Extreme chemical sensitivity of nonlinear conductivity in charge-ordered LuFe$_2$O$_4$

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Nonlinear transport behaviors are crucial for applications in electronic technology. At the nonlinear critical turning point, the nonequilibrium states cause rich physics responses to environment. The corresponding study in this field is crucial for physics and industry application. Here nonlinear conductivity in charge-ordered (CO) LuFe$_2$O$_4$ has been demonstrated. Remarkable resistivity switching behavior was observed and the gas-sensing property can be reversibly tuned by a small alternation of partial pressure and/or chemical components of the environment. These facts allow us to use LuFe$_2$O$_4$ materials as a sensitive chemical gas sensor in technological applications. Careful analysis of the gas sensing process in LuFe$_2$O$_4$ suggests a novel sensing mechanism in sharp contrast with that discussed for the conventional gas sensors which depend fundamentally on surface chemical reactions.

Results

In order to characterize the essential transport nonlinearity in the layered LuFe$_2$O$_4$ crystal, we first performed our resistivity measurements on a number of single crystal samples along the relevant directions. Figures 1a and 1b show the current density-voltage field (J-E) curves obtained from a single crystalline LuFe$_2$O$_4$ sample for the current flowing respectively parallel (Elc) and perpendicular (E//ab plane) to the c-axis direction, illustrating the presence of visible nonlinear J-E characteristics along the c-axis and within the ab plane in a LuFe$_2$O$_4$ crystal. The nonlinear behavior in each measurement can be clearly recognizable as a clear anomaly cross the threshold electric field (Et), the Et in general appear at around 60 V/cm and 10 V/cm for E parallel and perpendicular to the c-axis direction. According to the empirical power-law relation of $I \propto V^a$, the nonlinear coefficients of the single crystal can be estimated to be about 200 and 30 for the $I//c$ and $I\perp c$ directions, these coefficients depend moderately on the current density used in transport measurements.

It has been commonly noted in previous investigations that visible alternation of resistance state could be triggered in a number of the CO systems. Our recent experimental investigations reveal that the nonlinear conductivity in association with CO melting in LuFe$_2$O$_4$ is extremely sensitive to the environmental conditions. Figure 2a shows nonlinear J-E behaviors taken from a well-characterized polycrystalline samples upon exposure
to different gaseous environments. It is recognizable that a jump-like transition of electric current yields a visible nonlinear conductivity at a threshold electric field, or corresponding threshold currents for each curve. The most striking phenomenon revealed in our measurements is the notable divergent behaviors above the threshold, demonstrating the existence of atmosphere-dependent J-E characteristics in the CO LuFe$_2$O$_4$ material. It is also noted that the sample in a He atmosphere shows a relatively high threshold current and a larger resistivity in comparison with the data obtained in O$_2$ and Ar atmosphere. According to the results shown in Fig. 2a, we can estimate the threshold current values for LuFe$_2$O$_4$ under different environmental conditions as: $J = 0.5 \text{ A/cm}^2$ for vacuum ($\sim 10^{-1}$ Pa), $0.7 \text{ A/cm}^2$ for O$_2$, and $0.9 \text{ A/cm}^2$ for He, respectively. Moreover, it is also noted that the gas sensitivity depends strongly on applied current in experimental measurements, i.e. the larger electric current is used, and the bigger difference appears in data of the resistivity. This feature is also recognizable in Fig. 2b which shows a series of resistivity curves under different testing currents from 0.3 A/cm$^2$ to 3.0 A/cm$^2$. This measurement was first performed on a LuFe$_2$O$_4$ sample under ambient conditions, and then the O$_2$ was pumped out to lower the chamber pressure progressively to $10^{-1}$ Pa. The remarkable effects of electrically driven non-linear resistivity and visible resistivity changes with alterations of the O$_2$ partial pressure are plainly illustrated.

Though there is no uniform definition for the gas-sensor sensitivity now, we can use the ratio of $S_R = \frac{R_{\text{vac}} - R_x}{R_{\text{vac}}} \times 100\%$ to qualitatively illustrate the sensitivity in our measurements. According our experimental data shown in Fig. 2b, $S_R$ depends strongly on the applied electric current, for instance, it is estimated to be $\sim 37.8\%$ and $72.7\%$ for $J = 0.3 \text{ A/cm}^2$ and $3.0 \text{ A/cm}^2$, respectively.

