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Synthesis and studying of reduced few-layered graphene coatings in gas sensor applications

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Abstract. In this work reduced few-layered graphene (rFLG) nanoparticles were synthesized using electrochemical pulse exfoliation method from waste graphite crucibles. The regular change in voltage polarity in the synthesis process ensures both the separation of graphite in layers and the reduction of graphene oxide. A method for synthesizing free-standing rFLG and nitrocellulose (NC) composite film has been developed involving creation of rFLG-NC ink that can be deposited on various substrates. It has been observed that a successful synthesis of a free-standing composite coating is possible with the mass ratio of rFLG:NC at least 9:1 of which resistivity is on the order of approximate 10 ohm-centimetres in dependence from temperature and surrounding atmosphere. Sensor electrode was prepared by simple dip-coating method and the response to humidity, organic solvent vapours and nitrogen containing gases was measured and conclusion made that rFLG-NC coating is sensitive to many kinds of gases (cross-sensitive) what may result in false detecting or can be used to multi-sensor chips for artificial olfaction devices.

1. Introduction

One of the biggest sources of energy at present day is through the fossil fuels. Burning of which releases dangerous side products. The most dangerous are considered to be nitrogen oxides NO and NO₂. For successful limitation of these pollutants gas sensors are required. A potential gas sensing material is carbon allotrope graphene [1,2]. Many methods have been developed other than first used micromechanical cleavage [2]. For preparation of relatively large size graphene monolayers chemical vapour deposition is widely used but this method is difficult to scale to industrial levels [3]. Other than graphite exfoliation through oxidation of graphite [4] electrochemical exfoliation is a potential method for scalable synthesis of graphene sheet stacks [5,6]. For even more effective exfoliation usually graphene sheet stack containing suspension is additionally subjected to ultrasonication [7].

For further applications variety of graphene-based materials are prepared ranging from thin gas permeable membranes [8] to three dimensional structures for energy storage [9].

One option for creation of larger structures is by creation of graphene – polymer composite through either *in situ* polymerisation or through dissolution [10]. In addition to create a relatively macroscopic material, some composite material properties can be tailored enhancing for example mechanical [11] or electrical [12] properties.

Gas sensors are classified by their detection mechanism, one of which is the chemical reaction or adsorption taking place in the surface of a semiconductor (e.g. tin dioxide is widely used [13]) in result



of which the electrical resistance increases or decreases depending on the reaction taking into account for the donor or acceptor presence in the semiconductor [14]. Sensor response S in percentage is introduced to characterise this change of resistance and described elsewhere [14,15].

2. Experimental

2.1 Synthesis and reduction of rFLG

Graphene sheet stack (GSS) powder was synthesised through electrochemical pulse exfoliation of waste graphite crucible from bronze metallurgy as the working electrode in 1 M H₂SO₄ electrolyte, counter electrode was platinum. Potential to the cell was applied periodically, +10 V for 3 seconds and -10 V for 5 seconds. The resulting suspension was vacuum filtered with DI water and dried in an oven. Dry GSS powder was then mixed with N,N-Dimethylacetamide in a sealable glass jar, which was further placed in sonication bath for multiple hours. After sonication the GSS powder was again vacuum filtered with DI water and dried in an oven. For further reduction dried powder was put in an alumina tube furnace purged with Ar/H₂ 95:5 gas mix at temperatures up to 800 °C.

2.2 Preparation of rFLG-NC films

Desired mass ratios between rFLG and NC was mixed in acetone and sonicated for around 3 hours to create the ink-like suspension.

For preparation of free-standing composite films aluminium foil was adhered to sample glass and used as a substrate. Ink was deposited on the aluminium foil layer by layer via tape casting in ambient conditions. To remove rFLG-NC film from substrate, it was slowly put into 0.5 M KOH solution with the aluminium side facing solution. Separated rFLG-NC film remained floating in the solution and was carefully taken out on PTFE strip and dried on a laboratory hot plate (around 50 °C) for an hour. Samples for gas and vapour sensing measurements were prepared by dip-coating method from the rFLG-NC-acetone suspension (rFLG:NC mass ratio of 4:1) on sample glass pieces (width 10 mm and length 15 mm).

