Room temperature methane sensing properties of $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles

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$\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ (0 ≤ x ≤ 0.17) nanoparticles were synthesized using an improved homogenous co-precipitation method. The effects of doped Cu on crystal structure of $\alpha$-Fe$_2$O$_3$ were investigated by field emission transmission electron microscopy, X-ray diffraction and Raman spectroscopy. Owing to the substitution of Cu$^{2+}$ at the Fe$^{3+}$ sites, the lattice parameters of $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ with an average particle size of ~40 nm and a single corundum structure increased with increasing doped Cu concentration. The shifting of Raman peaks for $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ to higher wavenumber was also observed due to the strong electron–phonon interactions and structural distortion after doping Cu. According to the conductivity measurements, doping Cu can increase the concentration of hole carriers and enhance the conductivity of the p-type $\alpha$-Fe$_2$O$_3$ semiconductor. Furthermore, CH$_4$ sensing characterization showed that the $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles are sensitive and have a good selectivity to CH$_4$ at room temperature, and the response of the material is evidently improved by doping with Cu. The maximum response to 2000 ppm CH$_4$ at room temperature and 50% relative humidity was obtained when x = 0.10, meeting the common requirements in application. These results suggest that $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles can be considered a potential candidate for methane detection at room temperature.

1. Introduction

Methane (CH$_4$), the second potent greenhouse gas, is often found in environment, industrial and domestic areas. It is the major component of natural gas, which is used widely in industries, automobiles and homes. However, it is necessary to detect CH$_4$ from coal mines, factories, farmland ventilation or natural gas-fueled appliances because it can form an explosive mixture in air if its concentration is in the range of 5–15%. There are several traditional techniques for CH$_4$ detection, such as gas chromatography equipped with a flame ionization detector (GC-FID) or infrared spectral radiometry. However, these common measurement methods for CH$_4$ have some disadvantages, requiring high cost equipment and strict working conditions. In the past few decades, metal-oxide semiconductors, such as SnO$_2$,$^2$ $\alpha$-Fe$_2$O$_3$, and ZnO,$^4$ have been investigated widely as CH$_4$ sensing materials because of their high response and simplicity in synthesis. Although these metal-oxide semiconductors have more advantages for CH$_4$ detection, there are also some problems including their low selectivity, particularly high working temperature (about 400–500 °C). The identification of CH$_4$ at temperatures lower than 350 °C is relatively difficult owing to its high thermodynamic stability compared to that of other hydrocarbons.$^5$ High working temperature in an atmosphere containing CH$_4$ is dangerous and may result in an explosion. Hence, there is strong demand for a reliable sensor that can detect CH$_4$ at or near room temperature. Nowadays, much effort has been devoted to reduce the gas-sensing temperature of metal oxides. For example, materials, such as Pd and Pt, catalyzing CH$_4$ decomposition at a relatively low temperature of 300 °C are loaded mainly in the stable metal oxides.$^6$ Unfortunately, the loading of noble metals has high cost and causes environmental pollution. Recently, great emphasis is being given to nanostructured$^{10,11}$ and doped metal$^{12}$ oxides as sensor materials to reduce the gas-sensing temperature. Nevertheless, the operating temperature of the vast majority of CH$_4$ sensors is not room temperature, and further studies are still necessary.

As a result, in the present study, $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles were selected and synthesized by an improved homogenous coprecipitation method. Based on the characteristics for the morphology, crystal structure and electric conductivity, the effects of doped Cu on crystal structure distortion and semiconducting property were investigated. The CH$_4$ sensing properties of the $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles were then examined. As expected, the sensor using $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles as a gas sensing material exhibited a receivable response to CH$_4$ at room temperature.

