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Free Standing Graphene Oxide Films for Gas Sensing Applications

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Abstract

Free standing films of graphene oxide (GO) were synthesized using an improvisation of Tour's method [ACS Nano, 4, 4806-4814 (2010)]. Reaction time and temperature were significantly modified to reduce the presence of graphitic residues in the as synthesized GO. These films were characterized for phase purity and we report their performance for ammonia sensors.

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*Keywords:*Ammonia sensor, Graphene Oxide, high yield

1. Introduction

Since the discovery of graphene as a two-dimensional material, graphene and related materials have attracted significant attention due to their unique electronic, optical, mechanical and thermal properties [1-4]. Transferable single and few layer graphene sheets were discovered by mechanical exfoliation of graphite by scotch tape [5], epitaxial growth [6] and chemical vapour deposition [7]. Although these methods are preferable for lab scale device assembly, they are less effective for large scale applications. Chemical routes [8-11] are promising practical approach for production of bulk graphene related materials. The primary challenge is synthesis of individual and

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few layer graphene. Typical chemical exfoliation involves intercalation of functional groups, thermal expansion, electrochemical exfoliation and oxidation leading to the formation of graphene oxide (GO). Reduction of GO yields reduced grapheme oxide (rGO) which can be used as a substitute for graphene for most practical applications. GO presents itself as a strong candidate for gas sensing application. Hummers and Offeman proposed the use of $KMnO$, $NaNO_3$ and H_2SO_4using a recipe (now popular as Hummers method) for the preparation of GO. Maracano *et al*. [12] proposed a modified recipe (popularly known as Tour's method) which avoids the usage of NaNO (Which otherwise leads to emission of harmful NO_x gases) and instead uses an increased concentration of $KMnO_4$and a 9:1 mixture of H_2SO_4:H_3PO_4. Here we report an improvised method where synthesis time and temperature are significantly modified to yield GO with a further reduction of graphitic residues and which allows for preparation of free standing films of GO.

2. Experimental details

GO has been synthesized using an improvisation of Tour's method [9]. Free standing films were prepared by slow drying of the dispersed GO sheets after washing. The synthesis temperature and time have been significantly modified so as to suit the requirements for the absence of graphitic residues in the GO films. X-ray diffraction (XRD) studies of the film were performed using Rigaku TTRX-III XRD employing Cu K_α radiation. The micro Raman studies weredone using 532nm excitation laser with a spot size of ~ 1μm and typical laserpower of 200 μW. Gas sensing experiments were performed in a home built chamber where the concentration of gases could be estimated within the reaction volume and the base temperature can also be changed conveniently from room temperature to over 400^{o}C.

3. Results and discussion

Figure 1 shows the XRD diffraction pattern of GO film (black line). The (002) peak at 9.11° (GO) confirms the formation of graphene oxide. The XRD pattern for the starting graphitic flakes is shown (red line) for comparison and one can see the absence of any graphitic peak in the synthesized GO film. The XRD peaks corresponding to the graphitic flakes are indexed using suitable data from ICDD database (ICDD card number 00-0056-0160). There are few unaccounted impurity peaks for the starting graphitic flakes however they seem not to affect the phase purity of resulting GO. Figure 2 shows the Raman spectra of the film obtained at room temperature in the wavenumber range of 1200-2000cm^{-1}. The D and G peaks are centred around 1350 cm^{-1} and 1600 cm^{-1}, respectively. The observed G peak originates due to the first order scattering from doubly generated E_{2g} phonon modes and contains information regarding the sp^{2}hybridization within the carbon network. The D peak on the other hand is due to the breathing mode of aromatic rings which corresponds to the presence of structural imperfections and is used as a measure of the degree of disorder in the film due to the presence of functional groups [13]. The higher intensity of the G peak compared to the D peak attests to the good quality of GO film. The inset in Fig. 1 shows an SEM image of the film which confirms the formation of large scale GO films. The inset in Fig.2 shows a portion of the FTIR data which suggests the absence of any graphitic residues in the GO film. Gas sensing properties of the film has been performed using a home-made customized setup utilizing a Keithley Model 2420. The current-voltage (I-V) characteristics were obtained at room temperature and for desorption of adsorbed gases, the film was heated with a simultaneous evacuation of the containing chamber to rotary vacuum. Different concentration of volatile gases were used for detection at various PPM levels. Figure 3 depicts ethanol gas sensing via change in I-V in air and in absence of air. Ammonia gas sensing is demonstrated in Fig.4 with different levels of concentration. Special care has been taken so that no additional gas sensitivity enhancer (e.g., gold pads, etc) are participating in the sensing process. The gas sensing experiment has been repeated several times and we found that our film recovers its property merely by degassing, which suggests that it does not require the presence of inert gases or any other further treatment to recover its original property.

