

Reduced graphene oxide obtained using the spray pyrolysis technique for gas sensing

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Abstract. Graphene oxide films were formed using the ultrasonic spray coating method and studied with micro-Raman spectroscopy, atomic force microscopy, and electrical dynamic response of resistance measurements. Effect of different gases (water vapor, ethanol, acetone, ammonia, and isopropyl) on the dynamic response of resistance of the Au / graphene oxide / Au structure has been studied. The dynamic response shows that adsorption of all mentioned gases results in increase of the resistance. For ethanol, acetone and isopropyl adsorption and desorption cycles are almost identical. At the same time, in the case of water vapor and ammonia the cycle of desorption is very weak, especially for the former, which attests different mechanisms of adsorption/desorption processes regarding to ethanol, acetone and isopropyl. The mechanisms of studied vapors adsorption/desorption are proposed.

Keywords: ultrasonic spray pyrolysis, graphene oxide, Raman spectroscopy, gas sensor.

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1. Introduction

In recent years, the interest in nanostructured gas-sensing materials, particularly in thin film form, has significantly grown up. The devices based on them have good response, wide operation temperature range and stable selectivity. Moreover, sensors based on thin film materials are essential for mass production technologies. For industrial applications, a low cost method, specifically an ultrasonic spray pyrolysis technique, appears to be an excellent choice. The ultrasonic spray pyrolysis method is based on formation of fine droplets with size distribution in the range of a few micrometers. Hence, the ultrasonic spray pyrolysis method could be the best approach for deposition of uniform thin films.

At the same time, graphene and graphene-based materials are considered as promising candidates for advanced applications in future electronics [1-3] because of their attractive physical and optical properties. It was found that graphene oxide (GO) shows good sensing properties towards H₂O [4, 5], NO₂ [6], NH₃ [7], H₂ [8] and other gases and vapors.

One of the most informative methods to investigate the conductivity of materials is impedance spectroscopy

[9], which has been already applied to distinguish oxidized and reduced graphene, evaluate the thickness of the different chemically modified graphene layers [10]. In Ref. [11], impedance spectroscopy with proper equivalent circuit model was used to study GO solution (in de-ionized water) with different concentrations.

In this work, we report GO-based sensors prepared by ultrasonic spray pyrolysis technique. The nanostructured GO is characterized by Raman spectroscopy and atomic force microscopy. The sensor resistances are measured by current-voltage characteristic in direct current mode, and measurements of current at vapor/dry air cyclic pumping (dynamic response) are performed. The sensors are used to detect ethanol, acetone, ammonia, isopropyl and water vapor.

2. Experimental

GO was synthesized using Hummers' method [12] and transformed into water solution. Evolution of chemical composition of this material, after annealing, was determined using XPS and FTIR spectroscopy, as reported in [13]. The carbon/oxygen ratio of pristine GO was found to be 2.31, which is in agreement with values

reported for similar oxidation processes [14, 15]. Then, an aqueous solution of GO was deposited onto the substrate. As shown in Fig. 1, the substrate is an Au interdigitated electrode array (IDA) on SiO_2/Si . Deposition (see Fig. 2) was performed using the ultrasonic spray coating technique with 120 kHz atomizer nozzle (Sono-Tek Corp., USA), power level – 6 W, flow rate – 3 ml/h, for 5 min. The substrate was located on a heated table (80–100 °C). To focalize the beam of drops, the focusing air shroud was made and used. In this way, GO flakes are immobilized on IDA after solvent evaporation [16]. To obtain reduced GO film (rGO), the samples were annealed at 230 °C for 15 min in ambient air.

Both measurements of current-voltage characteristic in direct current mode and measurements of current at vapor/dry air cyclic pumping (dynamic response) were performed using Agilent 4156C semiconductor parameter analyzer. The nano-relief and homogeneity of GO film surfaces were analyzed using the FemtoScan atomic force microscope (AFM) operating in the contact mode (Fig. 2). The control of GO layer quality was fulfilled by micro-Raman spectroscopy at room temperature (triple Raman spectrometer T-64000 Horiba Jobin-Yvon, equipped with electrically cooled CCD detector, and excited by the 515-nm line of an Ar-Kr ion laser).