2. Experimental

All the chemical reagents were analytically pure without further purification. $\alpha$-Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles were prepared by an
Table 1 Mol ratio of \(n(\text{Cu}^{2+})/n(\text{Fe}^{3+})\) for preparing the hydroxide of \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) nanoparticles

| Sample ID | Value of \(x\) | \(n(\text{Cu}^{2+})/n(\text{Fe}^{3+})\) | Sample ID | Value of \(x\) | \(n(\text{Cu}^{2+})/n(\text{Fe}^{3+})\) |
|-----------|----------------|-------------------------------------|-----------|----------------|-------------------------------------|
| CF-0      | 0              | 0                                   | CF-5      | 0.10           | 0.05                                |
| CF-1      | 0.02           | 0.01                                | CF-6      | 0.11           | 0.06                                |
| CF-2      | 0.04           | 0.02                                | CF-7      | 0.13           | 0.07                                |
| CF-3      | 0.06           | 0.03                                | CF-8      | 0.15           | 0.08                                |
| CF-4      | 0.08           | 0.04                                | CF-9      | 0.17           | 0.09                                |

3. Results and discussion

3.1. Morphological characteristics of the \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) nanoparticles

Fig. 2 presents FE-TEM images of \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) nanoparticles. Part (a) and (b) show the bright field TEM image and high resolution TEM (HRTEM) image of undoped \(\alpha-\text{Fe}_2\text{O}_3\) grains, whereas parts (c) and (d) provide the bright field TEM image and HRTEM image of \(\alpha-\text{Fe}_{1.92}\text{Cu}_{0.08}\text{O}_3\), respectively. Fig. 2a shows that the undoped \(\alpha-\text{Fe}_2\text{O}_3\) powder consists of irregular particles with sizes in the range from 20 to 80 nm. To obtain more detailed structural information, a corresponding HRTEM image was recorded on the edge of the nanoparticle, shown in Fig. 2b. From the magnified HRTEM image of the selected area (inset of Fig. 2b), the lattice fringes could be observed clearly and the lattice spacing was 0.362 nm, corresponding to the \(012\) plane of \(\alpha-\text{Fe}_2\text{O}_3\). In comparison, the Cu doped \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) nanoparticles with a mean particle size of \(~40\) nm showed monodispersity (see Fig. 2c). The corresponding HRTEM image (Fig. 2d) displays the \(104\) plane with the \(d\) spacing of 0.266 nm for \(\alpha-\text{Fe}_{1.92}\text{Cu}_{0.08}\text{O}_3\). However, the \(d\) spacing did not increase significantly as expected, comparing with the value of undoped \(\alpha-\text{Fe}_2\text{O}_3\). TEM analysis of \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) nanoparticles is comparable to that of the Cu-doped \(\alpha-\text{Fe}_2\text{O}_3\) cubes reported in Sun’s study.11

3.2. Structural characteristics of the \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) nanoparticles

The XRD patterns of the \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) nanoparticles are shown in Fig. 3a. For undoped \(\alpha-\text{Fe}_2\text{O}_3\), all the diffraction peaks can be indexed by a single phase with the rhombohedral crystal structure of \(\alpha-\text{Fe}_2\text{O}_3\), which is consistent with the standard data file (PDF # 033-0664). For the \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) \((0 < x \leq 0.17)\)

Fig. 1  Schematic of (a) \(\alpha-\text{Fe}_{2-x}\text{Cu}_x\text{O}_3\) gas sensors and (b) equipment for the sensor response measurements.
nanoparticles, all diffraction peaks can also be successfully indexed to rhombohedral hematite and no other evident trace of impurity phase particularly copper oxide is detected. This indicates that the added Cu could be doped into the crystal structure of $\alpha$-Fe$_{2}$O$_{3}$, retaining the rhombohedral structure of hematite. Furthermore, from the zoomed-in (104) and (110) diffraction peaks of the $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ nanoparticles, as seen in Fig. 3b, the diffraction peaks all shifted to lower 2$\theta$ angles compared to those of undoped $\alpha$-Fe$_{2}$O$_{3}$, and the offset of peaks increased with increasing doped Cu concentration. To investigate the effects of doped Cu on the crystal structure of $\alpha$-Fe$_{2}$O$_{3}$, the room-temperature lattice parameters of $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ nanoparticles were obtained by the software X’Pert HighScore Plus based on the XRD data, as depicted in Fig. 3c. The results show that the lattice parameters $a$, $b$ and $c$, all increased with increasing doped Cu concentration. The ionic radii (six-coordination in a rhombohedral structure) of Fe$^{3+}$ and Cu$^{2+}$ are similar at 0.0645 nm and 0.073 nm$^{12}$ respectively. Therefore, Cu$^{2+}$ can be doped into the crystal structure of $\alpha$-Fe$_{2}$O$_{3}$ and partly substitute Fe$^{3+}$. There is no doubt that the lattice parameters may increase when the substitutions exist. Hence, the shift of diffraction peaks and increase in lattice parameters are in association with the substitutions of Fe$^{3+}$ by Cu$^{2+}$. In addition, with increasing doped Cu concentration ($x$), the lattice parameters of $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ increased gradually, which was accomplished by the shift of the diffraction peaks to lower 2$\theta$ angles.

