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Improved Gas-Sensing Properties of Graphene-$CoFe_2O_4$ Composite Prepared via Homogeneous Precipitation

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ABSTRACT
Before studying the gas-sensing properties of graphene-$CoFe_2O_4$ composite, graphene-$CoFe_2O_4$ composite with different mixing ratio are prepared via homogeneous precipitation method with urea as precipitator and characterized by X-ray diffraction using CuKα. The experimental results reveal that the average grain size of $CoFe_2O_4$ with spinel-type structure is about 60 nm. The sensitive properties of pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are similar to the p-type semiconductor, and the sensor based on 5%G-$CoFe_2O_4$ shows the high sensitivity to ammonia, acetone vapor, formaldehyde vapor and acetaldehyde vapor with the temperature range from 80 to 300°C. Especially, the sensor based on 5%G-$CoFe_2O_4$ shows the sensitivity as high as 3 to 1000 ppm formaldehyde vapor when the operating temperature of sensor is 180°C. Thus, graphene-$CoFe_2O_4$ composite may be applied to measure the formaldehyde vapor at low temperature if the selectivity and response are improved further.

Keywords: Graphene, $CoFe_2O_4$, gas-sensing properties.

1. INTRODUCTION
$CoFe_2O_4$ is an important member of AFe_2O_4 composite oxide with spinel-type structure, which is mainly prepared by co-precipitation method[1], sol-gel method[2], hydrothermal method[3] and microwave method[4]. $CoFe_2O_4$ have attracted much attention due to its outstanding magnetic property[5,6], catalytic performance[7] and gas-sensing property[8,9]. Recently, graphene-$CoFe_2O_4$ composite are applied as photo-catalyst[10], water treatment agent[11] and an anode for lithium battery[12]. However, as far as we know, the application of graphene-$CoFe_2O_4$ composite on gas sensor is rarely reported in the present literatures. Thus, we attempt to prepare graphene-$CoFe_2O_4$ composite via homogeneous precipitation method and study the gas-sensing property of sensors based on graphene-$CoFe_2O_4$ composite.

In this paper, graphene mixed $CoFe_2O_4$ was prepared via homogeneous precipitation method and the responses to ammonia, acetone vapor, formaldehyde vapor, ethanol vapor, acetaldehyde vapor and acetic acid vapor were studied in detail. It was found that graphene mixing has great influence on the gas response, especially, the sensor based on 5 wt% graphene mixed $CoFe_2O_4$ (5%G-$CoFe_2O_4$) showed best gas-sensing performance to formaldehyde vapor.

2. EXPERIMENTAL
2.1 *Preparation and characterization of graphene (G), $CoFe_2O_4$ and G-$CoFe_2O_4$ composite*
The preparation method of graphene is similar to that reported in literature[13]. Graphene oxide (GO) was synthesized from graphite powder by Hummers method. Then, GO was reduced by hydrazine hydrate at 90°C for 2h to obtain graphene. The graphene was identified by FT-IR spectrometer and Raman spectrometer. The results are reported in literature[14].

Analytically pure $Co(NO_3)_2\cdot 6H_2O$ and $Fe(NO_3)_3\cdot 9H_2O$ reagents (the molar ratio of Zn/Fe is 1:2) were dissolved in distilled water. Then, urea as precipitator ($n_{urea} = n_{Zn2+} + 2/3n_{Fe3+}$) was added to the mixed solution. The mixture was then transferred into a teflon-lined autoclave (20 mL) and kept for 12 h at 180°C in an oven. The product was collected and washed with distilled water and ethanol to remove by-products, and finally dried at 80°C for 10 h.

The mixing ratio of G-$CoFe_2O_4$ composite was controlled by carefully adjusting the weight ratio of G/$CoFe_2O_4$. The preparation method of G-$CoFe_2O_4$ is similar to that of pure $CoFe_2O_4$. The difference between them is as follows: before $Co(NO_3)_2\cdot 6H_2O$ and $Fe(NO_3)_3\cdot 9H_2O$ reagents were dissolved in distilled water, graphene of different weight should be dispersed in distilled water by ultrasonic, the time of ultrasonic dispersion was 30 min. 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ were prepared. The phase composition of the samples was characterized by X-ray diffraction using CuKα (XRD, D8 Advance, 40 kV and 40 mA).

