ELECTROCHEMICAL PROPERTIES OF GRAPHENE NANOSHEETS SYNTHESISED IN MICROWAVE PLASMA TORCH DISCHARGE

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Abstract

In the present work, 2-dimensional graphene nanosheets were synthesized, characterized and subsequently modified for gas sensor and electrochemical measurements. We used microwave plasma torch discharge (2.45 GHz) operating at atmospheric pressure conditions. Argon was used as the working gas and ethanol vapors, carried by argon, were used as precursor for carbon nanosheets synthesis. Characteristic high surface-to-volume ratio of prepared material, together with structural defects and various chemical groups on the surface serve as powerful combination for fast conductance changes upon adsorption. Therefore, prepared material consisting of graphene nanosheets was modified to perform different electrochemical measurements including gas sensing of ammonia and cyclic voltammetry characterization using several redox species. Our samples were analyzed by scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy to obtain an exact insight into the behavior of prepared sensors.

Keywords: Graphene, electrochemistry, sensor, microwave plasma

1. INTRODUCTION

Graphene [1] and other two-dimensional atomic crystals became the center piece of interest of both fundamental and applied science in last ten years. Graphene and graphene related materials combine high mechanical strength and flexibility, exceptional electronic and thermal conductivity, high carrier mobility and optical transparency [2]. Carbon nanomaterials can be used in wide range of applications such as hydrogen and energy storage [3], reinforcement of polymer composites [4], electronics [5], electrochemical devices [6], or gas sensors [7].

Graphene related materials can be used for ammonia detection, in chemi-resistor configuration, when material surface is exposed to ammonia containing gas. Ammonia is noxious and, in high concentrations, dangerous gas frequently found in the chemical and food industry. Commercial ammonia gas sensors are based on metal oxide semiconductors operating at high temperatures (200-300 °C) and require high input power. Graphene and graphene oxide [8] are therefore used as a new platform for development of new ammonia gas sensors.

In the biology and medical science, the gas-solid interface is often replaced by liquid-solid interaction. In such a case, electrochemical characterization becomes very important. Screen printed electrochemical sensors based on modified carbon electrodes represent suitable platform for fast and cheap environmental characterization. Among advantageous properties of carbon electrochemical electrodes belong a low residual current, a wide potential window, a relatively inert electrochemistry and electro-catalytic activity for a variety of redox reactions. Application of carbon nanomaterials as electrode material can promote an electron-transfer in electrochemical reactions [9] and increase several times the active electrode surface [10]. In this work electrochemical properties of plasma synthesized graphene nanosheets are studied in chemiresistive gas sensor and screen-printed electrochemical sensor configuration.

2. EXPERIMENTAL

2.1. Carbon material synthesis

The experimental set-up for graphene sheet synthesis was described in our previous publication [11] and allowed us to modify following experimental parameters: the microwave power P, the flow of working gas - argon - through inner channel Ar_c, the flow of carrying argon with ethanol vapors Ar_b and the method of mixing these two argon flows. As a result, we were able to adjust the deposition process to such an extent, that the produced material showed broad range of properties, as will be discussed in the following chapter. Deposition conditions of the two experiments discussed in this article are summarized in **Table 1**.

Table 1 Deposition conditions of experiments discussed in this work.

Experiment	Ar_c [sccm]	Ar_b [sccm]	Power [W]	Ethanol delivery
GV30	1000	700	280	outer channel
GV37	500	1400	210	inner channel

2.2. Material analysis

Samples were characterized by **Raman spectroscopy**, **X-ray photoelectron spectroscopy** (XPS) and **scanning electron microscopy**. XPS analysis was performed using ESCALAB 250Xi (Thermo Scientific, UK) X-ray photoelectron spectrometer equipped with a conventional hemispherical analyzer. Monochromatized Al K_α (1486.6 eV) X-ray source was focused into elliptical spot size at 650 µm. The pass energies were set to 50eV for wide-scan and 20eV for high-resolution elemental scans, respectively. These pass energies correspond to energy resolutions of 1.0 and 0.1 eV, respectively. Charge compensation was performed with a self-compensating device using field emitted low energy electrons. Measurements were performed under ultra-high vacuum 10^{-6} Pa and room temperature. Raman spectroscopy was carried out using HORIBA LabRAM HR Evolution system with 532 nm laser, using 100x objective and 25 % ND filter in the range from 1000 to 3200 cm^{-1}. Samples were imaged with TESCAN scanning electron microscope (SEM) MIRA3 with Schottky field emission electron gun equipped with secondary electron (SE) and back-scattered electron (BSE) detectors as well as Oxford Instruments EDX analyzer.

