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Study on the Structure and Properties of Graphene Doped Tin Oxide Thin Film

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SnO_2 film is widely used in the field of coated glass for its excellent transmittance and conductivity of visible light, and its application prospect is very promising. Graphene, as a monolayer of graphite molecules, has many unique properties. With the introduction of graphene in SnO_2 film, higher carrier concentration can be produced, and thus a better transparent conductive film can be obtained. Based on the above ideas, graphene doped SnO_2 composites were synthesized by hydrothermal method, and their gas sensitivity to three toxic substances, such as ethylamine and formaldehyde, were studied. The aim is to develop an excellent gas sensitive material. The introduction of graphene can significantly improve the gas sensing properties of SnO_2 materials. Gas sensing properties of the composite to formaldehyde, acetaldehyde and other volatile organic compounds were better than pure SnO_2. In the 120□ test temperature, the graphene composite with doping amount of 0.6 wt.% exhibited the best sensing properties to formaldehyde.

1. Introduction

Graphene is a new type of carbon nanomaterial with the thickness of a single carbon atom and with the structure of two-dimensional honeycomb lattice. Graphene is the thinnest material in the world with a thickness of only 0.335 nm(Franklin et al., 2014; Fu et al., 2014; Wei and Kivioja, 2013). The basic structural unit of graphene is composed by six membered ring lattice. Its carbon atoms are for sp2 hybrid. The three sp2 hybrid orbitals of each carbon atom form a strong C-C (δ) bond with the sp2 hybrid orbits of its surrounding three carbon atoms.. The bond length of C-C is about 0.142 nm, and the graphene has excellent mechanical properties(Hsieh et al., 2014). In addition, each carbon atom does not participate in hybridization. The 2pz orbit which contains one electron forms a wide range of π-π conjugated structures perpendicular to the plane of graphene(Kanade et al., 2015; Zhang et al., 2014; Eminian et al., 2011). The appearance of graphene enriches the family of carbon materials, and the monolayer graphene is the basic unit of other carbon materials.

Tin oxide (SnO_2) is an important n- type semiconductor gas sensitive material, which has a good response to a variety of oxidizing and reducing harmful gases(Lin et al., 2012). In recent years, a large number of research reports on SnO2-based gas sensors have been released, which were studied to detect all kinds of toxic and harmful substances, including NH_3, NO_2, H_2S, CO, ethanol and formaldehyde. However, nano SnO_2 is usually small granular and easy to agglomerate, so pure SnO2-based gas sensors usually have the common faults of traditional semiconductor oxides with high working temperature and low sensitivity, and which limits their further development and application(Patil et al., 2013). Graphene has excellent properties such as large surface area, fast carrier mobility and so on. It can be used as a supporting material for SnO_2 particles. The combination of graphene and SnO_2 can not only effectively prevent the aggregation of SnO_2 and the overlap of graphene layers, but also improve the electrical, chemical and physical properties of the materials(Seo et al., 2013). Therefore, we can solve the above shortcomings of pure SnO_2 gas sensitive materials by introducing graphite.

At present, the research of gas sensor based on SnO_2/ graphene composite materials has become a hot spot. Some researcher reported that gas sensor based on SnO_2/ reduced and oxide graphene has better sensitivity than H2S gas sensor prepared by pure SnO2 material. Others have confirmed that SnO_2/ oxide graphene

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materials have good sensitivity to LPG. Others synthesized the SnO_2/ reduced oxide graphene nanocomposites, and proved that the composite has a better response to the NO_2 gas than the pure graphene. Based on the above reports, SnO_2/ oxide graphene composites were synthesized by hydrothermal method, and their gas sensitivity to three toxic substances, such as ethylamine and formaldehyde, were studied. And the aim is to develop a kind ofexcellent gas sensitive material.

2. Experiment

2.1 Experimental reagents and instruments

Table 1: The main experimental reagents

Reagent	Specifications	Manufacturer
Stannous chloride	Analytical reagent	Tianjin quartz clock factory
methanol	Analytical reagent	Tianjin wind boat chemical reagents Co., Ltd.
Anhydrous ethanol	Analytical reagent	Tianjin wind boat chemical reagents Co., Ltd.
CTAB	Analytical reagent	Tianjin Kermel Chemical Reagent Co., Ltd.

Table 2: The main experimental equipment and instruments

Instruments	Model	Manufacturer
Drying box	101-1A	Tianjin Taisite Instrument Co. Ltd.
Centrifuge	TG16G	Yancheng Kate experimental instruments Co., Ltd.
X ray diffractometer	XRD-6000	Shimadzu Corporation
SEM	S-4800	The Japanese company Hitachi
TEM	H-800	The Japanese company Hitachi
FTIR	Teneor27	German Brook company
Gas sensor test system	WS-30A	Zhengzhou Weisheng Electronic Technology Co., Ltd.

