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Research paper

RGO nanosheets modified $NiCo_2S_4$ nanoflowers for improved ethanol sensing performance at low temperature

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ABSTRACT

$NiCo_2S_4$/rGO, with the morphology consisted of flower-like $NiCo_2S_4$ and rGO nanosheets, was successfully fabricated based on a simple method of one-step solvothermal at 200 °C for 12 h. The composite was characterized by XRD, SEM and XPS, and the first time used as gas sensors. Compared with flower-like $NiCo_2S_4$, $NiCo_2S_4$/rGO possessed ascendant gas sensitive properties, such as lower working temperature about 100 °C, shorter response/recovery time and better selectivity to ethanol. The extraordinary performance was because of the introduction of rGO with fast electron transport rate. Also, the possible formation mechanism of $NiCo_2S_4$/rGO composite was preliminary discussed.

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1. Introduction

The research of new kinds of materials is an effective approach to enhance gas sensitive performance. The traditional gas sensing materials are transition metal oxide, transition metal sulfide such as ZnO [1–3], NiO [4–6], Co_3O_4 [7–9], WO_3 [10], TiO_2 [11,12]. $NiCo_2S_4$ is a common p-type semiconductor, which is widely used in supercapacitors [13], dye-sensitized solar cell [14], electrochemical energy storage/conversion devices [15], based on its unique redox characteristic, extraordinary electrochemical activity. However, it was used as gas sensing material rarely. In this manuscript, $NiCo_2S_4$ was selected as gas sensing material to detect ethanol, then rGO nanosheets were added into $NiCo_2S_4$ to prevent the agglomeration so that gas sensing performance could be enhanced. GO is a common 2D material, which was used widely in lithium-ion batteries [16,17], catalyst [18,19], supercapacitors [20,21] attributed to its rich active sites, high specific surface area and outstanding electrochemical activity. The materials related to rGO are frequent in gas sensors [22,23]. Usually, after mixing with rGO nanosheets, the operating temperature of the composite reduced and the response of the sensor both increased significantly. So, it is hopeful to improve the gas sensitive properties by designing a compound of $NiCo_2S_4$ and rGO and used as gas sensing material.

Herein, we synthesized a composite of flower-like $NiCo_2S_4$ and rGO nanosheets through in situ growth to enhance sensing performance of $NiCo_2S_4$. To explore the effect of mixing rGO on the properties of composite, gas sensors based on $NiCo_2S_4$/rGO composite, monophasic $NiCo_2S_4$ were fabricated and subsequently evaluated for gas sensing performances. Having investigated on the gas sensors, we found that $NiCo_2S_4$/rGO exhibited higher response to 100 ppm ethanol and lower operating temperature compared with $NiCo_2S_4$.

2. Experimental

2.1. Synthesis of graphene oxide

Graphene oxide (GO) was fabricated via the modified Hummers method [24,25]. Briefly as follows: after the addition of 5 g graphite powder into 100 ml H_2SO_4 (98%) in an ice bath, the mixed solution was stirred for 2 h. Next, 30 g $KMnO_4$ was mixed into the mixture slowly which was still kept below 5 °C in the ice bath. Afterwards, the solvent was transferred in the condition of water bath with stirring for 45 min at about 50 °C. In the meantime, the color of the mixture turned to brown. Next, 300 ml deionized water was injected into the solution, heated to 90 °C and stirred for 15 min. After that, 40 ml H_2O_2 (5%) and 200 ml deionized water were

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added into the solution to remove redundant $KMnO_4$. At this point, the mixed solution changed into golden yellow. At last, as-prepared GO was washed with HCl (3ωt%) and deionized water successively. When the PH of the mixed solution changed into 7, as-prepared GO was dispersed into single-layer sheets in deionized water at a concentration of 1 mg/mL with the assistant of ultrasound for further utilization.

2.2. Synthesis of $NiCo_2S_4$/rGO composite

Pre-obtained GO solution was used to synthesize the final product which was named flower-like $NiCo_2S_4$/rGO nanosheets compound by one-step process. In a typical process, 20 mg GO was dispersed in 64 ml mixed solution containing water and ethanediamine (1:1, v/v) along with ultrasonic processing for 90 min to ensure the GO exfoliated. Then, 1 mmol $Ni(NO_3)_2{\cdot}6H_2O$ and 2 mmol $Co(NO_3)_2{\cdot}6H_2O$ were added into it under magnetic stirring. The final reactant was acquired after adding 6 mmol CH_4N_2S with the process of stirring for 1 h and ultrasonic treatment for 1 min. Subsequently, the reactant was transferred into a 100 ml autoclave and kept it at 200 °C for 12 h. After the autoclave cooling down naturally, the deposition was collected through centrifuging and washed for several times with deionized water and absolute ethanol for several times, and dried at 60 °C for 12 h. The pure $NiCo_2S_4$ was synthesized by similar process without adding GO.