2.3. Electrochemical measurements

The **gas sensor** was characterized by measuring the sensor resistance under ammonia exposure. The measurements were performed using a setup with two gas channels: one for the carrier gas - synthetic air (Linde, Prague, Czech Republic), the second channel contained NH_3 diluted in N_2/synthetic air gas. The sensor was placed into the measuring chamber on the heater, operated by an Agilent U3606A DC power supply (Agilent, Santa Klara, California, USA). Its resistance was measured by the two-point technique between the gold electrodes by Keithley 2410 Source Meter (Keithley, Cleveland, OH, USA). A fixed bias voltage 1 V was applied. The sensor response was calculated as $\Delta R/R_0 = (R - R_0)/R_0$, where R and R_0 denote the sensor resistances in a gas mixture with NH_3 and in synthetic air, respectively. The ammonia concentration was varied from 100 ppm to 500 ppm. Each measurement cycle consisted of three 10 min cycles (for 100 ppm, 250 ppm and 500 ppm of analyte) alternated with three 10 min cycles in air flow. The total gas flow rate was kept constant at 500 sccm. All measurements were carried out at room temperature (25±2°C) and relative humidity 2-2.5 %.

Electrochemical measurements were performed with AUTOLAB PGSTAT 204 potentiostat/galvanostat controlled by Nova 1.10 software (Metrohm Autolab B.V., Netherlands). The electrodes were characterized by **cyclic voltammetry** using a three-electrode voltammetric cell with standard Ag/AgCl reference electrode (type 6.0729.100, Metrohm, Switzerland) and platinum auxiliary electrode (type 6.0343.000, Metrohm, Switzerland) in the equimolar solution of 2.5 mmol/L potassium ferro/ferricyanide in 0.1 mol/L KCl electrolyte solution (pH 5.8). The scan rate was 50 mV/s and potential range was from -1.0V to +1.0V for $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$. Two sets of differently modified working electrodes were prepared and subsequently treated by three different oxidative processes. The first set of working electrodes was prepared by screen-printing of commercial DuPont carbon paste for reference purposes. The second set was prepared from our graphene-based material in powder form, processed to paste form, screen-printed on a 625 μm thick corundum ceramics and thermally stabilized at 125°C.

3. RESULTS AND DISCUSSION

3.1. Structural and chemical characterization of synthesized graphene material

Since experimental conditions of our prepared samples slightly differed, as was mentioned previously, it was necessary to firstly investigate the chemical structure and morphology of our samples. XPS was used to characterize the elemental composition and Raman spectroscopy, as a versatile tool for graphene material structural analysis, to determine degree of defectivity and number of graphene layers. The XPS experimental curves were de-convoluted into a set of lines corresponding to the photoemission of electrons from atoms depending on their chemical surroundings. C1s peak gives the information on atomic concentration of carbon in different functional groups. In our measurements, the spectrum consisted of five peaks related to sp^2 hybridized carbon (~284.4 eV), sp^3 hybridized carbon (~285.1eV), carbon single bonded to oxygen C-O (~286.1eV), carbon double bonded to oxygen C=O (~287.2eV) and ester group O-C=O (~288.2eV) [12,13]. Elemental composition, relative atomic concentrations and positions are displayed in **Figure 1**. There is a significant difference between samples GV30 and GV37, concerning sp^2 and sp^3 components. Also, the concentration of carbon-oxygen functional groups differed, ~18 % and ~5% for GV30 and GV37, respectively. It must be mentioned, that minor contamination by iron spherical nanoparticles occurred in GV37 during synthesis. These nanoparticles originated from the nozzle and could not be avoided. **Figure 2** shows Raman spectroscopy of the samples. We can see an apparent difference between GV30 and GV37, namely in the relative intensity of D and 2D peaks to G peak. Greater D to G peak ratio is a sign of greater defectiveness [14], while increase in 2D to G peak intensity ratio corresponds to lower number of graphene layers [15]. The results of the analysis suggested, that sample GV37 showed lower defectiveness and presence of 3-4 graphene layers.