3. Results and discussion

3.1. Structure and surface morphology of GO film

AFM surface topology of GO film onto glass substrate, obtained with ultrasonic pyrolysis method, is presented in Fig. 3. GO films were aggregated to form clusters with the lateral sizes ranged from 500 nm up to several micrometers and the minimum thickness of about 3 nm. The root mean square (RMS) value of the GO height, averaged over an operation area $8 \times 8 \mu\text{m}^2$, equals to 5.4 nm. However, the local height of sharp thresholds between plateaus and valleys can reach 10–15 nm. The

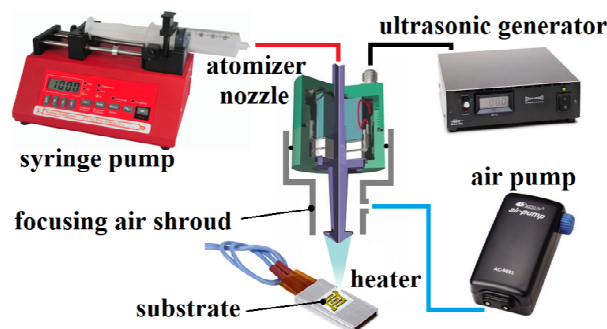


Fig. 2. Structural scheme of the ultrasonic pyrolysis system.

friction force map (Fig. 3b) illustrates a general homogeneity of mechanical and phase properties over the surface. At the same time, there is a local friction contrast of opposite sign (dark/light). The dark contrast associated with hole-like depressions in the relief (diameter 100...300 nm), where tip apex sticking and light contrast revealed fibrillar features of surface (wire-like features of $10 \times 100 \text{ nm}$ and length 1–2 μm) with a small friction. Probably, these fibrillar features are the multiple wrinkles formed at GO flakes spraying.

Raman spectra of GO and rGO films are presented in Fig. 4. Two typical peaks, with their maxima at $\sim 1350 \text{ cm}^{-1}$ and $\sim 1590 \text{ cm}^{-1}$ (D and G bands, correspondingly) are observed. Weak changes of I_D/I_G ratio from 0.92 to 0.91 could be associated with defect concentration growth after thermal treatment [13, 17], at the same time an oxidation degree remains significant [13].

3.2. Dynamic response of GO film resistance

The results of Raman measurements are confirmed by the relatively high resistance of the samples (see Fig. 5). Additionally, the current-voltage (I - V) characteristics of the samples are non-linear for investigated range of

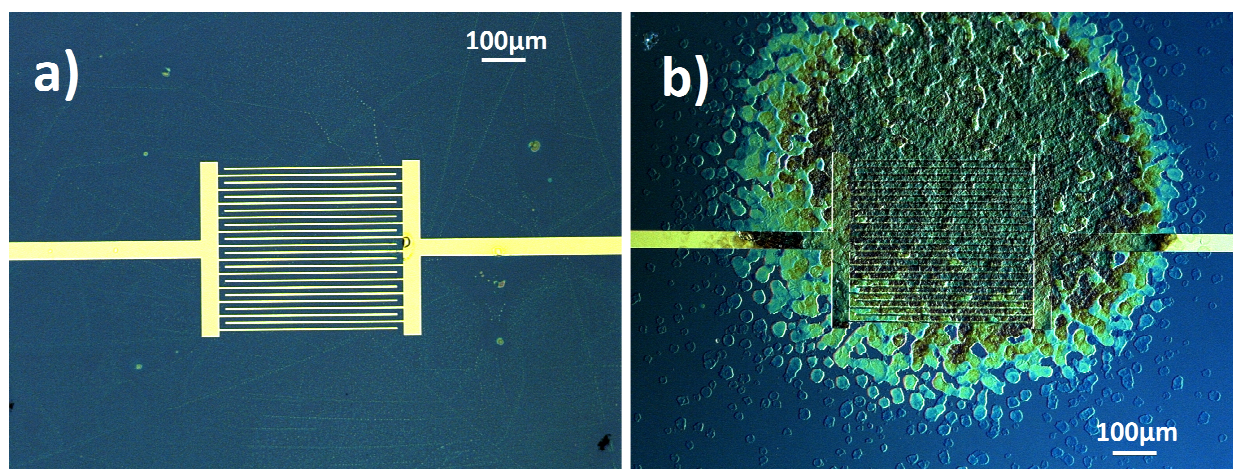


Fig. 1. Microscopic photo of Au electrodes (a) before, and (b) after spray deposition of GO film.