2.2 *Measurement of gas sensing performance[14]*
A paste was prepared from a mixture of the sample with terpineol, and then the paste was coated with a small brush onto an Al_2O_3 tube on which two gold leads had been installed at each end. The Al_2O_3 tube was about 8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter. The Al_2O_3 tube was heated in air at 100°C for 10 h to remove terpineol. A heater of Ni-Cr wire was inserted into the Al_2O_3 tube to supply the operating temperature that could be controlled in a range of 80°C-350°C.

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The response is defined as the ratio of the electrical resistance of the sensor in air (R_a) to that in the mixture of the detected gas and air (R_g) when the resistance of the sensor reaches a stable value. The preparing method for the mixture of the detected gas and air was depicted in our previous work. When measuring the electrical resistance of a sensor in air, the sensor was placed in a closed glass bottle filled with pure air and the surface temperature of the sensor was adjusted to operating temperature by changing the voltage and the current of the heater wire. The sensor was placed in the air bottle at least 5 min after the electrical resistance of the sensor was stable, then the sensor was taken out from the air bottle and placed in a closed bottle filled with the mixture of the detected gas and air. If the resistance of the sensor could not recover from the previous exposure, the operating temperature was adjusted to 80-300^{o}C and kept for about 10 minutes to let the detected gas desorb outside the air bottle. The resistance change of the sensor was recorded by a computer.

3. RESULTS AND DISCUSSION

3.1 *Phase Composition of G-$CoFe_2O_4$ Composite*

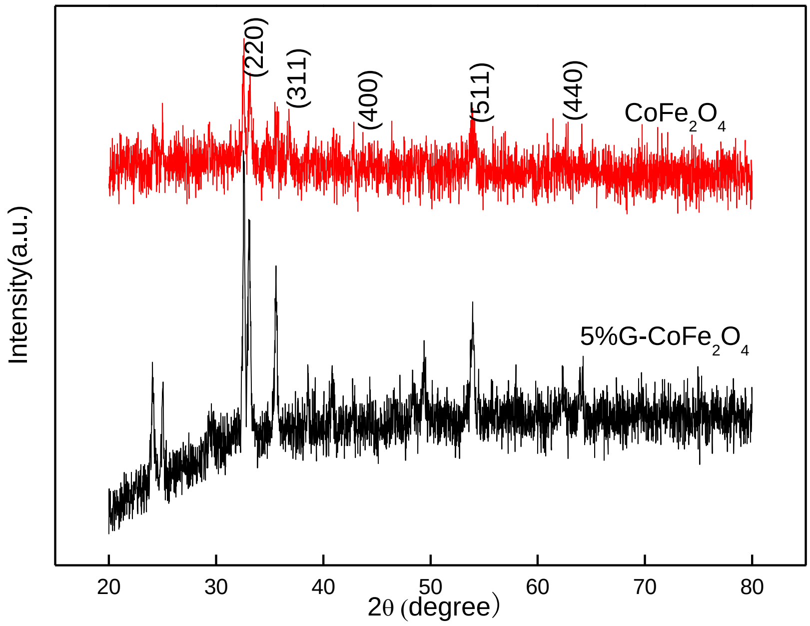
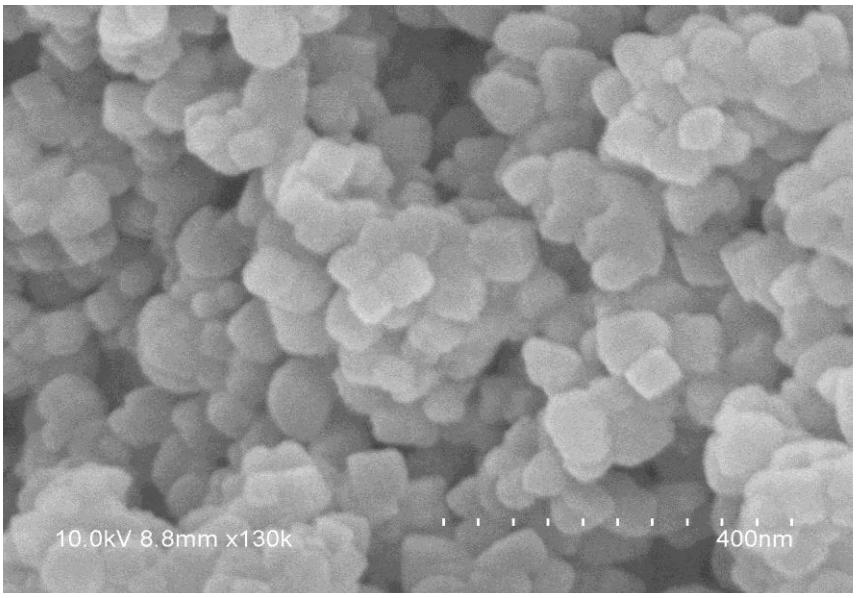