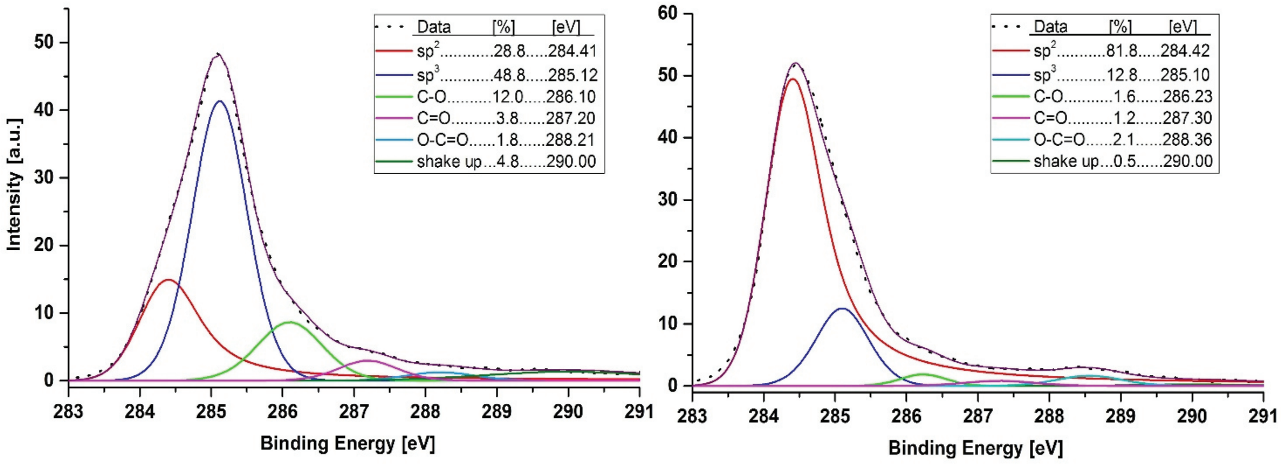

Figure 1 XPS spectroscopy of experiments GV30 (left) and GV37 (right)

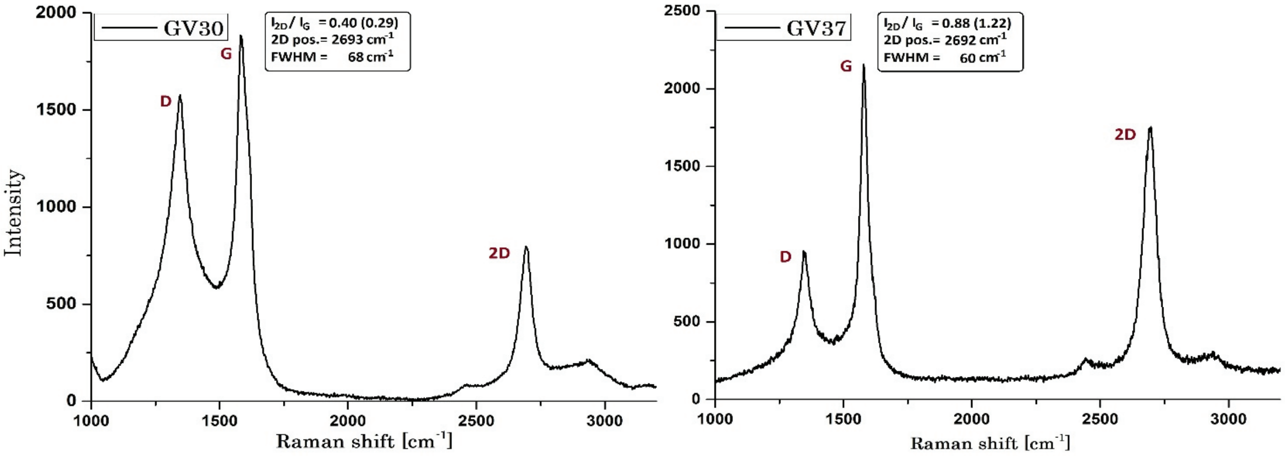

Figure 2 Raman spectroscopy of prepared material of experiments GV30 and GV37 together with important values of 2D/G peak intensity ratio, 2D peak position and FWHM of 2D peak