In order to understand the gas sensitivity in correlation with the charge order in LuFe$_2$O$_4$, we have checked the temperature dependence of the resistivity switching in the temperature range from 295 K to 520 K between vacuum and argon under testing current 0.3 A/cm$^2$. Inset shows details of R(T) curve at 440 K and 520 K respectively.
to 520 K and in the gaseous environment of Ar/vacuum in which the LuFe$_2$O$_4$ sample can be safely heated to high temperatures above the charge ordering transition temperature ($T_{co} \approx 500$ K). As shown in Fig. 2c, the switching of resistance state occurs when the sample chamber is pumped from argon to vacuum below 440 K, suggesting the environmental condition plays important role for the resistivity switching. This switching feature gradually disappears as the temperature rises to the CO transition value ($T_{co} \approx 500$ K) above which LuFe$_2$O$_4$ has a charge-disordered state with a relatively high conductivity. These facts demonstrate the presence of an essential correlation between charge ordering and gas sensitivity in present system.

In Fig. 3 the reversibility of the resistance switching in LuFe$_2$O$_4$ is discussed. We performed experimental measurements on a sample in the O$_2$ chamber. Decrease of oxygen pressure by pumping out the O$_2$ from the chamber to vacuum leads to a rapid resistance switch into low resistance states; then when the O$_2$ is reintroduced into the chamber, the experimental data switches reversibly to higher resistance state. Figure 3 shows a series of the experimental results as the sample was cycled between vacuum ($\leq 0.1$ Pa) and O$_2$, illustrating the remarkable resistance switching and high gas sensitivity for LuFe$_2$O$_4$ at room temperature. It is clearly recognizable that a rapid and reversible change in the resistance oscillates in response to the alternating environmental pressure. Similar resistivity switching behavior has been also observed by using the LuFe$_2$O$_4$ single crystal samples, demonstrating an essential bulk property of gas sensitivity instead of effects from surface or grain boundaries as commonly discussed for the conventional gas sensors. Besides, measurements in oxygen environment often show some additional complex changes, which are believed to be connected with the interstitial and/or deficient oxygen atoms in the layered LuFe$_2$O$_4$.

Considering the notable effects of interstitial oxygen ions on both microstructure and transport properties of LuFe$_2$O$_4$, we have also examined the changes of microstructure in association with nonlinear transition by using in situ TEM observation, which could be also important for understanding the sensing mechanism in present system. Figure 4 clearly shows the superstructure modulations in correlation with charge order and oxygen order as discussed in our previous investigations$^{11}$. Following the increase of applied electric field, the superstructure spots in the diffraction pattern gradually become invisible and disappear as illustrated in Fig. 4b. Based on our TEM experimental data, we estimate that the threshold electric field is approximately 45 V/cm. After the external electric field is removed, the CO satellite spots in the diffraction pattern re-emerge in the same crystal but the superstructure from oxygen order shows clear irreversibility in a high-vacuum column of TEM. When the sample was placed in air for more than 24 hrs, the superstructure spots of oxygen order appear again as showed in Fig. 4d. These facts suggest that certain microstructure features in present system also vary under the applied current, and their reversibility could also be important for technological applications of gas sensing materials.

**Discussion**

The gas sensing process and fundamental mechanism for the gas response in the CO LuFe$_2$O$_4$ as essential issues were also concerned in our investigations. Based on localized electron variable-range hopping (VRH) picture$^{12}$, the electric conductivity in the CO materials could be enormously sensitive to the modification of the

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**Figure 4** | The in situ TEM electron diffraction patterns taken along the [1–10] zone axis direction. (a) The diffraction spots in circle and rectangular is charge ordering and oxygen modulations respectively. (b) The charge-ordered (CO) state and oxygen modulations disappear when applied electric field is larger than $E_{th}$ ($\approx 45$ V/cm). (c) The CO state has recovered after the applied electric field is removed while the oxygen modulations fail to reappear. (d) The CO and oxygen modulations reemerge when the sample is placed in air for more than 24 hrs.