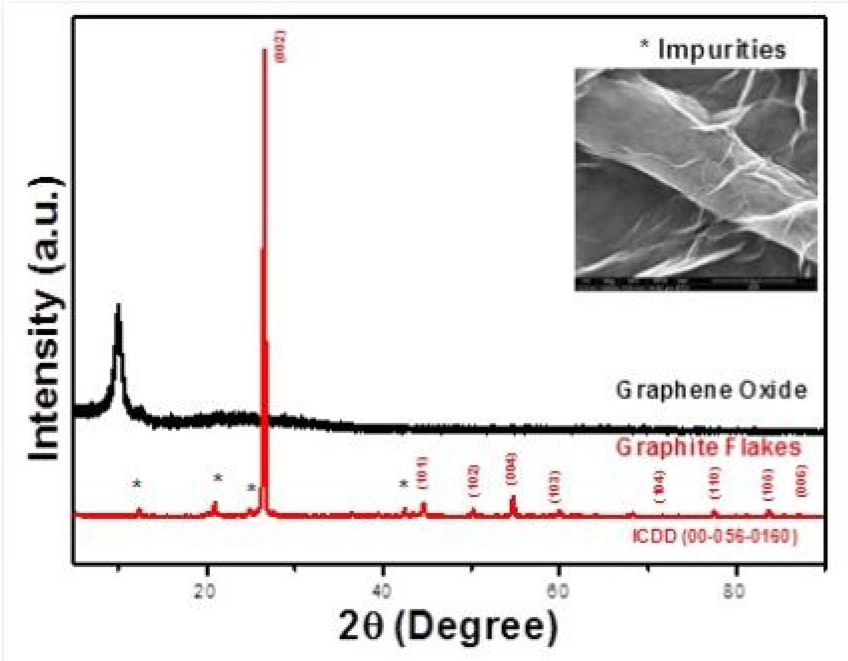

Fig. 1. XRD of GO thin film. The corresponding data for starting graphite flakes is shown in red.

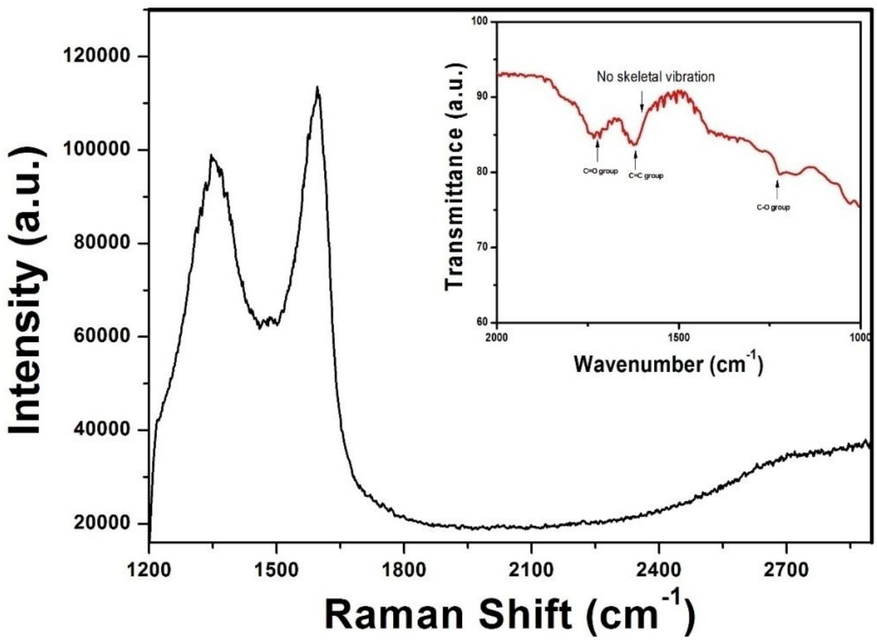

Fig.2. Raman spectra of graphene oxide thin film. Inset shows a portion of the FTIR data.