Fig-1: The typical XRD patterns of pure $CoFe_2O_4$ and 5%G-$CoFe_2O_4$ prepared at 180^{o}C for 12h

The typical XRD patterns of pure $CoFe_2O_4$ (180^{o}C, 12h) and 5%G-$CoFe_2O_4$ prepared at 180^{o}C for 12h are presented in Fig.1. The six broad peaks, centered at 2θ= 31.96°, 35.19°, 42.69° , 53.36° and 62.26°, respectively, match well with the $CoFe_2O_4$ crystal faces [220], [311], [400], [511] and [440], respectively. The main diffraction peaks in the pattern of pure $CoFe_2O_4$ can be indexed to spinel type structure $CoFe_2O_4$ (JCPDS card no.82-1049), and there is no peaks of impurity in the pure $CoFe_2O_4$ sample. Graphene peaks could be found in the XRD patterns of 5%G-$ZnFe_2O_4$, centered at 2θ=25°.



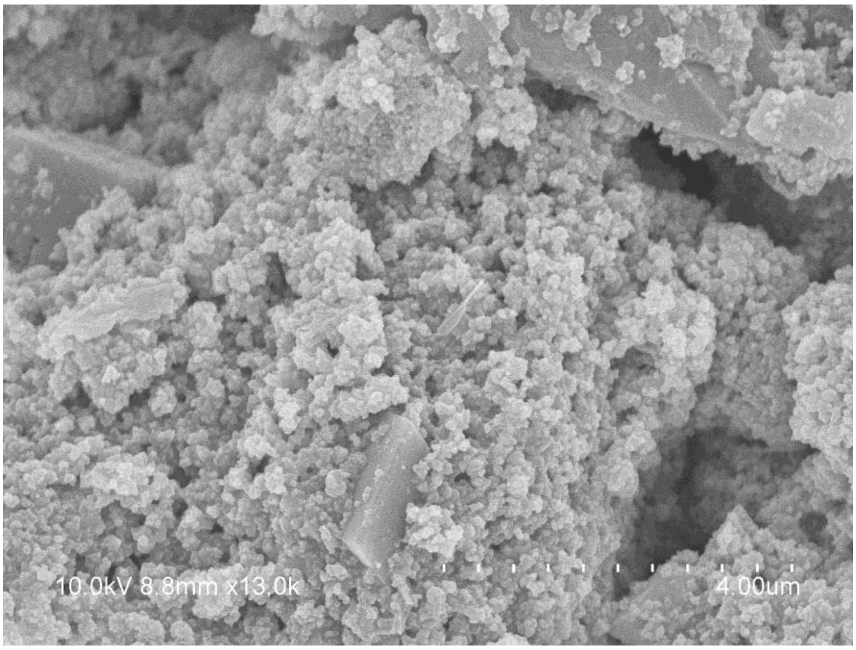


Fig-2: The SEM image of pure $CoFe_2O_4$ (a) and 5%G-$CoFe_2O_4$ (b)

The microstructure of pure $CoFe_2O_4$ (a) and 5%G-$CoFe_2O_4$ power are shown in Fig.2. The average grain sizes of $CoFe_2O_4$ were about 60 nm. A small amount of $CoFe_2O_4$ nanoparticles dispersed on the surface of graphene sheets. Due to the reassembling process between graphene sheets and $CoFe_2O_4$ nanoparticles, a large amount of voids exist between individual composites, which enlarge the specific surface area of composites.