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**Figure 3** | Period of resistance change when switching atmosphere between oxygen and vacuum regularly. The testing current is 0.3 A/cm$^2$. In the different regions divided by dashed lines, the $O_2^+$ is the oxygen region where sample was placed initially; $P^a$ is the region of pumping to vacuum; $O_2^-$ is the region of introducing oxygen again; $P^b$ is the region of re-pumping vacuum.
thermodynamic equilibrium. In a CO system, when nonlinear transition occurs above the threshold value, the melting of the CO state, together with the collective movement of charge stripes, can result in a strong electron-phonon interaction which contributes the Joule heating effect. Though the Joule heating could not change the essential feature of nonlinear conductivity, it indeed can induce visible alterations in the resistivity as discussed in our previous work on LuFe₂O₄ materials. In the present study, LuFe₂O₄ was exposed to variable gaseous environments, and the thermal equilibrium states of samples depend mainly on thermal balance between Joule heating and thermal diffusion.

If the applied current density does not reach to the threshold value to trigger nonlinear conductivity, no clear gas sensitivity can be observed in our measurements. On the other hand, if the applied current is larger than the threshold value, nonlinear conductivity depends strongly on temperature and the thermal equilibrium. Because the thermal conductivity/diffusion coefficients of gases are different for O₂, Ar and He, alternation of the composition and partial pressure of gases could lead to certain changes in the thermal equilibrium, which sequentially yields a visible change in resistivity as revealed in our experiments. Under a constant applied current, it is expected that the higher conductivity/diffusion coefficient of a gas should result in a bigger resistance state, which is in a good agreement with our experimental data. For example, the conductivity coefficients for He10, O₂ and Ar16 are 156.7, 26.3 and 17.9 mW/mK at 300 K (1 atm), respectively. The corresponding resistances are 847.7, 641.8 and 587.7 ohms in these gas environments under a constant testing current density of 1.5 A/cm².

Careful analysis of the gas sensing process suggests a novel sensing mechanism based on the thermal conductivity/diffusion coefficients of environment gases in stark contrast with the conventional gas sensors that depend chiefly on surface reactions. Moreover, in situ TEM observation suggests that certain microstructure features in present system also are sensitive to the vacuum environment, and their reversibility could also be important for technological applications of gas sensing materials.

The experiments on other CO materials also reveal very similar sensitivity phenomena as shown in supplementary materials. These observations open up new prospects for finding new functional applications and understanding interesting physics in CO materials and other nonlinear materials.

**Methods**

The well-characterized LuFe₂O₄ polycrystalline samples used in this study were synthesized by a conventional solid-state reaction. Polycrystalline samples of LuFe₂O₄ were synthesized from stoichiometric mixtures of Lu₂O₃ (99.99%) and Fe₂O₃ (99.99%) under a controlled oxygen partial pressure atmosphere using a CO₂-H₂ mixture at 1200 °C for 48 hours. In order to obtain the single crystals, the polycrystalline LuFe₂O₄ powder was heated up to 1620 °C in a platinum crucible and then the melted solid was cooled to 900 °C at a rate of 1 °C/min. The typical size of the polycrystalline sample used in our measurements is 2×5×1 mm³. A thermocouple as commonly used in previous studies was attached on the sample holder to detect the temperature, and an additional thermometer was attached directly on the sample for certain measurements. Silver contact pads with a radius of ~1 mm were deposited on samples. Current density-electric field (J-E) curves and transport testing were obtained by the two-probe and/or four-probe methods with a Keithley 2400/2611A source meter. In order to protect the samples, a compliance current of 200 mA was used during the testing of nonlinear J-E curves. Transmission electron microscopy (TEM) observations were performed at room temperature on a Tecnai F20 (200 kV) double-tilt TEM holder on which the in situ observations upon applied electric field can be performed.

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**Acknowledgements**

We would like to thank Professor Z.J. Ding for his help during manuscript preparation. This work is supported by the NSFC (Grant Nos. 90922001, 10904166, 11074292), the MOST (Grant Nos. 2011CBA00101, 2010CB923002, 2012CB821404, 2006CB921301), and the Chinese Academy of Sciences.

**Author contributions**

J.Q.L., S.C. planned and coordinated the experiments. S.C., J.L. carried out gas sensing resistivity experiments. Z.W., S.C. performed TEM measurement and analysis. L.J.Z. prepared the figure 1. Y.B.Q. grew LuFe₂O₄ polycrystal and single crystal samples. H.F.T., C. M. and H.X.Y. helped with data interpretation. J.Q.L., S.C. wrote the paper.

**Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports