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Effect of calcination temperature on the humidity sensitivity of TiO_2/graphene oxide nanocomposites

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ABSTRACT

The humidity sensitive elements of TiO_2/Graphene oxide nanocomposites (TGOs) were obtained by interdigital Ag-Pd electrode substrate. The resistance-temperature characteristic and humidity sensitivity of TGOs humidity sensors were characterized by voltammetry in the range of 25–80 °C and between a relative humidity of 11.3–93.6%RH. The results indicated that the calcination temperature obviously affected the resistance variation of the humidity sensitive elements. It can be seen that the resistance of TGOs humidity sensors decreased firstly and then increased with increasing calcination temperature. Meanwhile, the activation energy increased from 12.47 kJ/mol to 54.47 kJ/mol, then decreased to 16.72 kJ/mol, and finally increased to 19.66 kJ/mol. The resistance gradually reduced with the increase in environmental humidity for TGOs humidity sensitive elements calcined at 300 °C. The resistance of TGOs humidity sensors calcined at 350, 400, 450 and 480 °C increased first and then decreased with increasing environmental humidity. The humidity hysteresis of TGOs humidity sensors calcined at 300 °C increased to a maximum value of 24.33%, and decreased to 6.02% at 450 °C. Particularly, TGOs humidity sensors showed p-type nature of the semiconductors in the low RH range (< 62.1%RH) and showed n-type nature of the semiconductors in the high RH range (> 62.1%RH).

1. Introduction

Humidity measurement plays a significant important role in various areas of applications such as industry production, agriculture and animal husbandry, weather forecast, scientific research and other industries [1]. At present, the materials used for humidity measurement mainly include electrolytes [2,3], organic polymers [4,5], metal oxide films [6,7] and functional ceramics [8–10]. TiO_2 based humidity sensitive ceramics have been widely studied and applied due to their advantages such as low price, stable structure and high humidity-sensitive [11–13]. As a new two-dimensional carbon material, Graphene oxides (GOs) has been proved to be a promising humidity sensitive material due to its excellent physical and chemical properties, the existence of oxygen functional groups result in high reactivity [14–16].

It was found that many aspects of performance of TiO_2 would be significantly improved after graphene oxides modified [17–19]. Most of the previous studies [20–22] on TiO_2/graphene or graphene oxides composites are mainly focused on the preparation of TiO_2/GOs composites with different structures for enhancing the photocatalytic activity. Researchers [23–26] studied TiO_2 nanocrystals uniformly grown on graphene oxide nanosheets by hydrolysis and crystallized into a stable anatase structure, or the preparation of nanosized GOs-coated TiO_2 nanoparticles with the core/shell structure [27] and spherical TiO_2 agglomerates incorporated with reduced-graphene oxide (rGO) with a porous structure [28], which showed that graphene can significantly increase the specific surface area of the material, accelerate the separation of electron-hole pairs and improve the ion transport capacity, thereby improving the photocatalytic activity. Later, Zhang et al. [29] demonstrated that beyond the photocatalytic activity, TiO_2/GOs composites show an excellent electrical sensitivity towards environment humidity and the humidity hysteresis was very low, which has attracted more and more attention of scholars. Wang et al. [30] found that functionalizing single-layer graphenes by TiO_2 thin films show a reversible and linear sensitivity towards oxygen gas in the concentration range (5–100%) at room temperature and atmospheric pressure, with a minimum detection limit of 0.01%. Then, Zhang et al. [31] developed an UV light enhanced TiO_2/graphene sensitive device for oxygen sensing at room temperature, and found that hole-electron pair of TiO_2 film can be excited under UV light and the photogenerated electrons were percolate fast to the electrode by the graphene, while the

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photogenerated holes were recombination with the electrons within TiO_2 film. This process would deplete the electron and rapidly changing the conductivity of the device further, thereby the components would have better sensitivity characteristics. In order to explore the sensitive mechanism of the material, rGO/TiO_2 layered film deposition on the interdigital electrode substrate has been developed and the formaldehyde sensing performances were investigated over low detection concentrations from 0.1 ppmv to 0.5 ppmv, which revealed that the rGO/TiO_2 sensor exhibited rapid response, excellent selectivity and good reproducibility [32]. Till now, the studies of TiO_2/graphene (oxidized) composites are mainly focused on the photocatalytic properties of materials. However, the gas sensitivity and humidity sensitivity are seldom reported, especially the humidity sensitivity and its mechanism of TiO_2/graphene oxide nanocomposites.

We have studied the preparation of TiO_2/graphene oxide nanocomposites using intercalation-stripping-roasting method. It is found that anatase TiO_2 nanoparticles were uniformly loaded on the graphene oxide film and bonded with the hydroxyl of graphene oxide to form a Ti-O-C structure [15]. A lot of oxygen defects are existed due to the small size of TiO_2 particle on the surface of graphene oxide. With the increasing calcination temperature, graphene oxide in the composites were reduced gradually and TiO_2 increased, which may cause changes in the humidity sensitivity of composites. Hence, based on the above results, this paper will study the humidity sensitivity of TiO_2/graphene oxide nanocomposites to reveal the effect of calcination temperature on its humidity sensitivity and explain the humidity-sensing mechanism.

