

## Synthesis of Few-layer Graphene Sheets via Chemical and Thermal Reduction of Graphite Oxide

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Few-layer graphene sheets were produced from graphite oxide (GO) chemical and thermal reduction. For the chemical reduction of GO as reducing agents were used hydrazine hydrate, hydroxylammonium chloride, sodium borohydride and sodium sulfite. The reduced material was characterized by elemental analysis, thermo-gravimetric analysis, scanning electron microscopy, X-ray diffraction, Fourier transform infrared and Raman spectroscopy. A comparison of the deoxygenation efficiency of graphene oxide suspensions by different method or reductants has been made, revealing that the highest degree of reduction was achieved by thermal reduction and using hydrazine hydrate and hydroxylammonium chloride as a reducing agents.

**Keywords:** Graphene, Graphite oxide, Reduction.

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### 1. INTRODUCTION

Graphene sheets are planar monolayers of  $sp^2$ -bonded carbon atoms tightly packed into a two-dimensional honeycomb lattice [1]. Due to the extraordinary electronic [2], thermal [3] and mechanical [4] properties, graphene has been emerging as a fascinating material in electronics, optoelectronics, capacitor, and sensing applications. Large-scale production of graphene materials has been considered as rate-limiting step in the evaluation of putative applications of graphene. In spite of producing high-quality graphene sheets, the low productivity of micromechanical cleavage method makes it unsuitable for largescale applications. Reduction of GO, is considered to be an efficient approach to produce graphene sheets on a large scale.

As far back as 1840 Schafhäütl [5] and then Marchand [6] at graphite treatment by various oxidising agents formation of light-coloured products observed. Brodie in 1855 reported about the product of yellow-brown color, resulting in the wetted mixture of graphite and sodium chlorate by fuming nitric acid, and called its "graphitic acid" [7]. Staudenmaier in 1898 for graphite oxide production used  $KClO_3$  in a mixture of the concentrated sulfuric and nitric acids [8]. Boehm and coll. have shown that the basal planes of the graphene sheets in graphite oxide are decorated mostly with epoxide and hydroxyl groups, in addition to carbonyl and carboxyl groups, which are located at the edges [9]. Has re-emerged to it an intense research interest due to GO role as a precursor for the effective and mass production of graphene-based materials [10].

Currently, GO is prepared mostly based on the method proposed by Hummers and Offeman [11] in 1958, where the oxidation of graphite to graphite oxide is accomplished by treating graphite with a water-free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate. Reduction of the GO can be parted on physical and chemical methods. To physi-

cal methods concern thermal [12], microwave [13] and photo- [14] reduction. For the chemical reduction of GO to graphene used different reducing agents such as hydrazine [10], sodium borohydride [15], dimethylhydrazine [16], ascorbic acid [17], hydroiodic acid [18] and many other.

In this work we used chemical and thermal reduction for obtaining few-layer graphene sheets. For the chemical reduction of GO as reducing agents were used hydrazine hydrate, hydroxylammonium chloride, sodium borohydride and sodium sulfite.

### 2. EXPERIMENTAL

#### 2.1 Synthesis and chemical reduction of GO

GO was prepared using a modified Hummers and Offeman's method from natural graphite [19]. After washing by water from sulfuric acid tracks the obtained suspension of GO have treated on a sonication bath, and then it was refluxed with one of reducing agents: hydrazine (RGOG), hydroxylamine (RGOA), sodium borohydride (RGOB) or sodium sulfite (RGOS). RGO products was isolated by filtration on glass funnel, washed copiously with water and ethanol, and dried in vacuum at 80 °C. The produced RGOG was heated at 900 °C in a flow of argon within 3 hours.

#### 2.2 Thermal reduction of GO

The dried GO was thermally expanded to synthesize thermally reduced graphene oxide (TRGO) by rapidly heating it in a tube furnace. After the tube furnace was preheated to 900 °C, about ten milligrams of dry GO was placed in a quartz tube, through which flowed gaseous argon, and then the tube was rapidly moved into the middle heating zone of the furnace. Herewith the flow of argon removed obtained TROG from the heating zone of the furnace. The produced TRGO was heated in other tube furnace at 900 °C in a flow of argon within 3 hours. After thermal reduction GO, weight loss was about 60 wt%.