2.2 Experimental steps

Two portions of $SnCl_4$ $5H_2O$ were dissolved in 50 mL isopropanol, and then were mixed with a solution with a concentration of 0.05 mol/L. One of which was added to 0.05 g graphene. After mixing the mixed solution at room temperature for 4 hours at the magnetic stirrer, the solution is statically aged for 24 h. The quartz substrate was dried by acetone and deionized water after ultrasonic cleaning. The film is prepared by rotating coating on the homogenizing machine. After each coating, the substrate is baked in an oven for several minutes. The operation is repeated as the number of film layers. The quartz substrates were put in a muffle furnace under 450℃ atmosphere annealed for 2 hours.

2.3 Material characterization

The samples were characterized by XRD, SEM, TEM, Raman and FTIR. In addition, the solid phase ultraviolet visible spectrometer (UV-Vis), which was produced by the Shimadzu Corporation, was characterized by a UV-3600, with a scanning range of 200~800.

3. Results and discussion

3.1 XRD analysis

Figure 1 is the XRD spectrum of the non-doped and different layers of graphene doped SnO2 films prepared by the sol-gel method. From the graph, we can see that all the films appear diffraction peaks at 26.6 degrees, 34 degrees and 51.9 degrees, which correspond to diffraction peaks of SnO_2 (110), (101) and (211) crystal planes, respectively. There is no other diffraction peak in the X ray diffraction pattern. It indicates that there is no amorphous SnO_2, SnO_2 and t SnO_2 in other crystalline phases. The 25 degrees diffraction peak of graphene is not observed in the diagram, which may be covered by the strong diffraction peak of SnO_2 at 26.6 degrees.

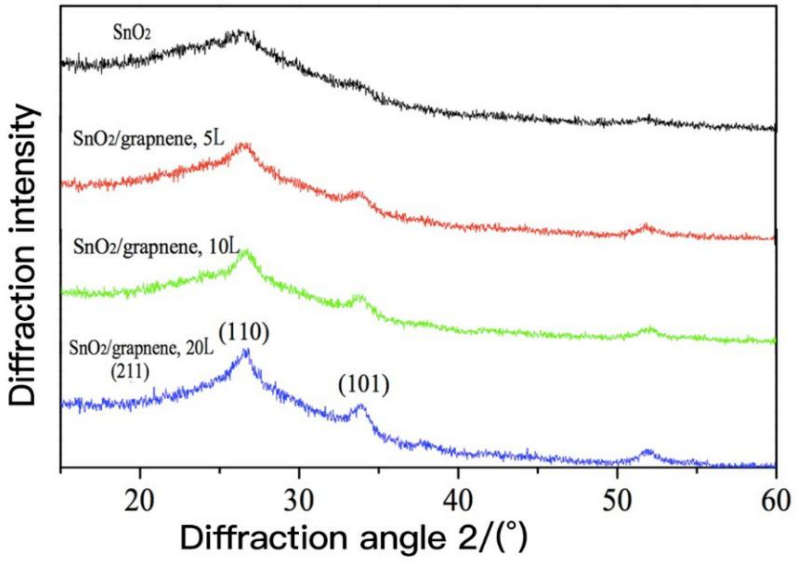

Figure 1: XRD spectra of tin oxide films doped with different layers of graphene (L-layer)

Calculation according to the Scherrer formula: $D=0.89\lambda/B\cos\theta$ (theta is the diffraction angle, λ is the excitation wavelength lambda, B is the peak value of modified XRD (101)), the grain size of graphene doped films were 7.127 nm, 7.129 nm and 10.69 nm (thin film doped layers is not obvious due to the low diffraction peak, so it is unable to calculate the grain size). It is indicated that the addition of graphene makes the grain size of SnO2 film increase, and the quality of crystallization is improved. The results of XRD indicate that with the increase of the number of deposition layers, the diffraction peaks of the crystal face tend to be sharp and the intensity is also increased, which is conducive to the grain growth and crystallinity of the films.

However, the transmittance of the film decreases sharply in the near ultraviolet region, which is due to the intrinsic absorption of the film material. The cutoff edges obtained by different annealed methods are obviously different. For the samples obtained by vacuum annealing, the "blue shift" occurs in the direction of the short wave, which is mainly caused by the change of the carrier concentration in the film. Annealed in vacuum environment, the defects of oxygen vacancies in the films increases because there is no oxygen. This leads to the increase in carrier concentration of the film, but also the transmittance decreased. And annealing treatment under normal circumstances, the zinc atoms on the film can be combined a lot of oxygen atoms in the air because of the amount of oxygen in the air. resulting in the decrease of the carrier concentration, which is conducive to improve the transmittance of thin films.