2.3. Characterization of as-prepared samples

The powder X-ray diffraction pattern of all as-prepared materials was carried out on a Rigaku X-ray diffractometer (XRD, Rigaku TTR-III) with CuK1 radiation in the scanning range of 5–60° (2θ) operating at 40 kV and 150 mA. The size and morphology of the samples were observed by field emission scanning electron microscopy (FESEM), which was carried through a JEOL JSM-7500F microscope with 20 kV of accelerating voltage. The surface chemical analysis of composites was measured by ESCALAB250Xi X-ray photoelectron spectroscopy.

2.4. Fabrication of sensor

The production process and test process of the sensor are similar to our group's earlier report [26]. First of all, a certain amount of powder dispersed into ethanol for 15 min to form a suspension under the aid of ultrasound. Next, the suspension was brushed onto the alumina tube whose diameter and length is 1 mm and 4 mm, respectively, and the both ends of Au electrode were linked to Pt wire. The Ni chrome resistance (28–30 Ω) which used as heater was put into ceramic tube to control working temperature. Finally, after being dried and aged for two days, the as-prepared sensor's sensing performance was tested.

3. Results and discussion

3.1. Materials characterization

Fig. 1(a) shows the XRD patterns of all the samples, consisting of GO, $NiCo_2S_4$ and $NiCo_2S_4$/rGO. The black line at $2\theta = 11.66°$ displays the diffraction peak of GO which is matching well to (0 0 1) crystal plane reported [27]. The pink line is the XRD pattern of $NiCo_2S_4$, all the diffraction peaks observed of which are well matched to the cubic phase $NiCo_2S_4$ (JCPDS: NO. 20-0782). The purple line belonging to $NiCo_2S_4$/rGO is almost the same as the pink one, but no evident peaks prove that rGO are observed which may be attributed to the low content of rGO in the materials [27]. Besides, there are no other peaks corresponding to impurity, confirming a high purity of $NiCo_2S_4$/rGO.

XPS measurement was adopted in order to prove the presence of rGO. The survey XPS spectrum is shown in Fig. 1(b) with only five elements about C, O, Ni, Co and S observed which are well coincident with the expected products. Fig. 1(c) shows the XPS spectrum of C 1s, which can be separated into three peaks located at 284.61 eV, 285.81 eV and 288.42 eV coinciding with C═C, C—O and C═O, respectively. The intensity of the last peak is very low which reveal a reduction from GO to rGO in the solvothermal process [28]. The Ni 2p and Co 2p spectrums are shown in Fig. 1(d) and

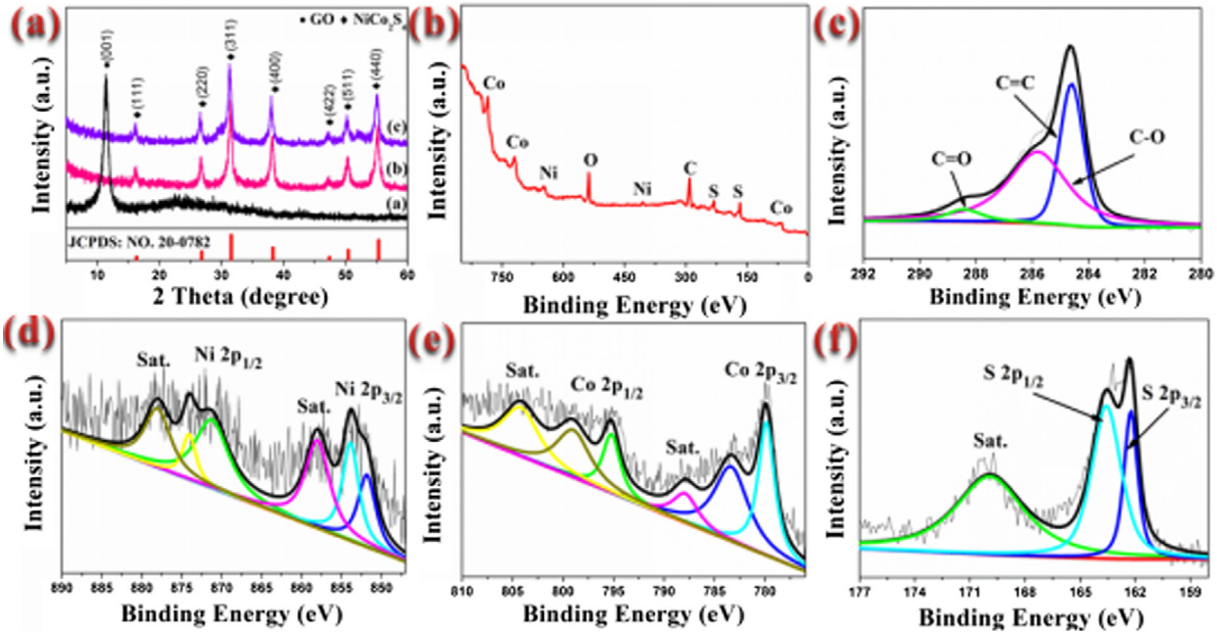

Fig. 1. (a) XRD patterns of standard card of cubic $NiCo_2S_4$, GO, $NiCo_2S_4$ and $NiCo_2S_4$/rGO from bottom to top, and XPS spectra of $NiCo_2S_4$/rGO: (b) survey, (c) C 1s, (d) Ni 2p, (e) Co 2p and (f) S 2p.

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