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### 2.3 Material characterization

All the samples were characterized by powder X-ray diffraction (XRD) using a DRON UM-2 Diffractometer (CuK $\alpha$  radiation, 0.05 degree resolution), Fourier transform infrared (FTIR) spectroscopy using a Perkin-Elmer Spectrum 100 FTIR spectrometer (0.5 cm<sup>-1</sup> resolution). Raman spectra were measured using a Horiba Jobin Yvon T64000 Raman spectrometer with an argon laser of 514.5 nm. C, H, N and O content analysis of the samples were carried out using a «Vario Micro cube» Elementar GmbH CHNS/O analyzer. The thermal properties of the samples were characterized by thermogravimetry (TGA) using Simultaneous Thermogravimetry Analyzer NETZSCH STA 409 C Luxx, and all the measurements were carried out under argon gas over a temperature range of 30–1000 °C with a ramp rate of 10°C min<sup>-1</sup>. Scanning electron microscopy (SEM) images were obtained using a scanning electron microscope Zeiss LEO SUPRA 25. Surface area was measured using the BET method from nitrogen gas adsorption–desorption isotherms at 77 K by Surface Area Analyzer QUADRASORB SI (Quantachrome).

### 3. RESULTS AND DISCUSSION

In all the cases, a black solid precipitates at the end of the chemical reduction reaction. This may be attributed to the reduction of hydrophilic GO to hydrophobic

graphene sheets, resulting in increased incompatibility with polar solvents. Chemical deoxygenation is related to removal of the oxygen functionalities and partial restoration of the aromatic graphene network. SEM image of fluffy RGOGT and TRGO powders shows agglomeration of the exfoliated platelets of few-layer graphene sheets (Fig. 1).

Characterization of GO and RGO shown in Table 1. Elemental analyses show an increase in C/O atomic ratio in the reduced material compared to the initial GO (2.7). In the number of RGOB, RGOS, RGOA, RGOG, TRGO C/O ratio increases to 4.29, 7.30, 9.62, 16.13, 43.49, respectively. After heating RGOG at 900 °C in an argon flow (RGOGT) C/O ratio is increased to 45.45. All samples which were used in obtaining the nitrogen containing reduction agents (hydrazine or hydroxylamine) have nitrogen in its composition. It can be related to reaction of hydrazine and hydroxylamine with carbonyl groups of the GO (Wolff–Kishner-type reaction).

Surface area measurement of the reduced GO sheets via nitrogen gas absorption yielded a BET value from 470 to 620 m<sup>2</sup>/g. However, it is lower than the theoretical specific surface area for completely exfoliated and isolated graphene sheets (~2,620 m<sup>2</sup>/g [12]), potentially due to the agglomeration of the graphene oxide sheets upon reduction.