3.2 Fluorescence spectrum analysis

Figure 2 is a photoluminescence spectrum of graphene doped tin oxide films at room temperature. It can be seen from the diagram that all the curves have the main band edge emission (396 nm) in the ultraviolet region, in which the band edge emission is produced by the electron hole free exciton compound. Compared with the undoped samples, the emission intensity of all doped samples increased, and the emission peak intensity gradually decreased with the increase of the number of deposition layers. However, the location of the photoemission peak did not drift with the doping concentration. The photoluminescence efficiency can be calculated by the following formula:

$$\eta = \frac{I_R}{I_R + I_{NR}} \quad (1)$$

Where η is the luminous efficiency, IR and INR are respectively the radiative and non-radiative transition probability. Non-radiative transitions are caused by crystal defects, such as point defects, dislocation and grain boundaries. For the tin oxide film, the main factors affecting the photoluminescence efficiency are the crystalline quality of the film and the stoichiometric ratio of the components in the lattice. In general, the crystalline quality is good, and the fluorescence emission intensity of the thin film near the stoichiometric ratio is higher. The emission intensity with the increase of deposited layers decreases gradually, and this phenomenon may be due to that the increase in the doping ratio of graphene film concentration is too large. On the one hand, it makes lattice defects increase due to non-radiative recombination increases. On the other hand, the quenching concentration is too large, which may make tin oxide luminescent center arc phenomenon, and weakens the luminescence intensity.

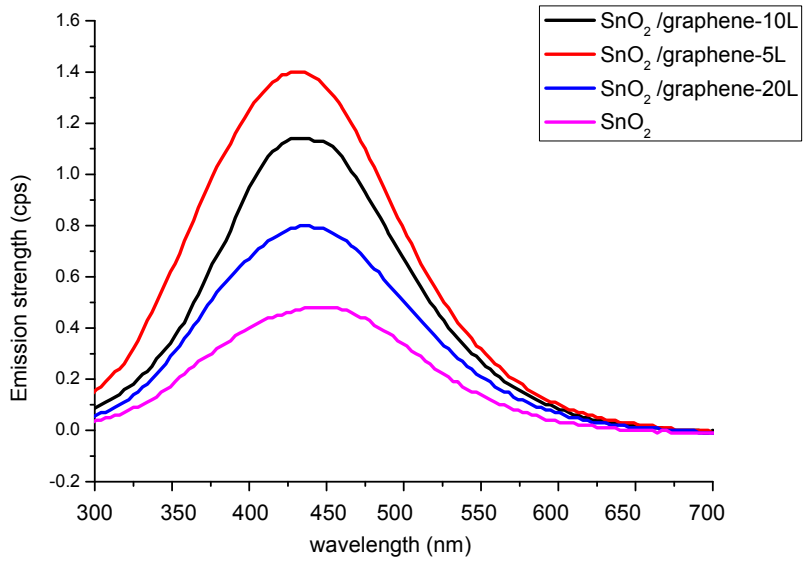

Figure 2: Photoluminescence spectra of tin oxide films with different layers of graphene doping concentration

From the transmission spectra it can be clearly seen that all the films are in the visible region (400~800 nm) in the range of high transmittance (>70%). With the increasing content of doped graphene film, the transmittance of the films decreases, the film is thicker, the density of the film is increased, and the grain grows slightly. The coarse grain increases the surface roughness of the film and increases the light scattering. At the same time, the light absorption path of the thick film is also increased, which results in the decrease of the transmittance of the film. In addition, with the increase of film thickness, the uneven distribution of defects, grain boundaries and other components also increases greatly, resulting in the scattering of light, resulting in the transmittance decreasing of the films . The transmittance of all the samples in the near ultraviolet region (near 400 nm) decreased rapidly, which was caused by the intrinsic absorption of the tin oxide band. It is obvious from the diagram that the absorption edge of the SnO_2 film is blue shifte with the doping of graphene.

3.3 Gas sensitive performance

Figure 3 shows the sensor responses of pureSnO_2 and different graphene doped SnO_2/ graphene complex annealed at 120℃ to different volatile substances, including methanol, ethanol, ethylene glycol, formaldehyde, acetaldehyde, acetone and three ethylamine. It can be seen that the response values of SnO_2/ graphene complexes to these harmful substances are all higher than those of pure SnO2, and the composites have good selectivity for formaldehyde especially. Although the response value of pure SnO2 to 50 ppm formaldehyde reached 40.9, it was far below the response value of SnO_2/ graphene-15L (187.5). and thus it can be seen that the proper doping of graphene with SnO_2 can significantly improve the selectivity of the material to formaldehyde.