3.2 *Responses of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ towards 1000 ppm of several vapors*

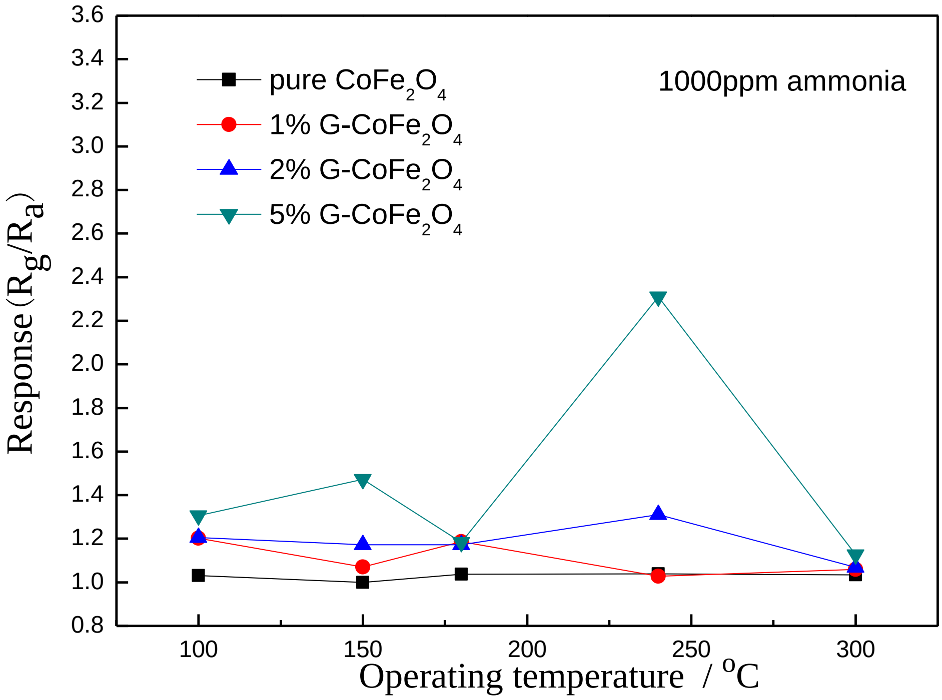


Fig-3: The responses to ammonia (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ (180°C, 12 h) with different mixing ratio

The responses to ammonia (1000 ppm) of sensors based on G-$CoFe_2O_4$ with different mixing ratio are shown in Fig.3. In the operating temperature range from 80°C to 300°C, the max responses to ammonia of sensors based on pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are 1.1, 1.2, 1.5 and 2.4, respectively. The sensors based on 5%G-$CoFe_2O_4$ show the highest response to ammonia at 240°C.