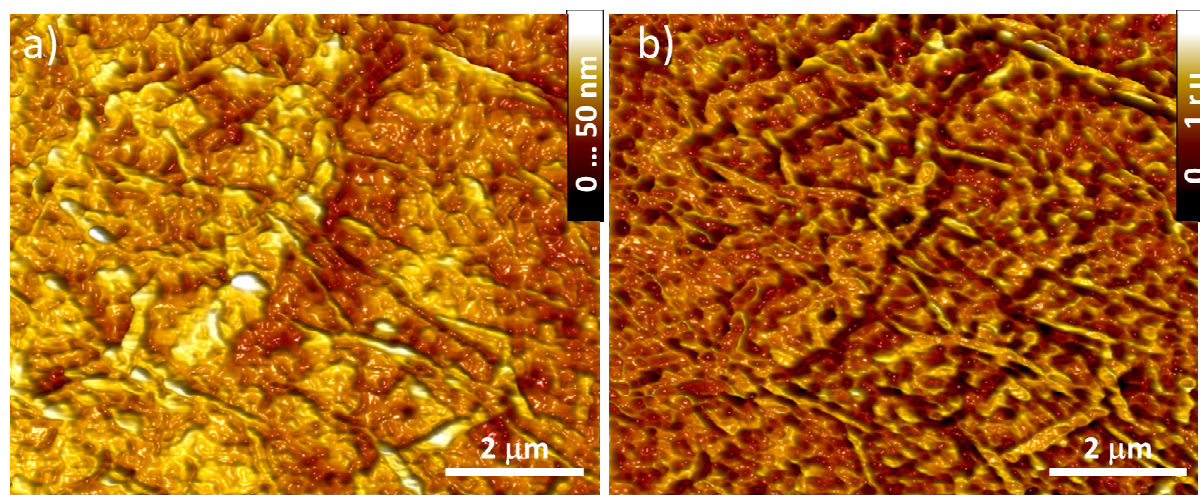


Fig. 3. AFM height (a) and friction (b) maps of the GO thin film deposited onto glass substrate with ultrasonic pyrolysis technique.

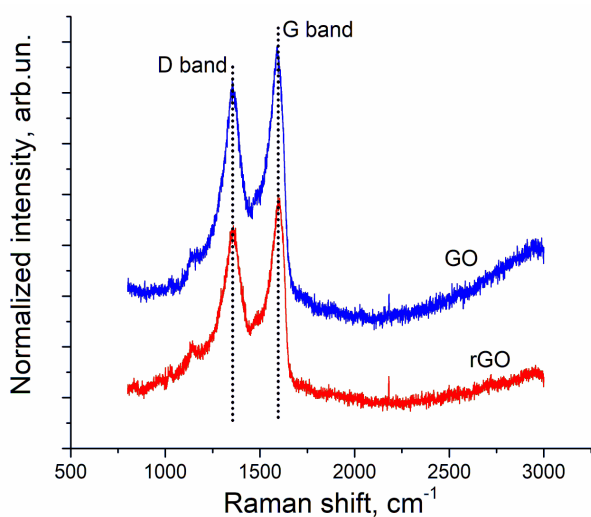


Fig. 4. Raman spectra of graphene oxide film before and after reduction.