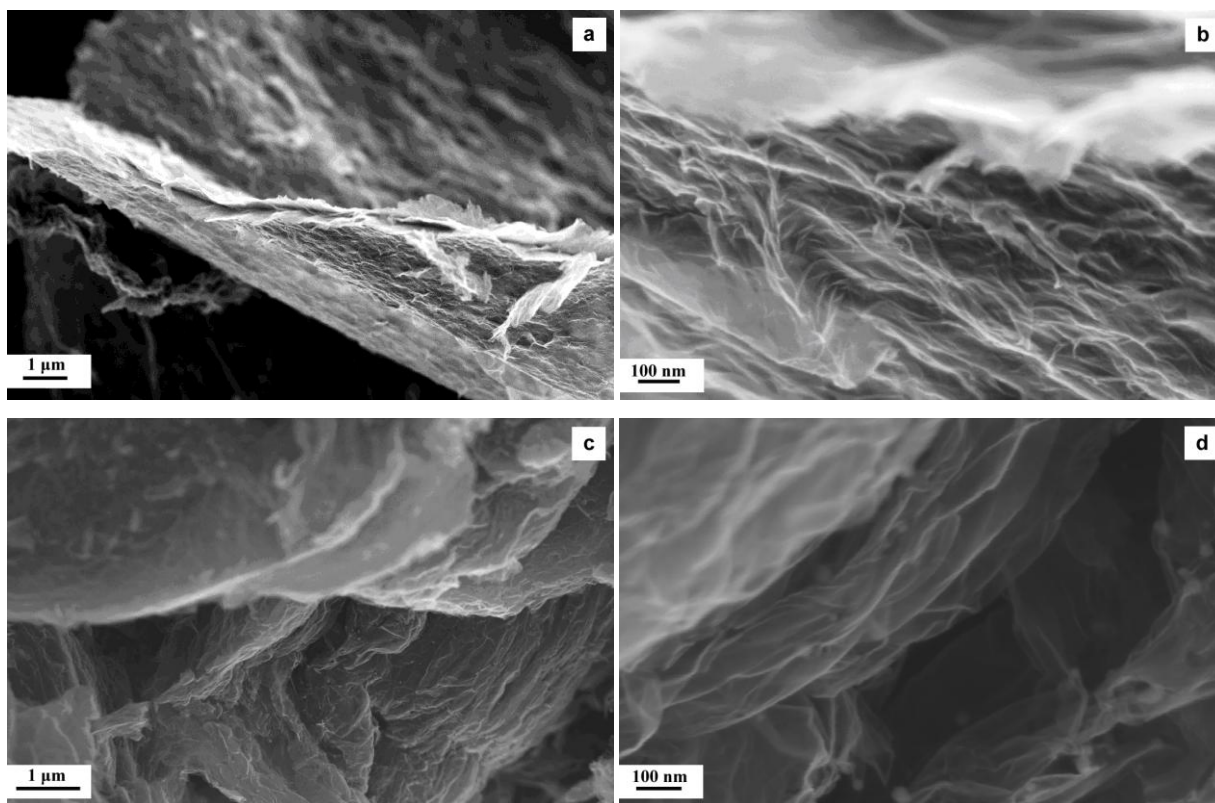
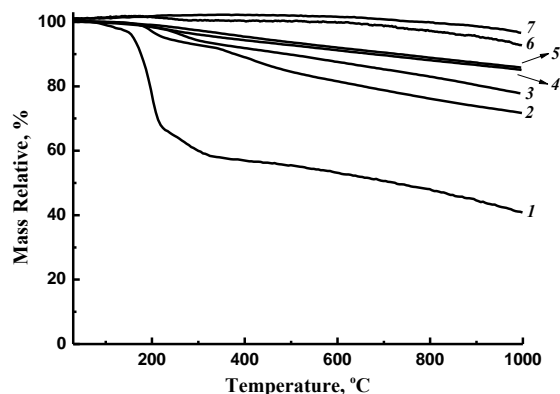


Fig. 1 – SEM images of RGOG (a), (b) and TRGO (c), (d)

**Table 1** – Characterization of GO and RGO

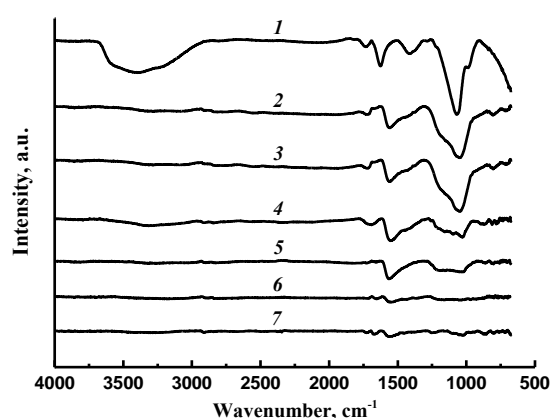
	Elemental analysis, wt%			C/O	Raman $I_D/I_G$	$S_{BET}$ , m <sup>2</sup> /g
	C	H	O			
GO	49.3	2.4	45.1	1.46	0.96	-
RGOB	60.8	1.7	18.9	4.29	1.10	560
RGOS	79.3	1.1	14.5	7.30	1.11	470
RGOA	81.8	1.1	11.3	9.62	1.26	490
RGOG	89.2	0.7	7.4	16.13	-	-
RGOGT	91.3	0.8	2.7	45.45	1.27	510
TRGO	90.8	1.0	2.9	43.49	1.26	620