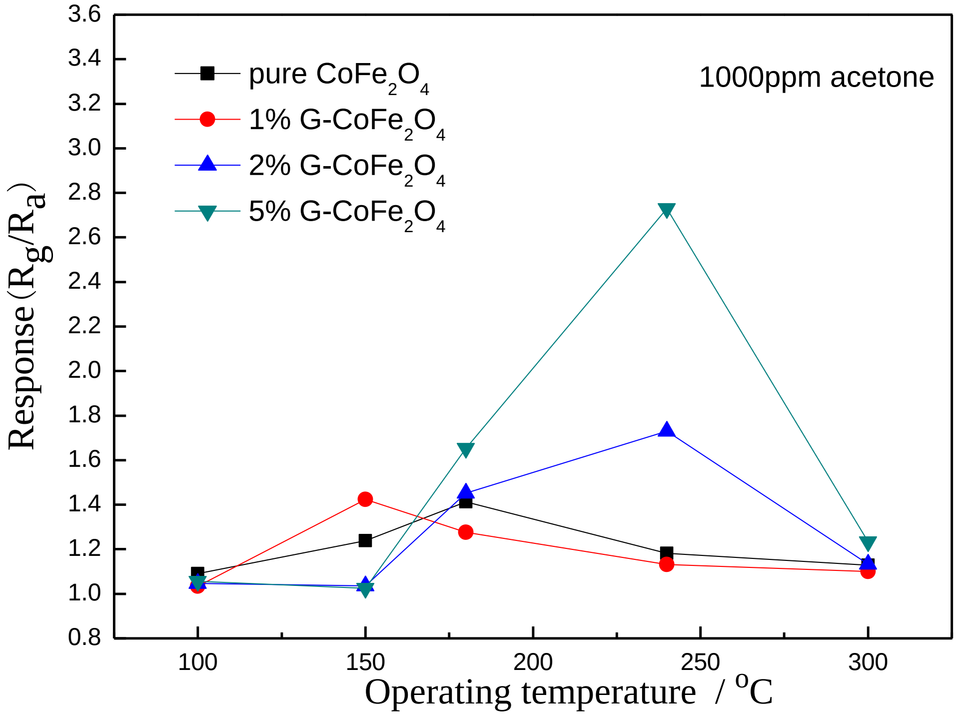


Fig-4: The responses to acetone vapor (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ (180°C, 12 h) with different mixing ratio

The responses to acetone vapor (1000 ppm) of sensors based on G-$CoFe_2O_4$ with different mixing ratio are shown in Fig.3. In the operating temperature range from 80°C to 300°C, the max responses to ammonia of sensors based on pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are 1.4, 1.4, 1.7 and 2.8, respectively. The sensors based on 5%G-$CoFe_2O_4$ show the highest response to acetone vapor at 240°C.

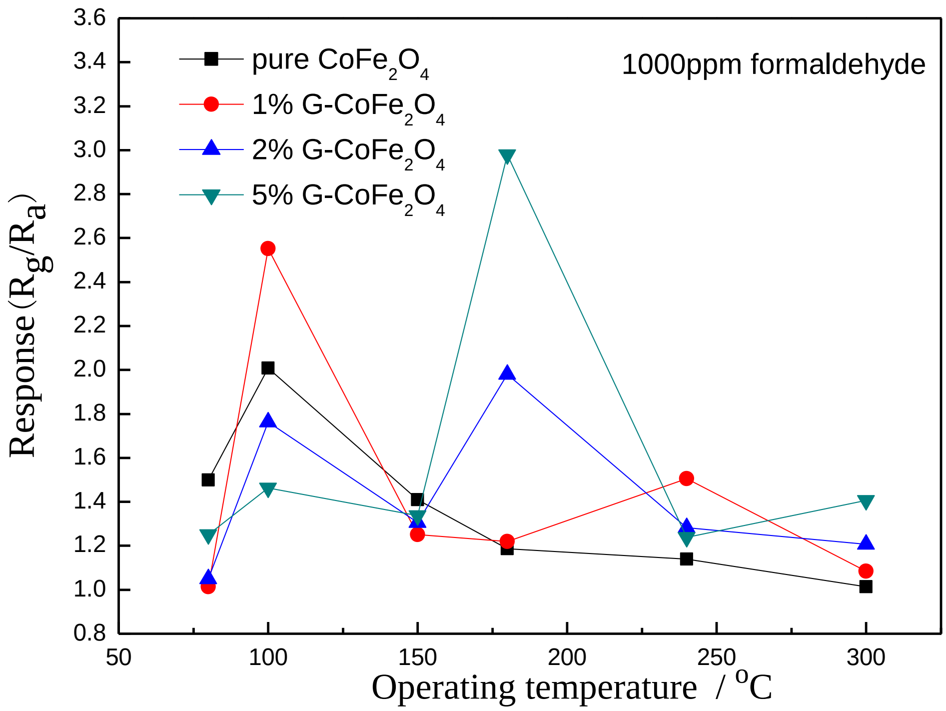


Fig-5: The responses to formaldehyde (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ (180°C, 12 h) with different mixing ratio

The responses to formaldehyde vapor (1000 ppm) of sensors based on G-$CoFe_2O_4$ with different mixing ratio are shown in Fig.5. In the operating temperature range from 80°C to 300°C, the max responses to ammonia of sensors based on pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are 2.0, 2.6, 2.0 and 3.0, respectively. The sensors based on 5%G-$CoFe_2O_4$ show the highest response to formaldehyde at 240°C. So, the sensors based on G-$CoFe_2O_4$ could not been applied in detecting formaldehyde vapor.