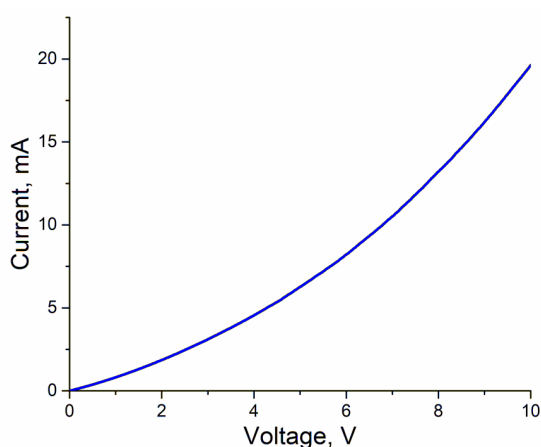


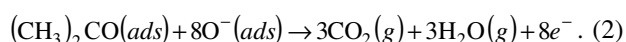
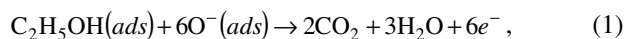
Fig. 5. *I-V* characteristic of a reduced graphene oxide film device (see Fig. 1).

applied voltage that can be associated with Schottky contact formation between Au and rGO.

Dynamic responses of the rGO film for ethanol, acetone, isopropyl, ammonia and water vapor are presented in Fig. 6. It can be seen all vapors under study (Fig. 6a-6e) provide the resistance increase in the rGO film. Additionally, the rGO film demonstrates the resistance responses ($\Delta R/R_0$), to isopropyl of about 4...5% (Fig. 6a), to ethanol about 5% (Fig. 6e), to ammonia about 15...18% (Fig. 6c) and to water about 25...30% in the first adsorption cycle (Fig. 6d). However, $\Delta R/R_0$ to acetone vapor is much lower, about 1...2% (Fig. 6b).

It should be noted that at room temperature adsorption of most molecules (ethanol, isopropyl, acetone, ammonia) do not reach saturation after 800 s, and desorption starts to appear. However, water vapor is in saturation at 200 s, and week desorption is observed (Fig. 6d). These facts suggest the adsorption/desorption difference between water and the molecules mentioned above. Probably, incorporation of water molecules into the interlayer regions of the multilayer rGO reduces electrical contacts between rGO flakes, hereby, increasing the resistance of the rGO film [18]. Desorption of interlayer water in GO film is observed at temperatures about 100 °C [13].

The sensing mechanism for organic vapors, namely: ethanol (C_2H_5OH), acetone ($(CH_3)_2CO$) and isopropyl (C_3H_7OH), is a complex process. Adsorption of organic vapors on rGO surface occurs through dissociation of the organic molecules to H^+ or OH^- ions to form many different intermediate states. The final reactions of ethanol and acetone with adsorbed oxygen species can be described in the following form [19]:



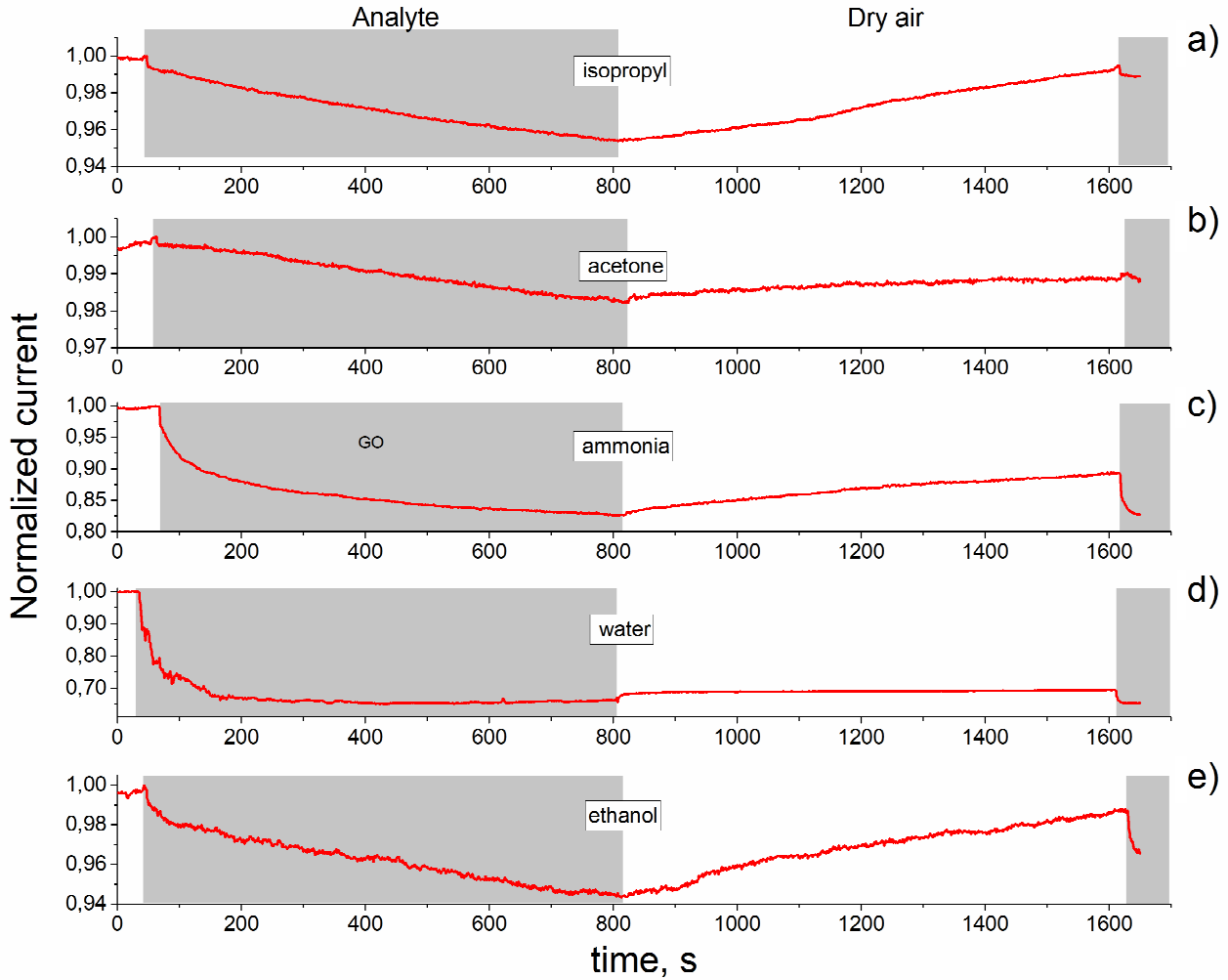
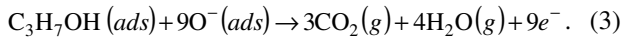
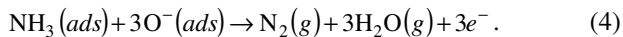


Fig. 6. Time dependence of normalized current (for 1 V applied voltage) for rGO samples, measured under (a) isopropyl, (b) acetone, (c) ammonia (d) water and (e) ethanol vapor.

Using the approach described in [19], the final reaction of isopropyl with adsorbed oxygen species can be also described by the following reaction:



The similar approach can be used to explain ammonia reaction on surface of rGO that contains adsorbed oxygen [20]:



The sensing mechanism of ethanol, acetone, isopropyl and ammonia is based on the fact that electrons from the chemical reactions mentioned above transfer to the graphene, which results in hole depletion of *p*-type graphene, thereby, increasing the resistance of the graphene film. If we compare the chemical reactions (1)-(4), we can conclude that for the reaction (4) we need only three charged oxygen on the graphene surface

whereas for ethanol – six ones. That is, the reaction (4) can perform faster than reactions (1)-(3). Indeed, resistance sensitivity of rGO film to ammonia is considerably higher than to ethanol and acetone.

4. Conclusions

The rGO films were formed using the ultrasonic spray coating method with low-temperature (230 °C) annealing in ambient atmosphere. It was shown that adsorption of such gases as ethanol, acetone, isopropyl, ammonia and water vapor results in increase of the resistance inherent to the rGO film. The water vapors demonstrate the highest sensitivity on the first step of adsorption, but a small desorption effect is observed. It is suggested that incorporation of water molecules into the interlayer regions of the multilayer rGO reduces electrical contacts between rGO flakes and increases of resistance of the rGO film. At room temperature, the maximum sensitivity for other studied gases is observed for ammonia which reaches 18%.

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