption edge of the $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ samples displays different shifts to the visible region. This has been confirmed by roughly estimating the band gap of samples according to the plot in Fig. 3b, which is obtained via the transformation based on the Kubelka–Munk function. The estimated band gap values of S1, S2, S3, S4 and S5 are approximately 2.40, 2.35, 2.30, 2.20 and 2.02 eV, respectively, clearly showing the narrowing band gaps.

![Fig. 2](image-url) (a) XRD patterns, (b) HRTEM images, (c) content of Mn element in $\text{YFe}_{1-x}\text{Mn}_x\text{O}_3$ according to EDS test, and (d) EDS mappings of the samples.
as compared to the estimated 2.40 eV of the pure YFeO₃. A smaller band gap means that electrons in the valence band can more easily transition to the conduction band, increasing the carrier concentration. The change of carrier concentration has an important effect on gas sensitive performance of the sensing material. Therefore, it can be concluded that Mn doping has an important effect on the gas sensitive performance of YFe₁₋ₓMnₓO₃.

As shown in Fig. 3a, Fe element doped in YFe₀.₉₅Mn₀.₀₅O₃ exists in mixed valence state, the Fe 2p₃/₂ peaks at 710.5 and 712.5 eV could be assigned to Fe²⁺ and Fe³⁺ ions, respectively.¹⁸,³⁶ As shown in Fig. 3b, the Mn 2p region consists of a spin–orbit doublet of Mn 2p₃/₂ and Mn 2p₁/₂, and the Mn ions doped in YFe₀.₉₅Mn₀.₀₅O₃ also exist in mixed valence state. The peaks of the Mn elements located at 640.7 and 642.5 eV correspond to Mn²⁺ and Mn³⁺ ions, respectively. These results are in good agreement with reports in the literature.¹²,²⁷ Because of the presence of Fe³⁺ ions, a small amount of oxygen in the reactor and the high temperature and pressure generated during the reaction (230 °C for 72 h), the oxidation of Mn²⁺ ions will be promoted to a certain extent to produce Mn³⁺ ions. The O 1s peak data for YFe₀.₉₅Mn₀.₀₅O₃ are presented in Fig. 3c, indicating an asymmetric peak that is usually fitted with three components. The fitted peaks located at 529.9, 531.5 and 532.7 eV were labeled as OL, Oᵥ and OC, respectively. OL, Oᵥ and OC was associated with lattice oxygen, oxygen vacancy, and adsorbed oxygen, respectively.¹⁸,³⁶ For other samples, the XPS peaks of Mn, Fe with different valence states and three kinds of oxygen, and their fitting peaks are shown in Fig. S4, S5 and S6,† respectively.

The proportion of two kinds of Mn ions and oxygens is calculated according to their corresponding peak area and listed in the Table 1. It is worth noting that with the increase of doping amount of Mn ions in YFe₁₋ₓMnₓO₃, the proportion of Mn²⁺ ion decreases, and the proportion of Mn³⁺ ions increases. However, the increase of Mn ions in YFe₁₋ₓMnₓO₃ reached 3.45, 8.41, 10.37 and 11.29% for the S2, S3, S4 and S5 respectively according to XPS results, which is consistent with the ICP results (Table 1). It can be seen that the increase of Mn ions in YFe₁₋ₓMnₓO₃ is significantly faster than the decrease of Mn²⁺ ion. This means that although the proportion of Mn²⁺ ions decreases gradually, the net concentration of Mn²⁺ ions increases with the increase of total doping amount of Mn ions. It is well known that electronegativity is a relative scale of the ability of atoms or ions to attract electrons. The greater the electronegativity, the greater the tendency to attract electrons. The Mn²⁺ ions have lower electronegativity than the Mn³⁺ ions. In other words, Mn²⁺ ions are beneficial to the adsorption of oxygen ions on the surface of YFe₁₋ₓMnₓO₃, while Mn³⁺ ions are not conducive to the adsorption of oxygen ions. Thus, the competition between Mn²⁺ ions and Mn³⁺ ions may lead to the increase of oxygen ions on the surface of YFe₁₋ₓMnₓO₃ and then decrease (Table 1).

