

Corporation Effect of CuO and Fe₂O₃ Composites in VOC Sensing

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Summary:

We demonstrated improved VOC sensing using composites of p-type CuO and n-type Fe₂O₃ metal oxide semiconductors. The composites were prepared using both chemical mixing (sol–gel method) and physical mixing. Both composites showed higher sensor signals and faster response and recovery speeds compared to the pure phase, while the physically mixed sample maintained the baseline resistance and sensitivity of Fe₂O₃. Operando DRIFTS measurements confirmed consistent surface chemistry, indicating that the improvements originate from the electronic coupling effect between CuO and Fe₂O₃.

Keywords: SMOX sensor, VOCs, CuO, Fe₂O₃, corporation effect

Introduction

Semiconducting metal oxides (SMOXs)-based gas sensors, as one of the most important types of chemical sensors, have attracted widespread scientific attention. However, their practical applications are still limited by several drawbacks, such as slow response and recovery speeds, especially toward low-concentration VOC gases. Our previous work demonstrated that Fe-containing materials exhibit better performance in VOC sensing; however, they also suffer from slow response and recovery kinetics, as observed in both Fe-containing perovskites and Fe₂O₃. This limitation can be mitigated by increasing the operating temperature to accelerate surface reactions and enhance charge carrier transport. However, elevated temperatures also increase power consumption and reduce the sensor signal. Fe-containing spinels, on the other hand, exhibit much faster response and recovery kinetics, despite their relatively poor sensitivity. Therefore, we explored another Fe-containing spinel, CuFe₂O₄. However, we accidentally obtained a mixture of CuO and Fe₂O₃, which exhibited improved performance, including higher sensor signals and faster response and recovery. We therefore performed a series of characterizations to elucidate the underlying mechanisms.

Materials and Methods

We first attempted to synthesize CuFe₂O₄ via a sol–gel method at different calcination temperatures ranging from 300 to 800 °C. The samples are denoted as CFO, followed by a suffix indicating the calcination temperature. CuO and Fe₂O₃

were synthesized using the same method and calcined at 500 °C. Characterization results revealed that the products obtained at lower temperatures (below 700 °C) consist of mixtures of CuO and Fe₂O₃. These mixtures, however, exhibited superior performance during the sensing tests. We then physically mixed CuO and Fe₂O₃ powders; the resulting material retained the baseline resistance of Fe₂O₃ while showing faster response and recovery speeds toward formaldehyde, as well as other VOCs. We therefore performed operando DRIFTS measurements to investigate the differences in surface chemistry among these materials. All sensors were fabricated using screen printing, and the sensing tests were conducted in a dynamic gas-mixing system with multiple VOC channels.

Results and Discussion

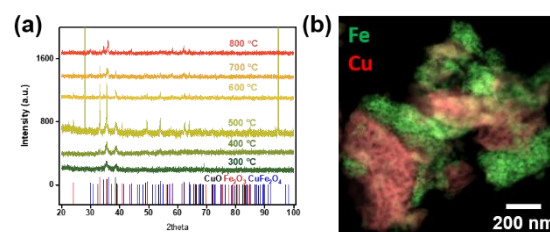


Fig. 1. (a) The XRD results of all synthesized materials. (b) The EDS mapping of CFO500 sample.

The crystallographic information was evaluated by X-ray diffraction (XRD), as summarized in Fig. 1(a). Incomplete crystallization at low temperatures (300 and 400 °C) leads to weak and broad diffraction peaks in the patterns. At 300 °C, only the CuO phase can be observed. Fe₂O₃ starts to

form at temperatures above 400 °C. Notably, the sharp peaks appearing at around 28 and 94.7° originate from the silicon substrate. At temperatures above 700 °C, CuO and Fe₂O₃ begin to convert into the spinel phase CuFe₂O₄, and at 800 °C, a pure spinel phase is obtained. Samples prepared between 400 and 700 °C consist of mixed phases of CuO and Fe₂O₃. The sample calcined at 500 °C shows better crystallinity and was therefore selected to evaluate the phase and elemental distribution by EDS mapping (see Fig. 1(b)). Clearly, the CuO and Fe₂O₃ particles are closely connected, which provides the possibility for forming more n-p heterojunctions.