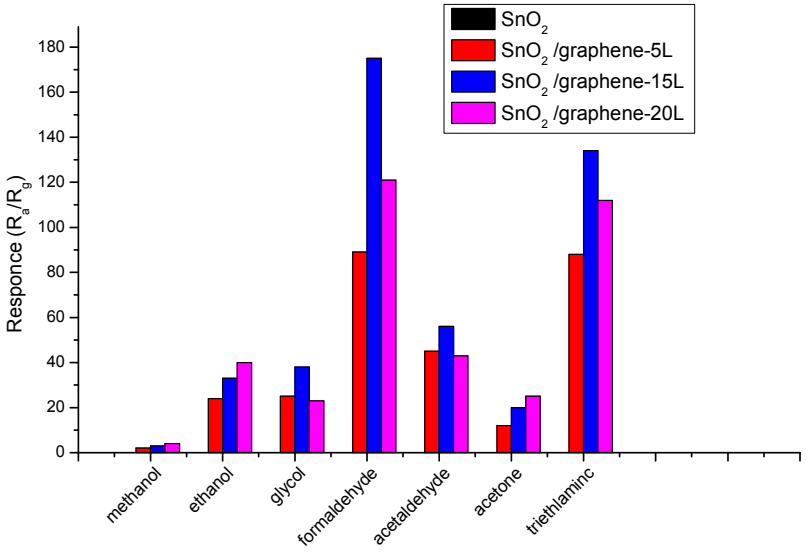

Figure 3: Sensor responses of pure SnO_2 and SnO_2/graphene to 50 ppm of different gases at 120 □

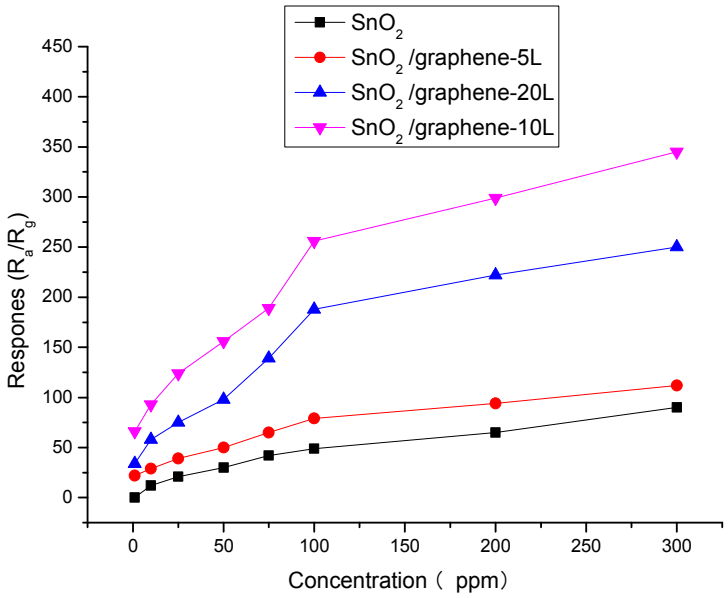

Figure 4: Responses of pure SnO_2 and SnO_2/graphene nanocomposites to acetaldehyde with various concentrations at 120 ℃

Figure 4 shows the response sensitivity of pure SnO_2 and SnO_2/ graphene composites at 120 ℃ to different concentrations of formaldehyde. From the figure, it can be observed that the response of the composite material to formaldehyde on 5~300 concentration in the range of ppm was significantly higher than that of pure SnO_2. the SnO_2/graphene composite materials with graphene doped 0.6 wt.% achieve the best sensitivity to formaldehyde and its response to 300 ppm of formaldehyde value is as high as 400.6. And the response of pure SnO2 on the same concentration of formaldehyde was 163.5. It can be seen that composite materials exhibit high sensitivity.

4. Conclusion

Three kinds of graphene doped SnO_2/ graphene nanocomposites were prepared by hydrothermal reaction process with two tin chloride and homemade graphene oxide as raw materials in methanol water system. The prepared samples have the structure of tetragonal rutile. The addition of graphene in tin oxide thin film improves the crystal quality. Optical edge of the thin film samples shifts towards the long wavelength, which produces "red shift" phenomenon. With the increase of the content of graphene, the photoluminescence intensity of tin oxide thin film showed a gradual quenching phenomenon. Under the optimum working temperature of 160 ˚C, SnO_2/ graphene nanocomposite has high sensitivity, fast response recovery and high selectivity for ethanolamine. Among them, the composite with graphene doped 1.25 wt.% has the best gas sensitivity to ethanolamine, and its response value to 1 ppm ethanolamine is 3.3 times higher than that of pure tin oxide.

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