Structure, temperature and frequency dependent electrical conductivity of oxidized and reduced electrochemically exfoliated graphite

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ABSTRACT

The article presents the influence of reduction by hydrogen in statu nascendi and modification by hydrogen peroxide on the structure and electrical conductivity of electrochemically exfoliated graphite. It was confirmed that the electrochemical exfoliation can be used to produce oxidized nanographite with an average number of 25 graphene layers. The modified electrochemical exfoliated graphite and reduced electrochemical exfoliated graphite were characterized by high thermal stability, what was associated with removing of labile oxygen-containing groups. The presence of oxygen-containing groups was confirmed using Raman spectroscopy. Influence of chemical modification by hydrogen and hydrogen peroxide on the electrical conductivity was determined in wide frequency (0.1 Hz–10 kHz) and temperature range (−50 °C–100 °C). Material modified by hydrogen peroxide (0.29 mS/cm at 0 °C) had the lowest electrical conductivity. This can be associated with oxidation of unstable functional groups and was also confirmed by analysis of Raman spectra. The removal of oxygen-containing functional groups by hydrogen in statu nascendi resulted in a 1000-fold increase in the electrical conductivity compared to the electrochemical exfoliated graphite.

1. Introduction

Electrochemical exfoliation of graphite is one of the most popular methods used to synthesize graphene and graphite oxide. Two different types of exfoliation were recently presented: cathodic and anodic exfoliation, in which anions such as SO4 2− or cations such as Li + are intercalated into graphene layers [1]. For example, Parvez et al. synthesized high quality graphene with 1–6 layers in 0.1 M H2SO4 solution using graphite flakes as working electrodes and platinum wires as counter electrodes [2]. Number of layers in synthesized material can be controlled by type of electrolyte and voltage between the electrodes. Shinde et al. reported that in higher potentials, thicker and more fragmented graphene sheets can be obtained and shear assisted electrochemical process yields large, single, bilayer and trilayer graphene with low defect concentration [3]. What is more, Ambrosi and Pumera showed that, using LiClO4 as electrolyte allowed to obtain highly oxidized graphene with C/O ratio close to 4.0 [4]. Additionally, different electrodes can be used to produce exfoliated graphite: highly oriented pyrolytic graphite (HOPG), graphite foil, flakes, powder and polycrystalline graphite rods [5,6]. On the other hand, organic and nonorganic intercalation agents can be used for the synthesis of electrochemically exfoliated graphite. Most popular is sulfuric acid or sodium sulphate [7]. The ionic liquids such as tetrafluoroborate and 1-Butyl-1-methylpyrrolidinium can be also used as electrolytes [8]. What is more, electrochemical exfoliation of graphite is a process, in which we can obtain not only graphene oxide but also nanographite powder (electrochemically exfoliated graphite – EEG) with low number of graphene layers. The EEG is characterized by relatively high thermal stability and disordered structure. Additionally, presence of oxygen containing functional groups change the conductivity of carbon based materials, what has been already shown. For example, insulating properties of graphene oxide are caused by the presence of functional groups in the structure [9]. As a result of the reduction of GO, its conductivity increases, which is related to the removal of functional groups and in consequence to the restoration of π conjugated system [9,10]. Changes induced by the reduction of oxidized graphite based structures can be observed in Raman spectra. In Raman spectra for disordered graphite base nanostructures (such as graphene oxide, graphite oxide and graphite nanoplates) four characteristic bands (D, G, 2D and D+iG) can be observed [11–13]. Additionally, D*, D' and D” bands can appear in Raman spectra for oxidized and disordered carbon based materials, what was recently reported [14,15]. Interpretation of characteristic bands for oxidized, disordered graphite...
Comparison of structural parameters (average height of the crystallite $H$, interlayer distance $d$, number of layers $n$) of synthesized materials and graphite resulting from the XRD patterns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ [°]</th>
<th>$H$ [nm]</th>
<th>$d$ [Å]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>26.44</td>
<td>37.9</td>
<td>3.37</td>
<td>113</td>
</tr>
<tr>
<td>EEG</td>
<td>26.33</td>
<td>8.3</td>
<td>3.38</td>
<td>25</td>
</tr>
<tr>
<td>mEEG</td>
<td>26.42</td>
<td>22.6</td>
<td>3.37</td>
<td>67</td>
</tr>
<tr>
<td>rEEG</td>
<td>26.34</td>
<td>14.7</td>
<td>3.38</td>
<td>44</td>
</tr>
</tbody>
</table>

Based on the obtained data, the structures of the synthesized materials were considered to be of graphite type, with typical layer distances $d$ equal to 3.37-3.38 Å.

**3. Results and Discussion**

**3.1. Electrical Conductivity**

Electrical conductivity was also studied in this work. Additionally, disordered structure of synthesized materials was confirmed by analysis of collected Raman spectra and by fitting the experimental data to show the presence of additional bands: $D'$, $D''$ and $D'''$.

**4. Conclusion**

This article presents the results of spectroscopy studies of structure and electrical conductivity of electrochemically exfoliated graphite (EG), EEG modified by hydrogen peroxide and reduced by hydrogen in situ. The influence of temperature on the electrical conductivity of graphite based materials was determined. Frequency dependent electrical conductivity was also studied in this work. Additionally, disordered structure of synthesized materials was confirmed by analysis of collected Raman spectra and by fitting the experimental data to show the presence of additional bands: $D'$, $D''$ and $D'''$.