2.3 Characterisation of rFLG-NC films

To find out the type of conductance of the prepared film, Hall effect measurement was carried out on HMS-5000 *van der Pauw* Hall effect measurement system.

The resistance as ohms per square was measured by placing two identical thin 5 mm long electrodes parallel to each other at a distance of 5 mm.

The microscopic images of the composite surface were obtained by the means of *Phenom Pro* desktop SEM with acceleration voltage of 10 kV.

2.4 Gas sensing measurements

Gas sensing measurements were carried out at room temperature. The prepared samples were placed in a sample holder and electrodes were pressed onto the sample film 2 mm apart. The holder was placed in a closed volume – desiccator. The electric measurements were carried out with potentiostat *VoltaLab PGZ 301*. Test substance was introduced, evaporated in a closed desiccator. To achieve complete evaporation of water and ammonia solution the desiccator was held at an elevated temperature of 64 °C. For tests with nitric oxide and nitrogen dioxide the gases were introduced by reacting copper metal with dilute and concentrated nitric acid respectively.

3 Results and discussion

3.1 Characterisation of composite films

The Hall effect measurement indicated that the conductance of synthesized rFLG-NC material is semiconducting p-type. The reason behind this is thought to be some oxygen containing functional groups on rFLG that most likely were introduced in the electrochemical exfoliation and persisted through reduction process. The resistivity dependence from the electrically conducting rFLG particle percentage in the composite (Figure 1) show an obvious trend of decreasing resistivity when the amount of rFLG in composite is increased. The film thicknesses in each of the rFLG percentages varies from 5 μm to 40 μm and are taken into account when calculating resistivity.

The free-standing (Figure 2 (a)) and supported (Figure 2 (b)) films show distinct differences on their structures. The supported film has rFLG sheets assembled more planar to each other in comparison to the free-standing film

likely due to the synthesis of each type of film. Utilization of relatively large amounts of ink in combination of quickly volatile solvent used in blade casting technique did not let the particles to align themselves with the least fill factor *i.e.* parallel to each other as it was observed in the dip-coating method where it is intuitively understandable that each planar rFLG particle would align as parallel as possible to the substrate surface.

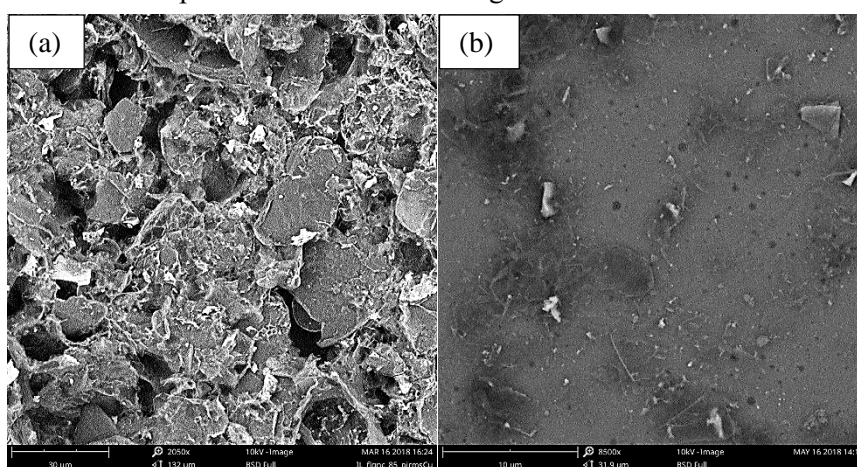


Figure 2. SEM images of two types of the made films. Scale lengths indicate 30 μm (a) and 10 μm (b).

3.2 Gas sensing measurements

Resistance over time of the film was obtained by applying a constant potential across the sample so that current would be on the order of few μA . This was done to make the resistance change due to Joule heating negligible.