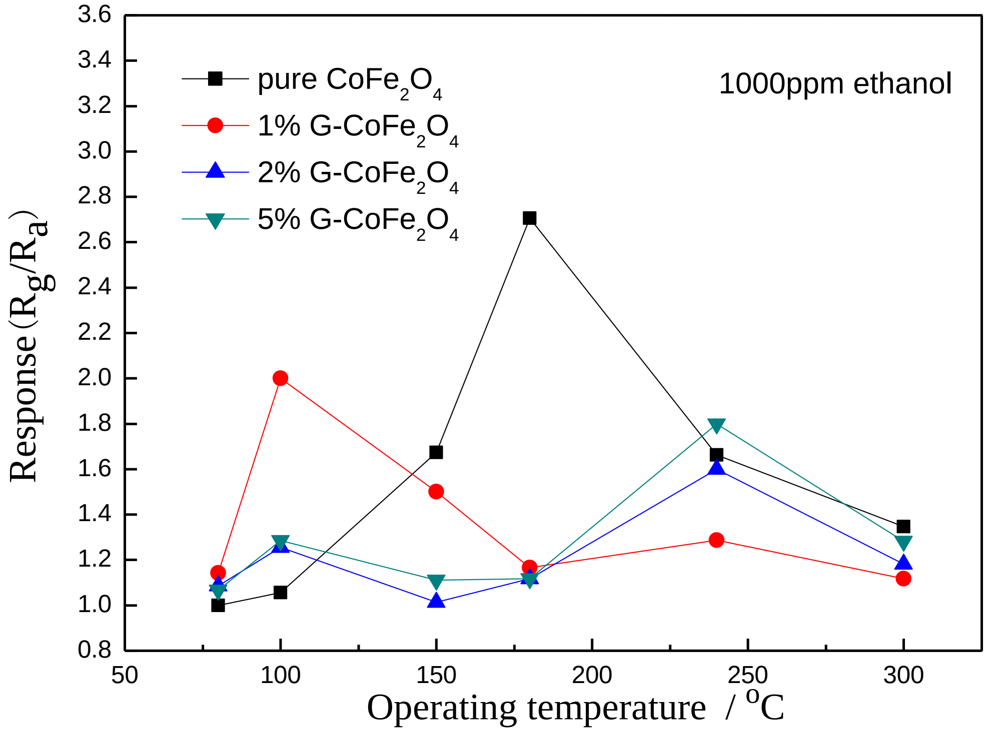


Fig-6: The responses to ethanol (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ (180^{o}C, 12h) with different mixing ratio

The responses to ethanol vapor (1000 ppm) of sensors based on G-$CoFe_2O_4$ with different mixing ratio are shown in Fig.6. In the operating temperature range from 80^{o}C to 300^{o}C, the max responses to ethanol of sensors based on pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are 2.7, 2.0, 1.6 and 1.8, respectively. The sensors based on pure $CoFe_2O_4$ show the highest response to ethanol vapor at 180^{o}C.