In addition, to further investigate the structural distortion of Cu-doped $\alpha$-Fe$_{2}$O$_{3}$ nanoparticles, the Raman spectra of the $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ nanoparticles at room temperature were collected (see Fig. 4). The Raman peaks located at 222 cm$^{-1}$ and 493 cm$^{-1}$ correspond to $A_{1g}$ modes, whereas the peaks at 241 cm$^{-1}$, 289 cm$^{-1}$, 405 cm$^{-1}$, and 606 cm$^{-1}$ are assigned to $E_{g}$ modes. This confirms the corundum structure of $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ ($0 \leq x \leq 0.17$), which is consistent with the values reported in the literature.$^{14,15}$ In general, substitutions of larger ions at the Fe sites may lead to an increase in the mean Fe–O bond length, resulting in a shift of the Raman peaks to lower wavenumbers. However, in the present study, it is puzzling that all of the Raman peaks of Cu doped $\alpha$-Fe$_{2}$O$_{3}$ shifted slightly to higher wavenumbers, compared to those of undoped $\alpha$-Fe$_{2}$O$_{3}$. According to Yogi and Varshney, similar Raman spectrum changes were also observed and attributed to the strong electron–phonon interactions and structural distortion in this system after doping Cu, accompanied with an increase in chemical bond strength.$^{16}$ These structural changes of the $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ nanoparticles induced by doped Cu are expected to have an effect on the electrical and CH$_{4}$ sensing properties.

### 3.3. Electrical properties of the $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ gas sensors

Fig. 5 shows the conductivities of the $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ gas sensors at room temperature. The conductivities of the sensors were calculated using eqn (1):

$$\sigma = \frac{1}{\rho} = \frac{L}{RS}$$

Fig. 2 TEM images of $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ nanoparticles: (a) bright field TEM image and (b) HRTEM image showing grain with the (012) plane of undoped $\alpha$-Fe$_{2}$O$_{3}$, (c) bright field TEM image and (d) HRTEM image showing grains with the (104) plane of $\alpha$-Fe$_{1.92}$Cu$_{0.08}$O$_{3}$.

Fig. 3 (a) XRD patterns, (b) zoomed-in (104) and (110) peaks, and (c) room-temperature lattice parameters of $\alpha$-Fe$_{2-x}$Cu$_{x}$O$_{3}$ nanoparticles.
According to Long’s research, the conductivity of the Fe$_2$O$_3$ semiconductor increases from 1.2 to 6.3 $\times$ 10$^{-5}$ S m$^{-1}$ with increasing $x$ in Fe$_{2-x}$Cu$_x$O$_3$ from 0 to 0.17. Clearly, Cu doping enhances the electric conduction capability of Fe$_2$O$_3$ gas sensor greatly.

According to Long’s research, Cu doped Fe$_2$O$_3$ annealed in air is a p-type semiconductor and the one annealed in oxygen usually is the conductivity level of the Fe$_2$O$_3$ semiconductor is enhanced, and the conductivity of the Fe$_{2-x}$Cu$_x$O$_3$ sensor increases with increasing doped Cu concentration.