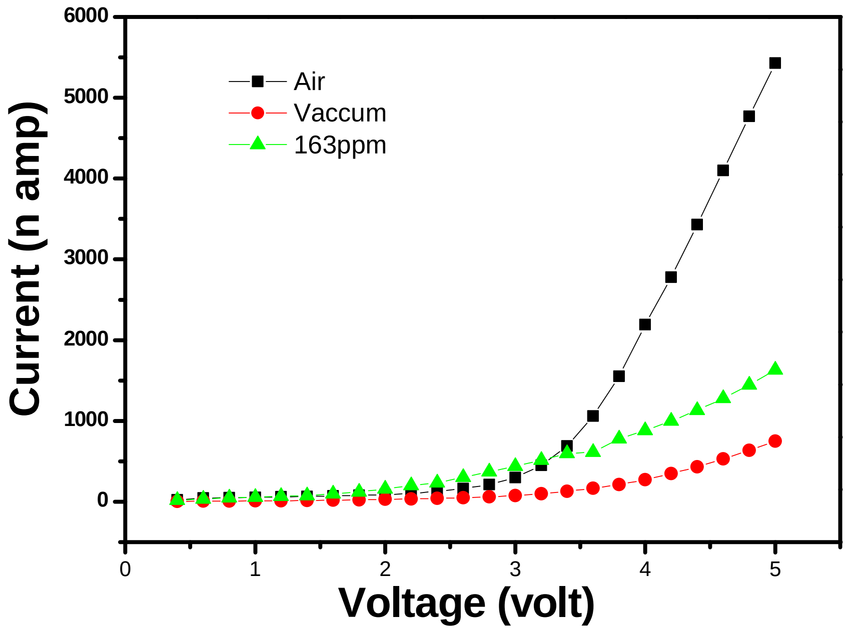

Fig.3. I-V characteristics of graphene oxide film in presence of ethanol

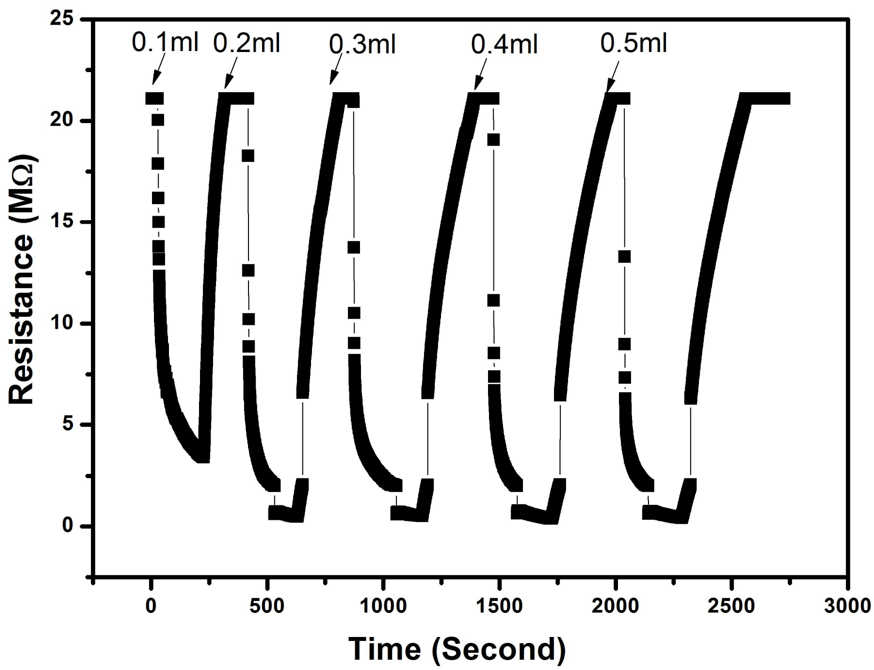

Fig.4. Chemresistive behaviour of free-standing GO film for ammonia sensing.

Conclusion:

Graphene oxidehas been prepared successfully by a modified Tour's methods. Free standing film of graphene oxide are made and shown useful in gas sensing.

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