Surface acoustic wave sensors with Graphene/PANI nanocomposites for nitric oxide detection

Beibei Wang[1], Lei Zheng[2] and Lingling Zhou[1]

[1]Chuzhou Vocational and Technical College, Chuzhou 239000, China

[2]School of Energy and Power Engineering, Jiangsu University, Zhengjiang 212013, China

Corresponding author e-mail: wangbeibei333@126.com

Abstract: Surface acoustic wave sensors with grapheme/PANI nanocomposite sensitive films for detecting nitric oxide (NO) were fabricated and experimentally studied. Morphological characterization and functionalization of the sensing material were explored using SEM and FTIR, respectively. The study of sensor response compared film sensitivity, response time, reversibility, and limit of detection for nanocomposite films, pure grapheme and pure PANI to the detection of NO. The response and recovery times were 40s and 20s when detecting 4ppm NO, respectively. The frequency response was discovered to be linear in the NO concentration range 1–50 ppm. The nanocomposite sensors had improved sensitivities compared to the polymer devices, and better response times.

1. Introduction

The selective and sensitive gas-sensing technology of surface acoustic wave sensor (SAW) is determined largely by the nature of the sensing film. Over the past few years, extensive research has been performed using nanocomposite sensitive films, because the combination of different compounds into one sensing layer has the potential to improve the sensitivity while retaining the advantages of its constituents and increasing its surface functionality.[1~5] The preparation of very thin and homogenous sensitive films is desirable for enabling high signal-to-noise ratio and short response time for sensor.[6] A drawback of the nanocomposite layers is that due to rather poor dispersion of the filler particles it is difficult to control structural features as inter-particle spacing and position on the surface; moreover the particles may tend to aggregate the composite material.[7]

Graphene is a two-dimensional material with an improved capability of gas sensing, which is due to two main facts: (1) the two-dimensional nature, with only a surface and no volume, enhances the effect of surface dispersion, (2) a high conductivity and low electrical noise. The effect of various p- and n-doped gases on the gas sensing properties of pristine grapheme has been investigated in the past few years. The adsorption/desorption of gaseous molecules which act as electron donors or acceptors on the graphene surface is responsible for the gas sensing mechanism in graphene through modifications of the carrier density, and hence the electrical resistance of graphene.[8~10]

Because of the lack of dangling bonds on the pristine graphene surface, gaseous molecules cannot be readily absorbed. One of the methods to improve the gas sensing properties of graphene is to composite it by polymers.[9] Polymer-based nanocomposites, produced by introducing nanoparticles, nanotubes, or nanowires into polymers, have enhanced absorption properties, mainly due to the increased surface area of the nanoscale materials. [11~13] As a versatile building block for the construction of adsorbents,

polyaniline (PANI) possesses high amine density and accessible primary amine sites on chain ends [14]. Therefore, PANI can easily interact with the oxygenated groups of graphene sheet, which is profit for the development of gas sensitive thin films.

Our interest was to study and compare the nanocomposite sensing films based on graphene nanosheets and PANI nanoparticles. In this paper, we report on the development of SAWS for detecting nitric oxide (NO). Graphene/PANI composite were used as the sensing film. Their sensitivity, responsivity, and reversibility for different gas concentrations were studied, and a comparison between these sensors and polymer sensors demonstrated a significant improvement in sensitivity.

2. Experimental

2.1. Synthesis of Graphene/PANI nanocomposite
The graphene/PANI doped with HCl synthesized by an in situ chemical oxidative polymerization, conducting in aqueous solution with Ammonium peroxydisulfate (APS; $(NH4)2S2O8$) as the oxidant. In a typical operation, 5mg graphene was sonicated for one hour in 20mL of ethylene glycol in the presence of 2mmol Aniline (Ani). Then 0.5mmol of APS in 10mL of 1.0M HCl was rapidly added to the mixture. The solution was cooled in an ice-water bath (0–5∘C) and magnetically stirred for 12h to continue polymerization. Finally, the obtained dark green precipitate was collected by filtration and respectively washed with deionized (DI) water, ethanol and hexane for three times. The resulting product was then dried in a vacuum oven at 25 ∘C for 24 h. As comparison, the PANI was prepared under the same process as those of graphene/PANI without graphene.