2. Experimental

2.1. Materials and reagents

Graphite oxide powder (GO, prepared by a modified Hummers' procedure [33], the mass ratio of $KMnO_4$ and graphite was 4:1) is as main raw material.

The used reagents include cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, Analytical Reagent), tetrabutyl titanate ($TiC_{16}H_{36}O_4$, Analytical Reagent), absolute ethanol (CH_3CH_2OH, Analytical Reagent), Polyvinyl alcohol ($(C_2H_4O)_n$, Analytical Reagent), ultrapure water (> 18.25 MΩ cm). Interdigital electrode substrate of Ag-Pd (13.4 mm × 7.0 mm, minimum width of 0.2 mm), as shown in Fig. 1a.

2.2. Sample preparation

2.2.1. Preparation of TiO_2/graphene nanocomposites (TGOs) samples

$Ti(OH)_4$/GOs samples were firstly prepared according to the well-established procedure described by Chen [34]. $Ti(OH)_4$/GOs samples were then placed in a muffle furnace and calcined for 1 h at different temperatures in air. Finally, TiO_2/graphene nanocomposite (TGOs) samples were obtained and respectively marked as TGOs-t, where t refers to calcination temperature (t = 300, 350, 400, 450 and 480 °C).

2.2.2. Preparation of humidity sensitive elements of TiO_2/graphene nanocomposites (TGOs)

5 mg of TGOs-t samples were dispersed into 5 ml of polyvinyl alcohol solution (2.5% (wt)) homogeneously, 50 μl of the dispersion was obtained with a pipette and dropped onto the interdigital Ag-Pd electrode substrate to connect the two electrodes. Then, the substrate was dried at 60 °C for 30 min and repeat the coating steps twice after removal. After the coating, leads were welded on both ends of the film interdigital electrodes to prepare TGOs humidity sensors TGOs-t. Repeated the above operation and control film area consistent, TGOs humidity sensors (TGOs-t) with different calcination temperature could be obtained.

2.3. Sample analysis

To test the humidity sensitivity of TGOs samples, according to the principle that the relative humidity on the top of the different saturated salt solutions inside the confined chambers remain constant, we measured the change in their DC electrical resistance as a function of relative humidity upon exposure to varying relative humidities. The nine different saturated salt solutions were prepared and their corresponding RH values [35] at the room temperature (25 °C) are listed in Table 1. the DC electrical resistance of the sample was measured by voltammetry using a VICTOR VC9808 + digital multimeter. The test circuit is shown in Fig. 1b.

3. Results and discussion

3.1. Structure characterization

Fig. 2 presents XRD patterns of the TGOs samples calcined at different temperatures. As can be seen from the figure, when the calcination temperature was 300 °C, no significant anatase TiO_2 diffraction peak was observed, which may be ascribed to the fact that the hydrated titanium oxide of the composites failed to crystallize and were composed of amorphous titania when calcined at low temperature. When the calcination temperature raised to 350 °C, the anatase TiO_2 (101) plane diffraction peak appeared with low intensity and the width of shows wider, which illustrated that a small amount of in situ dehydration took place and the formation of small crystal size of anatase TiO_2 crystalline in the composites after calcination at 350 °C. With the increasing calcination temperature, the anatase TiO_2 (101) plane diffraction peaks of the TGOs-400, TGOs-450, TGOs-480 samples increased in intensity and narrow in width gradually the characteristic diffraction peaks can be also observed at 2θ value of 53.98° and 55.12°, corresponding to the (105) and (211) crystal planes of anatase TiO_2, which indicating that the hydrated titanium oxide of the composites was catalyzed to in situ dehydroxylation and crystallization generate anatase TiO_2 with the increase of calcination temperature, and the crystallization degree of samples increases gradually.

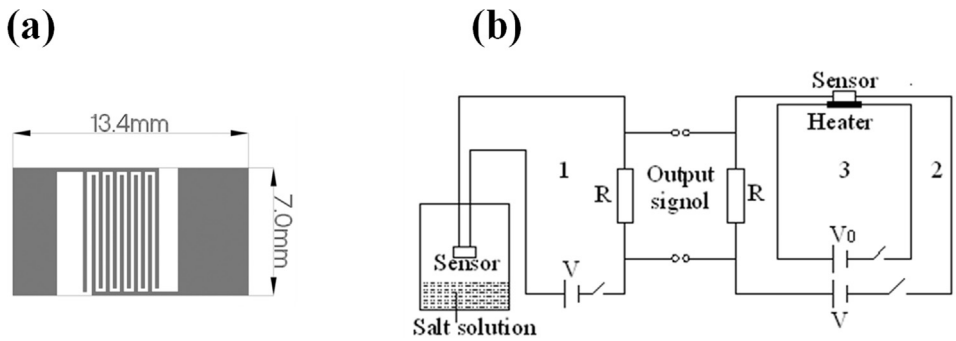

Fig. 1. a: Interdigital Ag-Pd electrode substrate and Test circuit. b: (1) Test circuit for humidity sensitivity, (2) Test circuit for resistance-temperature characteristic, (3) Circuit for heating.