Advantage or disadvantage in some cases of using composite material as the sensor material is that resistivity can change due to each part of the component of composite. Figure 3 shows the resistance change in interaction with solvent vapours – acetone, methanol and acetonitrile – each of which is known to dissolve polymer NC. The reversibility of resistance change in five or ten minutes is understandable, considering the volatile nature of solvents in ambient conditions. The reversibility also indicates that no structural changes are happening *i.e.* rFLG particles are not noticeably changing their distribution in the film. In addition, consecutive measurements under the same conditions in solvent vapours were carried out five times and these measurements did not show any significant

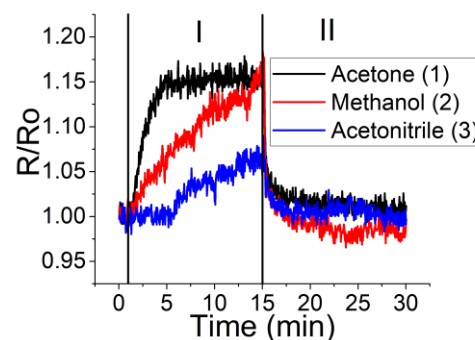


Figure 3. Resistance change of the rFLG-NC supported film under the influence of acetone, methanol, acetonitrile vapours. Part I shows the evaporation of target substance and the sensing reaction of film and II shows the purge of the closed volume.

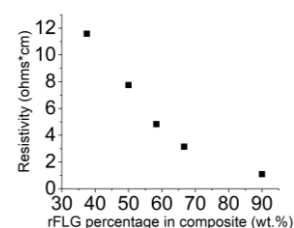


Figure 1. Composite resistivity vs the rFLG percentage in composite by mass.

difference or trend. It must be pointed out that for acetone and methanol sensors part of the contribution could be from chemical reactions between target gas and oxygen derivatives O^- adsorbed to rFLG surfaces [16,17]. The electrons generated by the reaction could recombine with the main charge carrier type (holes) in the composite and the overall resistance would increase. In the case for acetonitrile most likely there is no reaction happening and the response is purely due to interactions between the vapours and the nonconductive part of composite – NC. Although a sensing mechanism it must be pointed out that the resistance change to these organic solvents is relatively small in relatively large concentrations of solvent vapours and this reaction must be considered if composite is used as sensing material for other substances e.g. ammonia or nitrogen oxides described further.

Ammonia in water solution was evaporated in the closed container and Figure 4(a) shows the response values vs concentration to both ammonia and humidity. In contrast to exposure to nitrogen oxides where the resistance decreased the resistance due to ammonia increased. These observations agree with the fact that composite film is a p-type semiconductor. Ammonia a less electronegative compound adsorbs to rFLG sheets and donates electrons that recombine with holes in rFLG thus increasing the overall resistance [14]. Whilst the more electronegative nitrogen oxides when adsorbed to rFLG attract the electrons increasing the hole concentration in material and decreasing the overall resistance. It is important to note that the resistance change in exposure to nitrogen oxides is not reversible in short periods of time (15 minutes) as seen from Figure 4 (b). Reaction mechanism of nitrogen oxides is definitely adsorption to rFLG considering that there would be no possible reaction between the NC as it is fully nitrated, no more place available for nitrite ions to settle.

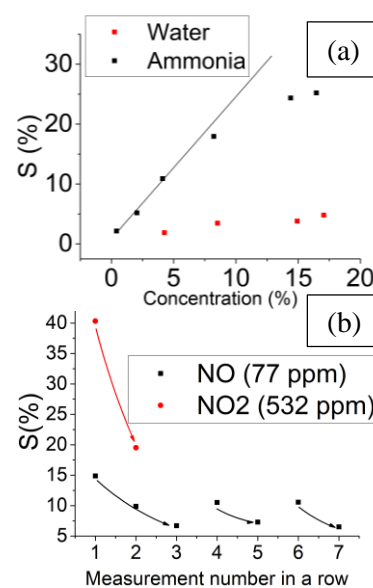


Figure 4. Response vs concentration for ammonia and water vapour (a) and response vs measurement number for nitrogen oxides showing the reversibility of sensor film, arrows indicate consecutive measurements (b).

Conclusions

We have synthesised rFLG through electrochemical exfoliation of waste graphite crucible and incorporated it into NC matrix in the form of free-standing and supported films. The supported films show a more planar orientation of rFLG sheets than in the case of freestanding. The composite film shows p-type conductance both from Hall and gas sensing measurements. We have shown that utilisation of composite material for sensor material can provide response reaction from both parts of the composite – NC solvent vapours and gases interacting with rFLG NH_3 , NO_2 and NO . Composite film is able to detect nitric oxide at concentrations as low as 77 ppm but the film electrical resistance in relatively short periods of time is partly non-reversible not as in the case of solvents, water and ammonia.

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