### 3.4. CH$_4$ sensing properties of the Fe$_{2-x}$Cu$_x$O$_3$ gas sensors

Fig. 6 depicts CH$_4$ gas response of the Fe$_{2-x}$Cu$_x$O$_3$ gas sensors in an atmosphere containing CH$_4$ (2000 ppm) at 25 °C and 50% relative humidity (RH); the inset shows the gas response of the undoped Fe$_{2-x}$Cu$_x$O$_3$ gas sensors to CH$_4$ with different concentrations at 25 °C and 50% RH. The undoped Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles have a lower response to 2000 ppm CH$_4$ gas at room temperature. In contrast, the response of the Fe$_{2-x}$Cu$_x$O$_3$ gas sensor is significantly higher at room temperature and at the same concentration of CH$_4$ gas. The maximum response to 2000 ppm CH$_4$ at room temperature was obtained when $x$ in Fe$_{2-x}$Cu$_x$O$_3$ $\approx$ 0.10. Although the maximum response is only $\approx$ 1.06, this material is also a potential candidate for methane gas sensor applications because the working temperature is much lower in the present case. The sensor using Fe$_{2-x}$Cu$_x$O$_3$ nanoparticles as gas sensing material exhibits a receivable response to CH$_4$ at room temperature. The inset in Fig. 6 indicates that the response increased almost linearly with increasing concentration of CH$_4$ gas from 500 to 4000 ppm, meeting the common requirements in application.

Moreover, for environmental monitoring of methane emissions at room temperature, the selectivity of the Fe$_{2-x}$Cu$_x$O$_3$ gas sensors was also evaluated. Fig. 7a shows the response of the Fe$_{2-x}$Cu$_x$O$_3$ gas sensors to different test gases (1000 ppm), i.e., CO$_2$, C$_2$H$_5$OH and NH$_3$ at 25 °C and 50% RH. In the CO$_2$, energy level (usually called isolated energy level) can be introduced between the valence band and conduction band if the substitutions of Cu$^{2+}$ ions occur at the Fe sites. The acceptor impurities on the acceptor energy level will ionize and lead to an increase in conductive holes in the valence band. As a result, the conduction capability of the Fe$_2$O$_3$ semiconductor is enhanced, and the conductivity of the Fe$_{2-x}$Cu$_x$O$_3$ sensor increases with increasing doped Cu concentration.
sensing testing, only 700 ppm CO₂ was injected because clean air contains around 300 ppm CO₂. This shows that the response of the sensors to CH₄ is the highest, indicating that the α-Fe₂₋ₓCuₓO₃ sensor has good selectivity for CH₄, even though it exhibits a certain response to C₂H₅OH. As expected, Cu doping can significantly improve the selectivity of the sensor for CH₄. Fig. 7b displays the effect of humidity on the sensor response at 1000 ppm CH₄ at 25 °C.

In a vacuum

In clean air

In an atmosphere containing CH₄

The CH₄ sensing mechanism (depicted in Fig. 8) of α-Fe₂₋ₓCuₓO₃ nanoparticles is a surface controlled process and can be understood as follows. In vacuum, there are a great number of unstable active sites on the surface of the p-type α-Fe₂₋ₓCuₓO₃ semiconductor, with holes as majority carriers. When α-Fe₂₋ₓCuₓO₃ nanoparticles are exposed to air, a certain amount of oxygen from the air is adsorbed on the surface of α-Fe₂₋ₓCuₓO₃ in the form of O₂⁻ or O⁻, by transferring electrons from the conduction band to the adsorbed oxygen atoms. In this process, the formation of chemisorbed oxygen species results in a decrease in the free electron concentration in the material conduction band. Consequently, the conductivity of the p-type semiconductor will increase. It should be noted that the amount of chemisorbed oxygen species may be affected, even decreased, with the increasing adsorption of water vapor on the surface of α-Fe₂₋ₓCuₓO₃, which is not conducive to improving the gas sensing performance. Once the α-Fe₂₋ₓCuₓO₃ nanoparticles are exposed to an atmosphere containing CH₄, surface reaction between the adsorbed oxygen species and CH₄ molecules will occur, resulting in the release of electrons trapped in the ionized oxygen species back into the materials and electron–hole recombination, thereby decreasing the concentration of hole carriers and lowering the measured conductivity.