3.2. Electrochemical measurements

Prepared material was examined as gas sensors, by measuring the sensor resistance under ammonia exposure. Time-dependent characteristics, showed in **Figure 3**, consisted of two modes - steep rise of relative resistance caused by physisorption in the first stages and subsequent slower increase caused by chemisorption in the later stages of NH_3 exposure during a single cycle [7]. According to the sample analysis, there is significant difference between structural and elemental composition of the samples, sp^2/sp^3 concentration ratio (0.6 → 6.4) and amount of carbon-oxygen functional groups (18% → 5%). This difference is clearly visible in sensor response curve, where sample GV37 exhibited up to 10 times higher response. This difference can be attributed to the change in sample structure, which influenced NH_3 adsorption on carbon nanosheets surface. Also, 10-minute time interval was not sufficient for full recovery of active surface area from ammonia molecules. Recovery can be optimized by increase of sensor's temperature during the recovery phase.

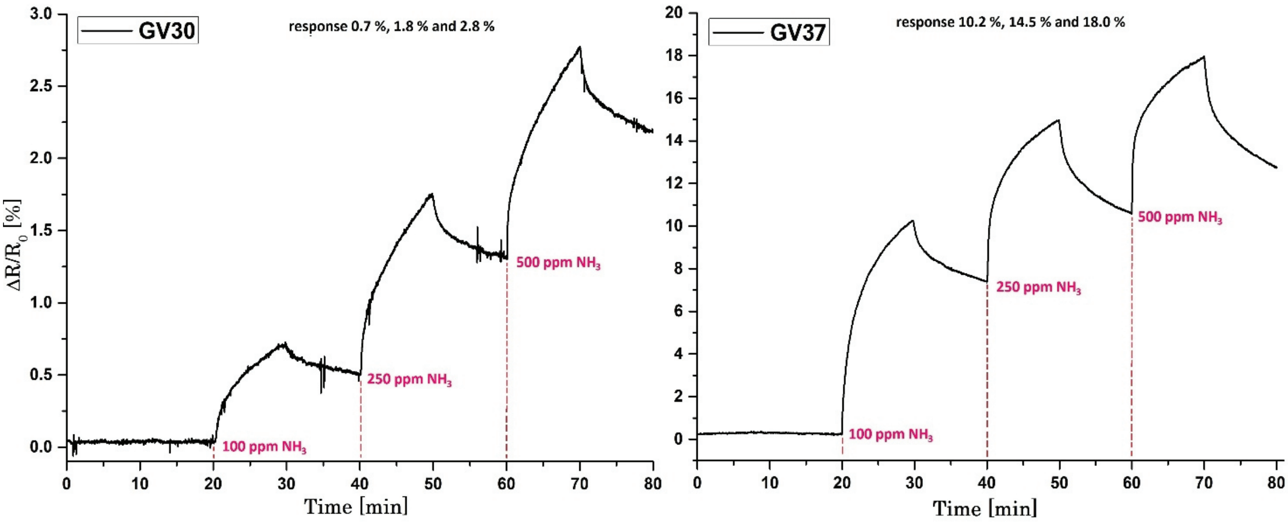

Figure 3 Response of graphene based gas sensors to NH_3 at three different concentrations. The response to 500 ppm of NH_3 is ~3% and ~18%, respectively, depending on the synthesized material