2.2. Fabrication of high frequency SAW devices
The sensors were "delay line" type, with a center frequency of 69.4 MHz. An interdigitated transducer (IDT) with 50 straight finger pairs, a 2500μm aperture width and a periodicity of 40 μm was patterned on a piezoelectric substrate. The 150-nm-thick gold IDTs were deposited on 10-nm-thick chromium using standard photolithographic techniques. The active area was 8 mm^2 with a parallelogram geometrical configuration of the quartz substrate in order to reduce acoustic wave reflection at the substrate edges.

Before the film deposition, IDTs were rinsed with DI water and ethanol, and dried in vacuum oven at room temperature for 24 h. The graphene/PANI were added in 10 mL solutions (1 mg mL-1) with 3 mL ethanol and 7 mL DI water. The resulting solutions were sonicated for 15 min before used as uniform coating solution, and then applied on the IDTs by drop-coating method. After natural evaporation of the solvent in a drying box at room temperature for 2 h, the NO sensing thin films coated IDTs were obtained.

The sensing properties of the fabricated SAW sensors were measured within an enclosure containing various NO gas concentrations. A computerized multi-channel gas calibration system was used for generating NO gas in a synthetic air balance. The NO and dry air were transported using mass flow controllers with a precision mass flow meter to change the ratio of NO gas to dry air. A temperature controller maintained a constant temperature of 25∘C. The response to the NO gas was monitored as change in frequency of the SAW sensor using a frequency counter .

2.3. Characterization and testing instrumentation
Fourier transform infrared (FTIR) spectra (KBr dispersed pellets) in the range of 400–2500 cm-1 were recorded on a fully computerized Nicolet 5700 spectrometer. The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM, CARL ZEISS Supra 55).

## 3. Results and discussion
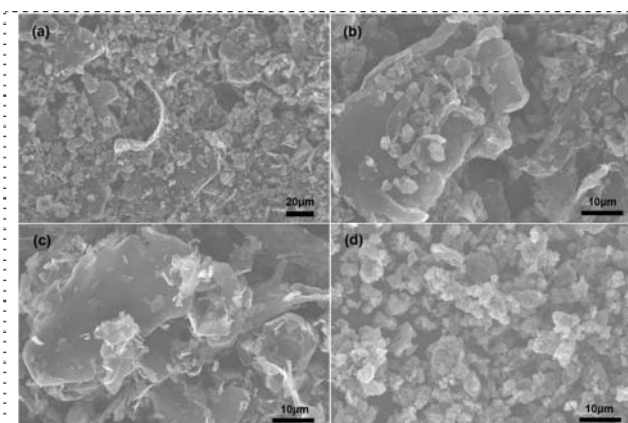
Figure 1. FESEM images of the surface morphology of sensing films: (a) and (b) Graphene/PANI; (c) Graphene; (d) PANI
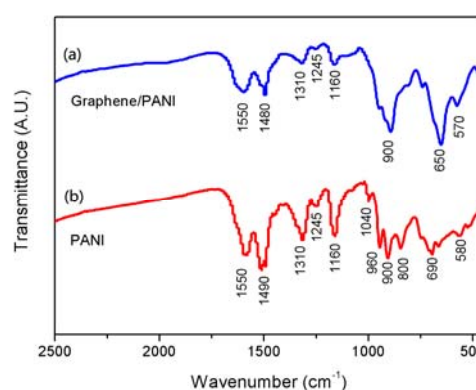

Figure 2. FTIR spectra of (a) graphene/PANI and (b) pure PANI.