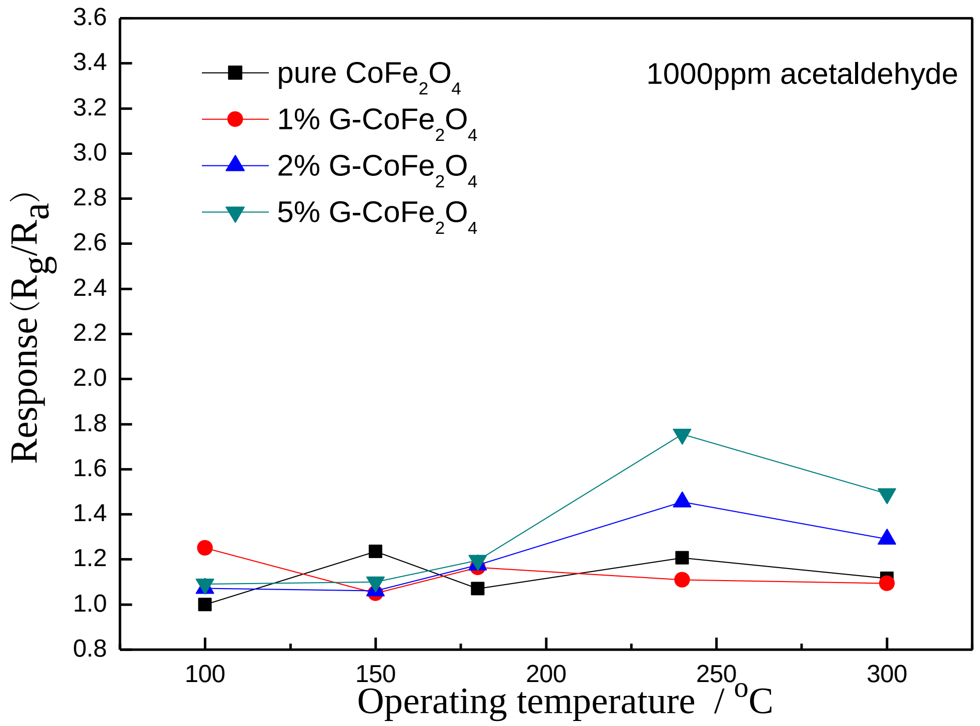


Fig-7: The responses to acetaldehyde (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ (180^{o}C, 12 h) with different mixing ratio

The responses to acetaldehyde vapor (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ with different mixing ratio are shown in Fig.7. In the operating temperature range from 80^{o}C to 300^{o}C, the max responses to acetaldehyde vapor of sensors based on pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are 1.3, 1.3, 1.4 and 1.8, respectively. It is observed that the response of all sensors increase with the mixing weight of graphene increasing the sensors based on 5%G-$CoFe_2O_4$ show the highest response to acetaldehyde vapor at 240^{o}C.

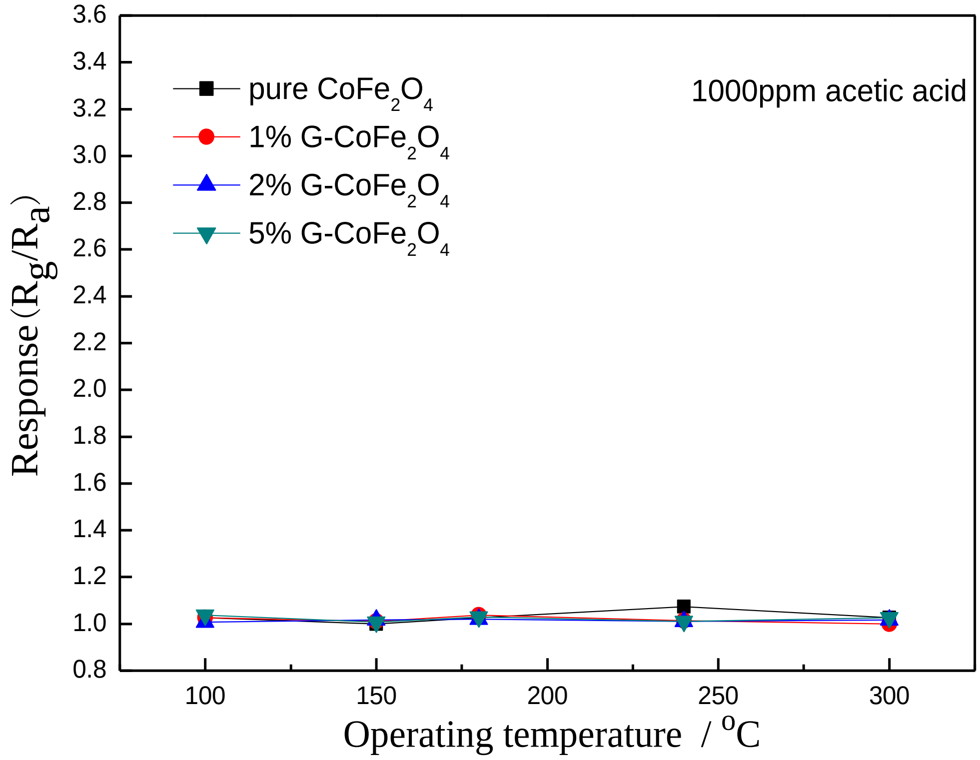


Fig-8: The responses to acetic acid (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ (180°C, 12h) with different mixing ratio

The responses to acetic acid vapor (1000 ppm) of sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ with different mixing ratio are shown in Fig.8. The responses to acetic acid vapor of sensors based on pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are low (not exceeding 1.5) in the operating temperature range from 80°C to 300°C. So, the sensors based on pure $CoFe_2O_4$ and G-$CoFe_2O_4$ could not been applied in detecting acetic acid vapor.