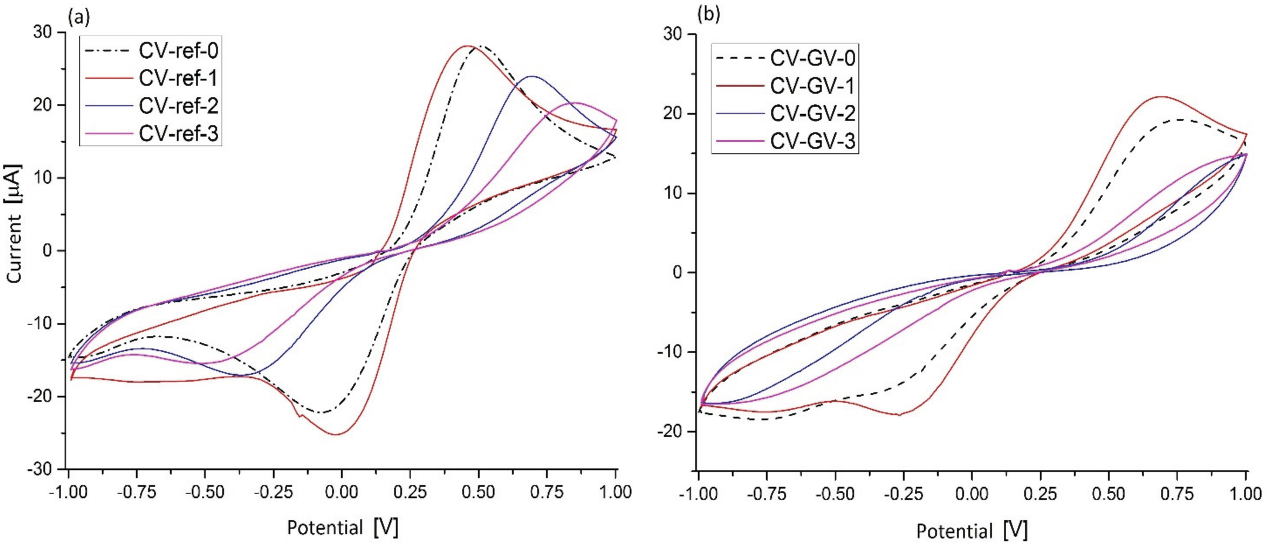

Figure 4 Cyclic voltammograms of (a) reference working electrode in comparison to (b) graphene-based working electrode

Cyclic voltammogram of both sets of working electrodes (WE) measured in the presence of 2.5 mmol/L potassium ferro/ferricyanide in 0.1mol/L KCl (pH 5.8) are given in **Figure 4 (a)** and **(b)**, representing reference WE (CV-ref) and the electrode made from graphene-based material (CV-GV). As mentioned in experimental chapter, different oxidative treatments of WE were applied to investigate change in sensor's response. These treatments are represented by numbers (0,1,2,3), which stands for: 0- as prepared, 1- plasma treated in low-pressure capacitively-coupled radio frequency discharge in Ar/O_2 gas mixture for 90 seconds, 2-annealed at 214°C in CVD oven and Ar/O_2 atmosphere for 5 minutes, 3- immersed in 5% water solution of H_2O_2 for 5 minutes. From voltammograms we could quantify reversibility as the peak-to-peak separation value and electrochemical response as the ratio of cathodic to anodic current. Best results were obtained with 90 second plasma treatment of working electrodes, where we were able to see an increase in reversibility (from 1.14V to 0.96V) and also, current response improved. Other applied treatment techniques, as showed in **Figure 4**, did not lead to improvement and resulted in low current and the change in peak-to-peak separation value was negligible. In comparison to the reference working electrode and longer time treated multi-wall carbon nanotube electrode, the current response was lower, but comparable to other types of electrodes. The results suggested that longer treatment time could lead to improvement in sensor performance.

4. CONCLUSION

Presented work covers synthesis of graphene nanosheets, surface and structural characterization of prepared material, modification and application as ammonia and electrochemical sensors. The sensor response considerably depended on material structure. This can be understood in terms of change in ratio sp^2/sp^3 hybridized carbon and content of carbon-oxygen functional groups, as showed by XPS, which led to increase of active surface area for NH_3 adsorption. Prepared electrochemical sensors showed comparable results to other carbon material-based electrodes and sensor characteristics could be improved by plasma treatment. This opens possibility to improve sensor performance by studying plasma treatment parameters and further enhance reversibility and current response of as prepared working electrode.

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