



## Synthesis of nanostructured conducting composite films based on reduced graphene oxide and o-phenylenediamine

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### ABSTRACT

The chemical interaction of reduced graphene oxide (RGO) and poly-o-phenylenediamine (PPD) was studied. A simple method was proposed for synthesis of thin flexible electroactive conducting films based on reduced graphene oxide and poly-o-phenylenediamine. Thus obtained films were characterized by means of cyclic voltammetry, electrochemical impedance, IR, Raman and XP spectroscopy.

### 1. Introduction

The sustained growth in the popularity of graphene continues for more than ten years. It began in 2005, when the group of Geim was the first to observe the quantum Hall effect at room temperature with a graphene specimen obtained by mechanical peeling of highly-oriented pyrolytic graphite [1]. The studies of graphene and its derivatives became an individual field of research, which is now dominating in the science of carbon nanomaterials, being in advance of carbon nanotubes and fullerenes.

In addition to the own unique properties such as two-dimensional (2D) structure, high conductivity, high specific surface area, chemical stability and some others, graphene is attractive as the basis (substrate, additive) in synthesis of the materials to be applicable in electrochemical power sources, sensors (including biosensors), sun cells, nanoelectronics, fuel cells, supercapacitors, and electrocatalysis [2–5].

The major problem in practical application of graphene is the difficulty of its commercial production. This problem has not been solved yet. Therefore, researchers paid attention to graphene-like materials based on graphene oxide and reduced graphene oxide, which consist of graphene nanosheets assembled in nanostacks with different number of oxygen-containing groups. These groups prevent aggregation of nanostacks and decrease electronic conductivity but provide good wettability with polar solvents and hence ionic conductivity. Available ways were found to synthesize graphene oxide by oxidation of pristine

graphite (Hummers method and modifications thereof [6,7]). GO may be reduced to RGO (reduced graphene oxide) either chemically (by means of hydrazine [8,9], ascorbic acid [10]), or by other means, for example, electrochemically [11,12]. Removal of oxygen-containing groups results in higher electroconductivity, but at the same time phase transitions occur because no oxygen-containing groups now prevents closer interaction of nanostacks, and the specific surface of material decreases in the course of oxide (GO) reduction.

GO is also applicable in synthesis of graphene composites with various organic and inorganic molecules that enables to obtain new carbon-containing materials with tailored properties.

It is interesting that virtually all the application fields of graphene and derivatives thereof are also attributable to another wide group of compounds, namely conducting polymers (CP). Conducting polymers in doped state can retain charge not only due to formation of electrical double layer with counter-ions but also as a result of Faradaic charge transfer (pseudocapacity). Thus the specific capacity of CP-containing electrodes is higher than the double layer capacity of pure carbon materials [13–16].

Conducting polymers themselves have a number of disadvantages, some of which are low strength and chemical instability in the course of long charge-discharge cycling. Therefore, composites of electroactive polymers with carbon materials and especially those with graphite-like nanomaterials are widely applied.

RGO-CP composites are often obtained in situ [13] by oxidative

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polymerization of monomer, for example, EDOT with ammonium persulfate in aqueous dispersion of RGO nanosheets [17].

But if GO rather than RGO is used as one of precursors, then the methods for synthesis of CP composites are similar in many respects to the methods of GO reduction.

Similarly to GO reduction, it is possible to synthesize RGO-CP composite electrochemically [18].

Another method for synthesis of RGO-CP composite is based on the fact that GO exhibits expressed oxidative properties.

As is known, most conducting and electroactive polymers are synthesized by oxidative polymerization of monomer. Such oxidizer may be GO, which is reduced to RGO. RGO composites with polypyrrole, polyaniline and polythiophene were synthesized by a similar method [19]. But in all three cases, the reaction was carried out upon heating.

In other cases, in addition to the oxidative properties of GO, microwave radiation was also applied. For example, in synthesis of GO-PPD composite [20]. On the other hand, it is known that GO can be reduced either by heating [21,22] or by means of UHF radiation [23] or without additional use of any reducer. Our prior studies showed that the synthesis of modified RGO-based materials may use GO rather than only RGO as the precursor, which will act to oxidize the monomer [24,25].

This paper describes a method for synthesis of a flexible film based on RGO and PPD as a new electroconducting composite material.

## 2. Experimental

### 2.1. Materials

This paper represents a comparative study of electrochemical behavior of GO-PPD nanocomposites in two forms: (i) as a coating applied on a current-conducting substrate and (ii) as a flexible film electrode.

In the first case, in order to apply GO films on a substrate, we used a GO (5 g/l) aqueous dispersion produced by GRAPHENEOX LLC.<sup>1</sup> A several-fold diluted aqueous dispersion of GO was applied on a substrate with a micropipette, evenly spread over the surface, and dried in air under a lamp. Such drying resulted in strong film coatings, which could not be separated from the substrate undamaged. As a substrate, we used glassy carbon plates having the dimensions of 0.5 x 2 cm. In order works, we also used glasses with sputtered SnO<sub>2</sub> and stainless steel plates [25,26].