3.3 *The electrical resistances of pure $CoFe_2O_4$ sensor and G-$CoFe_2O_4$ sensors in air*

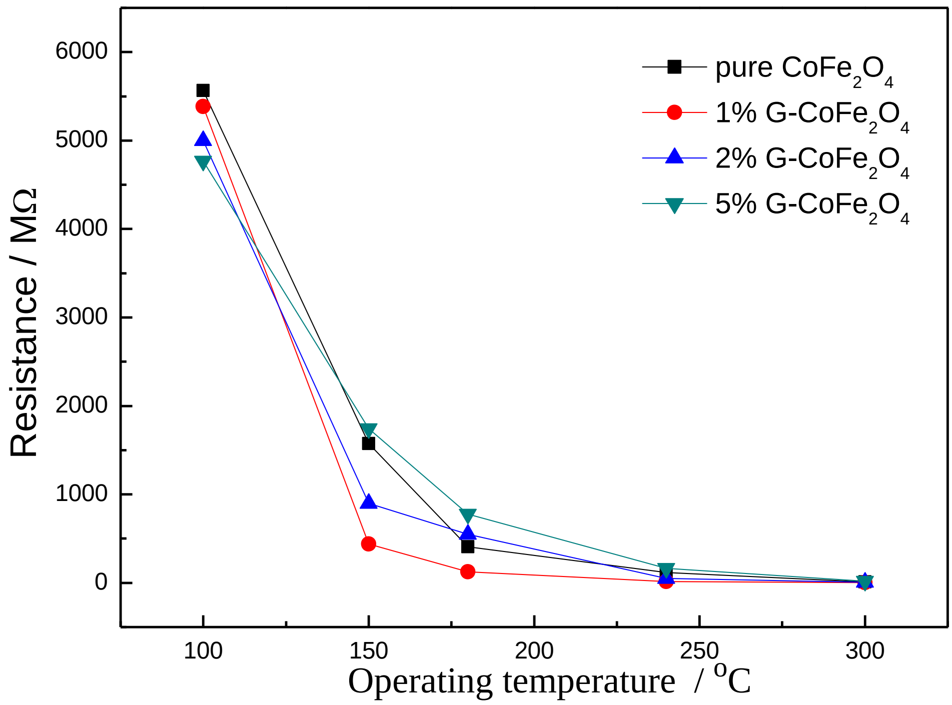


Fig-9: The electrical resistances of pure $CoFe_2O_4$ sensor and G-$CoFe_2O_4$ sensors in air at different operating temperatures

Fig-9 shows the electrical resistances of pure $CoFe_2O_4$ sensor and G-$CoFe_2O_4$ sensors in air at different operating temperatures (preparation conditions of pure $CoFe_2O_4$ and G-$CoFe_2O_4$: 180°C, 12 h). The resistances of all sensors decrease with the operating temperature increasing because the resistance of semiconductor material decreases with temperature increasing.

4. CONCLUSIONS

In summary, graphene-$CoFe_2O_4$ composite with different doping ratio are prepared via solvothermal method with urea as precipitator. The average grain size of $CoFe_2O_4$ with spinel-type structure is about 60 nm. The sensitive properties of pure $CoFe_2O_4$, 1%G-$CoFe_2O_4$, 2%G-$CoFe_2O_4$ and 5%G-$CoFe_2O_4$ are similar to the p-type semiconductor. The sensor based on 5%G-$CoFe_2O_4$ shows the high sensitivity to ammonia, acetone vapor, formaldehyde vapor and acetaldehyde vapor with the temperature range from 80 to 300°C. The sensor based on 5%G-$CoFe_2O_4$ shows the sensitivity as high as 3 to 1000 ppm formaldehyde vapor when the operating temperature of sensor is 180°C. This material may be applied to measure the formaldehyde vapor at low temperature.

5. ACKNOWLEDGEMENT

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