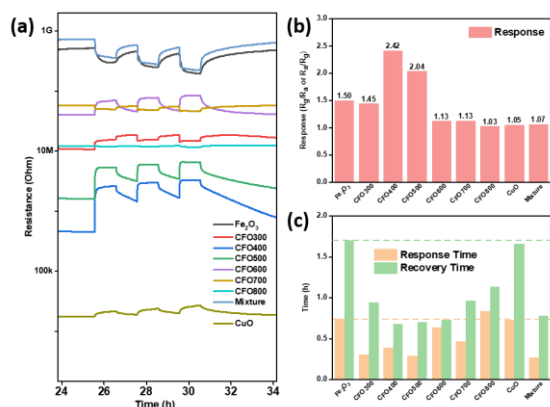


Fig. 2. (a) Output curves of all fabricated sensors toward 50, 100, and 200 ppb formaldehyde. (b) Calculated response values and (c) response and recovery times of all fabricated sensors toward 200 ppb formaldehyde. The sensor operating temperature was 150 °C.

The response curves of the fabricated sensors toward different concentrations of formaldehyde are shown in Fig. 2(a). Pure CuO, shown at the bottom, has a conductivity advantage, as indicated by its lowest baseline resistance. However, the limited sensor signals reveal its lower surface activity. The sample calcined at 300 °C exhibits an n-to-p conduction inversion, which is an intrinsic property of Fe₂O₃ [1]. However, this inversion is not observed in other mixtures, including the samples calcined at 400, 500, and 600 °C, nor in the physically mixed sample. The conduction type of Fe₂O₃ is inverted only when conduction band electrons are depleted and oxygen begins to extract electrons from the valence band. This strongly supports the interaction between CuO and Fe₂O₃. Electrons spontaneously transfer from the conduction band of Fe₂O₃ to the valence band of CuO, resulting in a decrease in the electron concentration of Fe₂O₃, which makes it more easily depleted, i.e., more prone to a change in conduction type.

The sensor responses are shown in Fig. 2(b). The samples calcined at 400 and 500 °C exhibit

higher sensitivity, which originates from the increased formation of n-p junctions within the material. At higher temperatures, particle growth occurs and the spinel phase, which exhibits poor sensitivity, begins to form, resulting in decreased sensor signals. The response and recovery times, summarized in Fig. 2(c), clearly show that both the response and recovery speeds of the mixtures, including the chemically mixed and physically mixed samples, are faster than those of the pure phases.

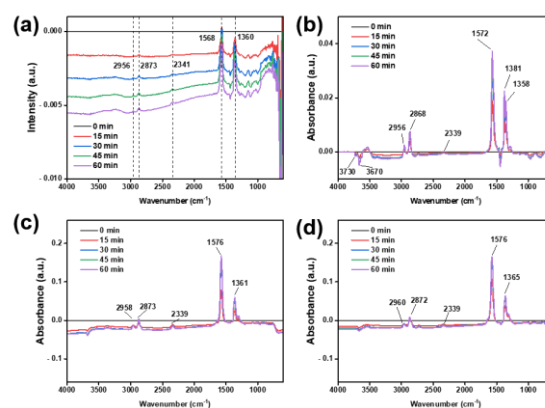


Fig. 3. DRIFT absorbance spectra of (a) CuO, (b) Fe₂O₃, (c) CFO400 and (d) CFO500 toward 10 ppm formaldehyde, collected with 15 min intervals.

The operando DRIFTS results are shown in Fig. 3. Intermediate products from the oxidation of formaldehyde, including bridged formate and dioxymethylene, can be clearly observed in the spectra of all samples[1]. Terminal formate species are observed in the spectra of Fe₂O₃. The peak at 2341 cm⁻¹ is attributed to carbon-containing species introduced by the organic precursors; this species is still under investigation. Apparently, the absorbance intensity of CuO is the lowest among the four samples. This further confirms its poor catalytic activity, which is consistent with the low sensor signal. The mixtures, including CFO400 and CFO500, exhibit significantly higher absorbance, indicating a higher concentration of surface species, which is induced by the cooperation between CuO and Fe₂O₃.

Referenc

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