In order to obtain a flexible electroactive carbon-containing material, we used ready GO films produced by Akko Lab<sup>2</sup> from graphene oxide synthesized according to the method of Hummers [6]. GO films were made by doctor blade by-layer application of GO aqueous suspension (concentration ca. 5 ÷ 6 g/l) on a smooth Teflon plate. Each application was followed by drying in air. Thus formed film was separated from the substrate and weighed. These films are characterized with a good anisotropy related to arrangement of GO scales primarily along the plane of application. By means of IR spectroscopy, XPS and C,H,N-analysis, we studied the qualitative and quantitative composition of the films: presence of C=O, –OH, C–OH, C(O)C groups, GO composition (wt.%) - C (58.0 ± 1.0), H (1.5 ± 0.5), O (39.0 ± 1.0), N (0); C/O molar ratio ca. 2/1. We used the films having the thickness of 4 μm.<sup>3</sup> Such films have sufficient strength be used, for example, as a working electrode of a symmetric electrochemical capacitor [26], Fig. 1.

O-phenylenediamine (OPD) monomer (Aldrich) was used as received.

In order to obtain a PPD composite, a GO film (free or applied on a substrate) was immersed in aqueous solution of 0.05 M OPD + 1 M

H<sub>2</sub>SO<sub>4</sub> for a given time and them rinsed and dried.

### 2.2. Measurements and instruments

The electrochemical studies were carried out with an IPC-compact potentiostat-galvanostat<sup>4</sup>. The measurements were carried out using a two-electrode circuit in a thin-layer cell with glassy carbon (GC) as the working electrode or a three-electrode circuit in a common electrochemical cell. In the thin-layer cells, the electrodes were separated with a membrane separator (Grays) for acid electrolytes based on polypropylene with silica gel with the thickness of 200 μm, which was wetted with 1 M H<sub>2</sub>SO<sub>4</sub> solution.

In the three-electrode cells, the electrode potential was measured against a saturated Ag/AgCl-electrode. The counter electrode was a Pt plate having the apparent dimensions of 1 x 1 cm. As the working electrode, we used conducting glass (CG) with sputtered SnO<sub>2</sub> or GC.

The impedance spectra were recorded using a Z-500-Pro impedance meter.<sup>5</sup> As to the geometry, the cell is a planar electrochemical capacitor [27], in which the capacity of the auxiliary electrode exceeds by 2,5–3 orders of magnitude the capacity of the working electrode. Such a scheme enables the working electrode impedance measuring without using the reference electrode. If the used electrodes have a relatively low conductivity (over 1 kHz), there may arise noises or induction abnormalities, which are most probably caused by a poor contact between the electrode and current collector. In our case, the current collector is a graphite foil impregnated by an inert polymer and has a negligibly small capacity as compared to that of the working electrode.

In order to record Raman spectra, we used a Bruker Senterra spectrometer. As the radiation source, we used a laser with emission wavelength (λ) of 532 nm and power of 0.5 mW<sup>6</sup>.

The conductivity of films was measured by the four-probe method using a combination of Keithly 236 and Keithly 2601 instruments. The measuring scheme is represented and describe with more details in [28].

The conductivity measurement error was within 5%.

IR spectra were recorded with a Perkin Elmer System 2000 FT IR spectrometer using a diffuse reflection unit.

## 3. Results and discussion

### 3.1. Chemical synthesis of RGO-PPD composite on substrate and further electrochemical study

Earlier we showed that GO contact with OPD aqueous acid solution results in a redox reaction, in which GO is partially reduced into RGO, while OPD is oxidized and polymerized to form RGO-PPD composite [24,25]. We propose to use Scheme 1 describing the processes independently taking place in a binary system consisting of GO nanostacks and OPD solution distributed between:

A – formation of hydrogen bonds with protons at nitrogen atoms in OPD (note that this interaction takes place in an acid medium that promotes to protonation),

B – interaction of aromatic rings lying in parallel planes from GO and OPD (π-π stacking),

C – start of redox reaction between GO and OPD and polymerization of OPD molecules attached to GO nanosheets,

D, E – formation of RGO-PPD composite (copolymer)

Fig. 2 shows CVA for GO films in 1 M H<sub>2</sub>SO<sub>4</sub> as applied on GC from diluted (1:10) GO aqueous dispersion and immersed for two days in

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<sup>5</sup> Produced by Elins (Chernogolovka)

<sup>6</sup> Measurements carried out with the facilities of the Collective User Center for Physical Research Methods at the Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences

<sup>1</sup> www.graphenox-ru.com

<sup>2</sup> http://www.akkolab.ru/en/

<sup>3</sup> Data of manufacturer

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