### 3.2 Fabrications and testing of sensor array

The effect of Mn doping on the gas sensing performance of YFe₁₋ₓMnₓO₃ is reflected by their sensing curves in Fig. 4. It can be seen from the sensing curves that YFe₁₋ₓMnₓO₃ with different doping concentrations have a relatively stable response to 1000 ppm of CH₂O, C₂H₆O and H₂O₂ vapors as well as 100% RH at room temperature. With the increase of Mn doping

![Fig. 3 XPS peaks and the Gaussian fitting peaks of (a) Fe 2p, (b) Mn 2p, (c) O 1s for YFe₀.₉₅Mn₀.₀₅O₃ (x = 0.05) powder.](image)

![Table 1 Mass ratio of Mn to Fe calculated by XPS and ICP, and the percentage of different fitting peaks of Mn and O element](table)

| Sample | Mn/Fe<sup>a</sup> | Mn/Fe<sup>b</sup> | Mn³⁺ | Mn²⁺ | Oᵥ | OL | OC |
|--------|-----------------|-----------------|------|------|----|----|----|
| S1     | 0.0%            | 0.0%            | 0.0% | 0.0% | 17.2% | 22.4% | 60.4% |
| S2     | 3.45%           | 3.54%           | 47.7% | 52.3% | 22.6% | 29.2% | 48.2% |
| S3     | 8.41%           | 5.25%           | 48.5% | 51.5% | 35.3% | 32.4% | 32.3% |
| S4     | 10.37%          | 11.33%          | 49.2% | 50.8% | 26.0% | 27.3% | 46.7% |
| S5     | 11.29%          | 11.68%          | 52.3% | 47.7% | 20.5% | 22.7% | 56.8% |

<sup>a</sup> Represents mass ratio of Mn to Fe calculated by XPS. <sup>b</sup> Represents mass ratio of Mn to Fe calculated by ICP.
concentration, the response of YFe$_{1-x}$Mn$_x$O$_3$ to four kinds of target atmospheres first increases, then decreases. In general, the gas sensing performance of YFe$_{1-x}$Mn$_x$O$_3$ is the best when $x = 0.05$ in the YFe$_{1-x}$Mn$_x$O$_3$. In addition, it can also be seen that the YFe$_{1-x}$Mn$_x$O$_3$ after doping has the highest sensitivity to H$_2$O$_2$ vapor, followed by CH$_2$O vapor. When the sensor based on YFe$_{1-x}$Mn$_x$O$_3$ are exposed to CH$_2$O and C$_2$H$_6$O vapors, surface adsorbed oxygen (O$_2^-$, $<100$ °C; O$, 100–300$ °C; O$_2^-$, $>300$ °C) will react with CH$_2$O and C$_2$H$_6$O as follows,

\[ \text{CH}_2\text{O} (g) + \text{O}_2^- (s) \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{e}^- \] (2)

\[ \text{C}_2\text{H}_6\text{O} (g) + 3\text{O}_2^- (s) \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 3\text{e}^- \] (3)

In the above reactions, e$^-$ represents a conduction electron and O$_2^-$ (s) represents a surface adsorbed oxygen ion. CH$_2$O (g) and C$_2$H$_6$O (g) represents adsorbing CH$_2$O and C$_2$H$_6$O molecules, respectively. It can be seen that the reduced gas molecules release electrons into YFe$_{1-x}$Mn$_x$O$_3$ during the reaction and the electric current of YFe$_{1-x}$Mn$_x$O$_3$ increases quickly, which shows the sensing characteristics of n-type semiconductor. However, the sensing signal to H$_2$O$_2$ is abnormal, which is in the same direction as the reductive gas. It is reported that H$_2$O$_2$ will react with the following two ways depending on the concentration of H$_2$O$_2$. At high H$_2$O$_2$ (of about 10 vol%) concentrations the mechanism is as follows:

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \] (4)

At lower concentrations (2.1 vol%) the net reaction is:

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + 0.87\text{O}_2 + 0.08\text{O}_3 \] (5)

In our work, the H$_2$O$_2$ with a mass fraction of 30% was used. According to the eqn (4), the main product of H$_2$O$_2$ decomposition is H$_2$O and O$_2$. Therefore, the produced O$_2$ and H$_2$O$_2$ vapor will capture electrons from the YFe$_{1-x}$Mn$_x$O$_3$, and H$_2$O will release electrons into YFe$_{1-x}$Mn$_x$O$_3$. In this way, there is a competition between the oxidizing atmosphere and the reducing atmosphere in the sensing performance. Finally, the reductive atmosphere prevails, showing the sensing characteristics of reductive gas.

Fig. 4 Sensing curves of different sensors based on YFe$_{1-x}$Mn$_x$O$_3$ to 1000 ppm of CH$_2$O, C$_2$H$_6$O, H$_2$O$_2$ and 100% RH at room temperature.
In order to better evaluate the effect of manganese doping on the sensing performance of YFe$_{1-x}$Mn$_x$O$_3$, the average responses, response time and recovery time of five sensors to four target analytes are shown in Fig. S7.† From the histogram, it is clear that the response of YFe$_{1-x}$Mn$_x$O$_3$ to the target analyte increases first and then decreases with the increase of manganese doping. As shown in Fig. S7a,† the average response of S1 to 1000 ppm of CH$_2$O, C$_2$H$_6$O, H$_2$O$_2$ and 100% RH is 36 851%, 8750%, 51 010% and 30 441%, respectively. As for the S2, the average response to 1000 ppm of CH$_2$O, C$_2$H$_6$O, H$_2$O$_2$ and 100% RH is increased to 52 083%, 17 858%, 83 422% and 46 409%, respectively. However, the average response of S3 to 1000 ppm of CH$_2$O, C$_2$H$_6$O, H$_2$O$_2$ and 100% RH is up to 344441%, 136711%, 465226% and 274374%, respectively. Compared with the S1, the response of the S3 to 1000 ppm of CH$_2$O, C$_2$H$_6$O, H$_2$O$_2$ and 100% RH is increased by 835%, 1462%, 812% and 801%, respectively. When the doping amount of Mn ions increases further, the sensitivity of the YFe$_{1-x}$Mn$_x$O$_3$ begins to decrease. As a result, the response of the S4 to 1000 ppm of CH$_2$O, C$_2$H$_6$O, H$_2$O$_2$ and 100% RH is 92 455%, 35 380%, 237120% and 24 864%, respectively, which is still better than that of S1. It can be seen that the effect of Mn doping on the gas sensing of YFe$_{1-x}$Mn$_x$O$_3$ is obvious. In terms of response and recovery rate, Mn doping has little effect on response time and recovery time of YFe$_{1-x}$Mn$_x$O$_3$ (Fig. S7b and c†). The response time of all sensors is less than 10 s, and the recovery time is less than 2 s, reflecting the sensing characteristics of fast response and fast recovery. This is because that good crystalline quality and one dimensional structure of YFe$_{1-x}$Mn$_x$O$_3$ is accounts for the higher electron mobility in gas sensors.

Although YFe$_{1-x}$Mn$_x$O$_3$ displayed good sensitivity to the above four atmospheres, it does not show good selectivity. An obvious advantage of sensor array compared with an individual sensor is that it can realize the discriminative detection to unknown analytes, based on certain mathematical analysis, and possibly, both kinetic and thermodynamic$^{12,42}$ or PCA.$^{43,44}$ Therefore, we prepare YFe$_{1-x}$Mn$_x$O$_3$ with different Mn doping amount into a sensor array to evaluate the feasibility of forming a sensor array. The responses of sensor array to four kinds of target atmosphere are used for principal component analysis (PCA) to evaluate the performance of sensor array. As shown in the Fig. 5a, on the two-dimensional PCA diagram, the data points corresponding to CH$_2$O and C$_2$H$_6$O are almost overlapped, indicating that the sensor array cannot distinguish CH$_2$O and C$_2$H$_6$O well. Furthermore, three-dimensional PCA (Fig. 5b) is used to evaluate the recognition ability of sensor array. Compared with the two-dimensional PCA, the three-dimensional PCA has improved the discrimination and basically achieved the discriminative detection of four analytes, but the data points corresponding to CH$_2$O and C$_2$H$_6$O are still relatively close. This may be because the performance of the sensors in the array is similar, so their discriminative ability is limited.

By combining the thermodynamic parameters and dynamic parameters, the digital signals can be transformed into graphic signals, and the visual detection of analytes can be realized by combining the image recognition technology. The response and response time are corresponding to the thermodynamic and kinetic parameters respectively. Therefore, five sensors have five response values and five response times for each analyte. For each analyte, the ratio of five responses to the corresponding five response times leads to five new parameters with thermodynamic and kinetic parameters. These five new parameters are used to build a visual pentagon and shown in Fig. 6. It can be seen from the Fig. 6 that because the S3 has the highest sensitivity, the pentagon looks like a triangle, which reduces the identification of the analyte. Therefore, we reduce the response of S3 to one tenth of the original response under the condition that other parameters remain unchanged, and build a visual pentagon again (Fig. 7). As a result, the visual recognition of four analytes is improved. Thus it can be seen if one wants to build a sensor array with high recognition ability, one need to select and optimize the sensors in the array.

Detection limit is an important parameter for estimating gas sensors. The relation between responses and vapour concentrations at RT were shown in Fig. 8. For H$_2$O$_2$ and CH$_2$O vapors, a nearly linear dependency between the response and the concentration in the low concentration range was observed (Fig. 8b and d). At higher concentrations, the response increases more slowly as the concentration increases, which shows that the adsorption of target molecules on the surface of sensing materials gradually reaches saturation. The linear relationship shows that the adsorption of H$_2$O$_2$ and CH$_2$O vapors on YFe$_{0.95}$Mn$_{0.05}$O$_3$ has not yet reached saturation in the low
concentration range. According to the fitting results in Fig. 8b and d, the estimated LOD (defined as LOD = 3S_D/m, where m is the slope of the linear part of the calibration curve and S_D is the standard deviation of noise in the response curve) for H_2O_2 and CH_2O is determined to be 1.75 and 2.55 ppb, respectively. These results show the high sensitivity of the YFe_{0.95}Mn_{0.05}O_3 to H_2O_2 and CH_2O vapors. This shows that perovskite YFe_{1-x}Mn_xO_3 can be used to measure both high and low concentration atmospheres and it is a very promising gas sensing materials.

According to the results of XPS analysis, with the increase of doping amount of Mn ions in YFe_{1-x}Mn_xO_3, the proportion of Mn^{3+} ion increases and the proportion of Mn^{2+} decreases. It can be seen that the increase of Mn ions in YFe_{1-x}Mn_xO_3 is significantly faster than the decrease of Mn^{2+} ion (Table 1). This means that although the proportion of Mn^{2+} ions decreases gradually, the net Mn^{2+} concentration increases with the increase of total doping amount of Mn ions. Electronegativity is a relative scale of the ability of atoms or ions to attract electrons. The Mn^{2+} ions have lower electronegativity than the Mn^{3+} ions. It means that Mn^{2+} ions are beneficial to the adsorption of oxygen ions on the surface of YFe_{1-x}Mn_xO_3, while Mn^{3+} ions are not conducive to the adsorption of oxygen ions. Thus, the competition between Mn^{2+} ions and Mn^{3+} ions may lead to an increase and then a decrease in the adsorbed oxygen on the surface of YFe_{1-x}Mn_xO_3 (Fig. 9a).

It is known that the depth of charge depletion layer (w) decide the sensing properties of chemiresistive sensors. The classical expressions for the w formed in the semiconductor upon gas adsorption:\cite{45, 46}

\[ w = L_D(2\beta V_S)^{1/2} \]  \hspace{1cm} (6)

where \( L_D \) is the Debye length, \( V_S \) the surface potential barrier, and \( \beta = q/kT \), where q is the electron charge, k the Boltzmann constant, and T the temperature. While, \( V_S \) can be expressed as the following equation:\cite{47}

\[ V_S = \frac{eN_t^2}{2\varepsilon\varepsilon_0 N_d} \]  \hspace{1cm} (7)

where \( N_t \) is the surface density of adsorbed oxygen ions (O^{2-}, O^{-} or O_2^{-}), the \( \varepsilon\varepsilon_0 \) permittivity of the semiconductor, and \( N_d \) the carrier concentration. Clearly, the \( V_S \) value depends on temperature, atmosphere, and dopant concentration; each of these parameters influences the \( V_S \), w and thus sensitivity.\cite{47}

Therefore, the competition between Mn^{2+} ions and Mn^{3+} ions results in the dynamic equilibrium of the oxygen absorption of the YFe_{1-x}Mn_xO_3 (Fig. 9a and b). XPS analysis (Table 1) shows that with the increase of Mn ions in YFe_{1-x}Mn_xO_3, the content of adsorbed oxygen increases first and then decreases (17.2%, 22.6%, 35.3%, 26.0% and 20.5%), reaching the maximum at x =
Fig. 7  Characteristic fingerprints deduced by combining kinetic and thermodynamic parameters from sensing data of (a) 100% RH, (b) saturated vapors of H$_2$O$_2$ at room temperature, (c) CH$_2$O, (d) C$_2$H$_6$O.

Fig. 8  Relation between responses of S3 and vapor concentrations at RT of (a) H$_2$O$_2$, (c) CH$_2$O; the fitting plots of response vs. concentration of (b) H$_2$O$_2$, (d) CH$_2$O.
0.05 for YFe$_{1-x}$Mn$_x$O$_3$. In addition, the increasing defects of YFe$_{1-x}$Mn$_x$O$_3$ caused by the doping of Mn ions may reduce the adsorption efficiency of oxygen ions for YFe$_{1-x}$Mn$_x$O$_3$, contributing to the tendency of first increase and then decrease of adsorbed oxygen. Accordingly, with the increase of Mn ions, the charge depletion layer of the material also increases first and then decreases (Fig. 9b). Therefore, the sensing performance of YFe$_{1-x}$Mn$_x$O$_3$ is the best when $x = 0.05$. When the $w$ is constant, the wider the width of the basic unit quadprism, the lower the proportion of $w$ in the whole quadprism, also resulting in the lower sensitivity. The dynamic equilibrium results in the increase of gas sensing properties of YFe$_{1-x}$Mn$_x$O$_3$ first and then decrease, which means that the doping of Mn ions can effectively control the gas sensing properties of YFe$_{1-x}$Mn$_x$O$_3$.

4. Conclusion

Perovskite YFe$_{1-x}$Mn$_x$O$_3$ with hierarchical structure was prepared by simple hydrothermal method and used as gas sensing materials. The gas sensing test showed that YFe$_{1-x}$Mn$_x$O$_3$ with different Mn doping amount displayed fast response and recovery characteristics to multiple target analytes as well as the good stability and recoverability. With the increase of Mn doping concentration, the response of YFe$_{1-x}$Mn$_x$O$_3$ to four kinds of target atmospheres first increases, then decreases. The gas sensing performance of YFe$_{1-x}$Mn$_x$O$_3$ is the best when $x = 0.05$. Compared with the S1, the response of the S3 to 1000 ppm of CH$_2$O, C$_2$H$_4$O, H$_2$O$_2$ and 100% RH is increased by 835%, 1462%, 812% and 801%, respectively. According to the PCA and radar chart analysis, the sensor array based on YFe$_{1-x}$Mn$_x$O$_3$ can basically identify four kinds of target analytes, and shows higher recognition ability after further data processing. It is feasible to realize the visual and discriminative detection of the target analyte by constructing sensor array through radar chart analysis and database construction.

Conflicts of interest

The authors declare no conflict of interest.

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