The surface morphology of graphene/PANI, graphene and PANI sensitive films was analyzed using FESEM. The graphene/PANI sensitive layer (Fig. 1(a)) had a uniform and porous structure, which seem to benefit for the short response time and good reversibility of the sensor. This is due to the fact that gas diffusion and absorption occurs more easily in porous structures, and the reaction between gas molecules and the thin film therefore occurs easily. Morphology of polyaniline is known to vary depending on the synthesis conditions.[15] In the present study, the mechanism of the formation of PANI particles on the graphene that aniline monomer is firstly adsorbed onto the surfaces of the graphene because of electrostatic attractions. Therefore, the graphene act as a role of support stabilizer to form graphene/PANI nanocomposite by chemical polymerization. Fig. 1c shows the large flake-like morphology of graphene with slightly folded edges and flat surfaces. Fig. 1d shows the PANI nanoparticles with spherical morphology prepared by the intrinsic polymerization condition.

FTIR spectroscopy is important tool to study the chemical nature of nanocomposites. Fig. 2 displays the FTIR spectra of graphene/PANI. The main characteristic peaks of pure PANI (Fig. 2b) are assigned as follows: the bands at 1550 and 1490 cm^{-1} are attributed to ring stretching mode of vibration for the quinonoid and benzenoid units of PANI; the bands at 1310 and 1245 cm^{-1} are attributed to C-N stretching mode for benzenoid unit; the aromatic C-H in-plane band at 1160 cm^{-1}; the out-of-plane deformation vibration of C-H bond in 1,2,4-disubstituted benzene at 960 and 900 cm^{-1}; the out-of-plane deformation vibration of aromatic C-H bond at 800 cm^{-1}; the vibration of C-Cl group at about 1040 cm^{-1}. For graphene/PANI nanocomposite (Fig. 2a), the FTIR spectrum are almost identical to that of pure PANI, but all bands shift slightly. Moreover, the bands at 1040, 960 and 800 cm^{-1} have disappeared. Those results indicate some interaction between PANI and graphene.
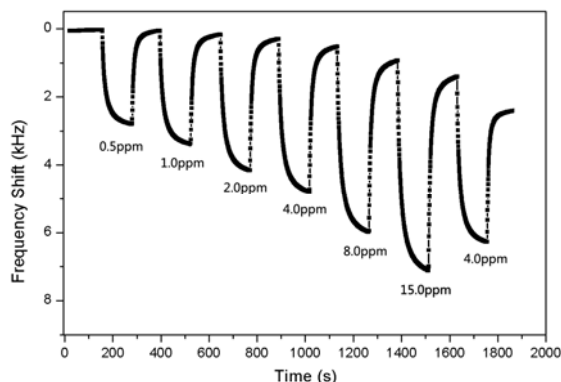
Figure 3. Dynamic response of nanocomposite SAW sensors towards NO gas at room temperature
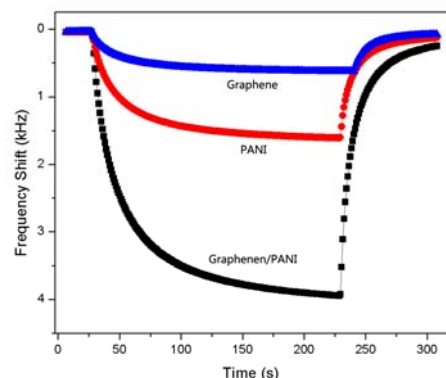

Figure 4. Dynamic responses of SAW sensors using pure PANI, pure graphene and graphene/PANI exposed to 4 ppm NO