4. Conclusion

α-Fe₂₋ₓCuₓO₃ (0 ≤ x ≤ 0.17) nanoparticles were synthesized by an improved homogenous co-precipitation method. The morphological and structural characteristics showed that α-Fe₂₋ₓCuₓO₃ (0 < x ≤ 0.17) nanoparticles with an average particle size of ~40 nm also have a single phase with a rhombohedral...
corundum structure. Owing to the substitution of Cu\(^{2+}\) at Fe\(^{3+}\) sites, the lattice parameters of \(\alpha\)-Fe\(_2\)\(_x\)Cu\(_x\)O\(_3\) increase with increasing doped Cu concentration. The shift of Raman peaks for \(\alpha\)-Fe\(_2\)\(_x\)Cu\(_x\)O\(_3\) to higher wavenumbers was observed due to the strong electron–phonon interaction and structural distortion after doping Cu. Doping Cu can also increase the concentration of hole carriers and enhance the conductivity of p-type \(\alpha\)-Fe\(_2\)O\(_3\) semiconductor. The CH\(_4\) sensing characterization shows that the \(\alpha\)-Fe\(_2\)\(_x\)Cu\(_x\)O\(_3\) nanoparticles are sensitive and have good selectivity to CH\(_4\) at room temperature, and the response of the \(\alpha\)-Fe\(_2\)\(_x\)Cu\(_x\)O\(_3\) \((0 < x \leq 0.17)\) gas sensor is significantly improved by doping Cu. The maximum response to 2000 ppm CH\(_4\) at room temperature and 50% RH was obtained when \(x\) in \(\alpha\)-Fe\(_2\)\(_x\)Cu\(_x\)O\(_3\) = 0.10, meeting the common requirements in application. Based on these results, the \(\alpha\)-Fe\(_2\)\(_x\)Cu\(_x\)O\(_3\) \((0 < x \leq 0.17)\) nanoparticles can be considered potential candidates for methane detection at room temperature.

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## References

1. J. Hill, C. McSweene, A. D. G. Wright, G. Bishop-Hurley and K. Kalantar-zadeh, *Trends Biotechnol.*, 2016, 34, 26.
2. Z. K. Horastani, S. M. Sayedi, M. H. Sheikhi and E. Rahimi, *Mater. Sci. Semicond. Process.*, 2015, 35, 38.
3. A. Das, V. Bonu, A. K. Prasad, D. Panda, S. Dhara and A. K. Tyagi, *J. Mater. Chem. C*, 2014, 2, 164.
4. T. Sarangi, M. Naja, S. Lal, S. Venkataramani, P. Bhardwaj, N. Ojha, R. Kumar and H. C. Chandola, *Atmos. Environ.*, 2016, 125, 450.
5. S. Maduskar, A. R. Teixeira, A. D. Paulsen, C. Krumm, T. J. Mountziaris, W. Fan and P. J. Dauenhauer, *Lab Chip*, 2015, 15, 440.
6. J. A. Sinclair, P. G. J. Irwin, S. B. Calcutt and E. L. Wilson, *Icarus*, 2015, 260, 103.
7. B. Dong, Z. Han, Y. B. Zhang, Y. Y. Yu, A. G. Kong and Y. K. Shan, *Chem.–Eur. J.*, 2016, 22, 2046.
8. J. Hu, F. Q. Gao, Z. T. Zhao, S. B. Sang, P. W. Li, W. D. Zhang, X. T. Zhou and Y. Chen, *Appl. Surf. Sci.*, 2016, 363, 181.
9. S. M. Sedghi, Y. Mortazavi and A. Khodadadi, *Sens. Actuators, B*, 2010, 145, 7.
10. A. Amutha, S. Amirthapandian, A. K. Prasad, B. K. Panigrahi and P. Thangadurai, *J. Nanopart. Res.*, 2015, 17, 289.
11. P. Sun, C. Wang, X. Zhou, P. F. Cheng, K. Shimanoe, G. Y. Lu and N. Yamazoe, *Sens. Actuators, B*, 2014, 193, 616.
12. H. F. Liu, T. J. Peng, H. J. Sun, L. Fan and B. G. Guo, *Adv. Mater. Res.*, 2010, 96, 105.
13. R. D. Shannon, *Acta Crystallogr.*, 1976, 32, 751.
14. A. Yogi and D. Varshney, *Mater. Sci. Semicond. Process.*, 2014, 21, 38.
15. L. Kopanja, I. Milosevic, M. Panjan, V. Damnjanovic and M. Tadic, *Appl. Surf. Sci.*, 2016, 362, 380.
16. N. V. Long, Y. Yang, M. Yuasa, C. M. Thi, Y. Cao, T. Nann and M. Nogami, *RSC Adv.*, 2014, 4, 8250.
17. A. Mirzaei, B. Hashemi and K. Janghorban, *J. Mater. Sci.: Mater. Electron.*, 2016, 27, 3109.
18. S. Yamaguchi, *Mater. Chem.*, 1981, 6, 505.