The dynamic response of the sensors towards NO gas at room temperatures was shown in Fig 3. NO gas, at different concentrations in a balance of synthetic air, was introducing to the chamber and exposed to the sensors. The SAW sensor exhibited a negative frequency shift during exposure to the analyte gas. The frequency shift was proportional to the concentration for the sensor and no saturation was observed up to 15.0 ppm. After purging out the NO gas through the introduction of dry synthetic air, the operational frequency of the SAW sensor increases and return back to the baseline. The NO sensing mechanism of the graphene/PANI nanocomposite is not fully understood. Here we think the reasons that the frequency shift of graphene/PANI thin films sensor increases with the NO concentration mainly is: When the adsorption of NO gas on the sensitive layer, some quinoid bands of PANI were converted into benzenoid bands. This indicates that the layer was reduced during the NO oxidation process. When the sensor was purged by dry air, the sensitive layer was reoxidized. Consequently, the adsorbed NO desorbed from the surface and the sensitive layer recovered its original chemical structure. Therefore, the sensing signal could be recovered to the baseline.

Fig. 4 depicts response curves of the sensors coated with different sensing films (pure PANI, pure grapheme and graphene/PANI) as a function of time. It could be seen that the graphene/PANI layered film sensors show superior performances than pure grapheme and PANI sensors. The real response time was calculated by subtraction of 3–4 s from the measured response time. It is remarkable that graphene/PANI film coated sensors exhibit faster response rates among all sensors. The response of about 40 s was found for the graphene/PANI sensors (to reach 90% of maximum signal). For the pure PANI and pure graphene sensors, the response time was 85 s and 105 s, respectively.
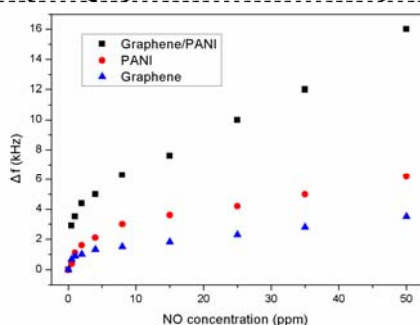
Figure 5. Comparison of frequency shifts at different gas concentrations.
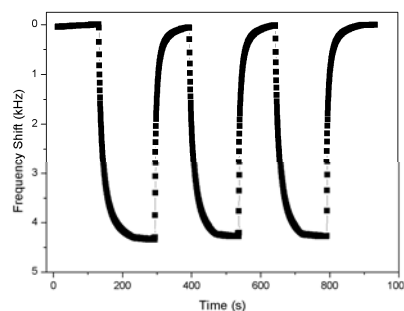
Figure 6. Typical response and recovery curve of graphene/PANI sensors exposed to 4 ppm NO

The sensitivity, defined as the frequency shift in Hz per unit analyte concentration in ppm, was determined from the slope of the data as illustrated in Fig. 5. All of them exhibit almost linearity of frequency shift for NO concentrations ranging from 1 to 50 ppm. The inset depicts the situation at low NO concentration. The results show that the response value and response rate to graphene/PANI sensor were much higher than that of PANI and grapheme sensor.

Repeatability, selectivity and long-term stability are all key factors for SAW sensors; especially the minimization of hysteresis behavior is an important condition for practical application of sensors. To investigate the sensor's repeatability, the graphene/PANI sensor was tested at a fixed concentration repeatedly for three cycles, as shown in Fig. 6. It can be seen that the sensor exhibits reproducible adsorption and desorption kinetic behaviors with very little response fluctuation under the two humidity levels, indicating the good repeatability and baseline stability.

4. Conclusion

In summary, we have reported the synthesis of the graphene/PANI nanocomposite by chemical oxidative polymerization of aniline in the presence of graphene dispersion solution. A SAW gas sensor is fabricated by graphene/PANI nanocomposite using drop-coating method, and provided a comparison of graphene and PANI to detect NO gas. The result reveals that the nanocomposite films sensor exhibits much higher sensitivity and faster response time than that of grapheme or PANI, and shows approximate linearity over a wide range of concentrations from 0 to 50 ppm. Moreover, the graphene/PANI thin films sensor has good reproducibility for NO gas. The PANI nanopartical are homogeneously dispersed on graphene, which may increase the surface-to-volume ratios and therefore increases the sensitivity of graphene/PANI thin films.

Acknowledgments

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