Thermogravimetric analysis (Fig. 2) shows curve changes of specimens weight as variation of temperature under an argon flow. Weight loss (~3 wt%) of the GO up to 120 °C could be primarily due to evaporation of water molecules held in the samples. A comparatively small amount ( $\leq 1$  wt%) of weight loss in this temperature region indicates that RGO does not contain much water because of its hydrophobicity. While GO exhibited significant weight loss (~40 wt%), contributed by combination of evaporation of water and removal of labile oxygen functional groups) from 120 to 350 °C, the RGOGT and TRGO did not lose weight, suggesting that a significant amount of the water and labile oxygen groups were removed by the reduction. Other RGOs lost up to 9 wt% in this region, indicating that the degree of reduction of RGOs was reduced by hydrazine (without heating), hydroxylamine, sodium borohydride and sodium sulfite is lower than that of RGOGT and TRGO.

**Fig. 2** – TGA analysis of GO (1), RGOB (2), RGOS (3), RGOA (4), RGOG (5), TRGO (6) and RGOGT (7)

In the FTIR spectrum of GO (Fig. 3, curve 1), the absorption peaks at  $\sim 3420$  cm<sup>-1</sup> can be assigned to the O-H stretching vibrations in the water and hydroxyl groups in the GO; the C=O stretching vibrations in the carboxyl group at 1733 cm<sup>-1</sup>; the C=C ring stretching at 1624 cm<sup>-1</sup>; the O-H deformation from the hydroxyl groups attached to the aromatic graphene network at 1407 cm<sup>-1</sup>; the C-O (epoxy) stretching at 1068 cm<sup>-1</sup>, and the C-OH stretching at 1228 cm<sup>-1</sup>. In the FTIR spectrum of RGOB, RGOS, RGOA and RGOG (curve 2, 3, 4, 5, respectively) the intensity of the peaks for oxygen functional groups (1733, 1407, 1068 and 1228 cm<sup>-1</sup>) were decreased very much but did not disappear com-

pletely as is the case of RGOGT and TRGO (curve 6 and 7). The absorption peaks related to skeletal vibration of the aromatic rings were observed in all samples of RGO but the peak position shifted from 1624 to 1560 cm<sup>-1</sup> with respect to GO.

**Fig. 3** – FTIR spectra for GO (1), RGOB (2), RGOS (3), RGOA (4), RGOG (5), RGOGT (6) and TRGO (7)

The changes of structure from GO to RGO by chemical and thermal reduction are also reflected in the Raman spectroscopy. The Raman spectrum of the pristine graphite, as expected, displays a prominent G peak as the only feature at 1580 cm<sup>-1</sup>, corresponding to the first-order scattering of the E<sub>2g</sub> mode [15]. In the Raman spectrum of GO (Fig. 4, curve 1), the G band is broadened and shifted to 1603 cm<sup>-1</sup>. In addition there is a D band at 1354 cm<sup>-1</sup>, indicating the destruction of sp<sup>2</sup> character and the formation of defects in the sheets due to extensive oxidation. The Raman spectrum of the RGO (Fig. 4, curve 2-6) also contains both G and D bands (at 1592 and 1346 cm<sup>-1</sup>, respectively); however, with an increased D/G intensity ratio ( $I_D/I_G$ ) compared to that in GO (Table 1). Besides the highest value  $I_D/I_G$  achieved in the case of RGOA, RGOGT and TRGO. These observations further confirm the formation of new sp<sup>2</sup> graphitic domains after the reduction of GO.

It is known that pristine graphite exhibits a basal reflection (002) peak at  $2\theta = 26.6^\circ$  ( $d$ -spacing = 0.335 nm). Upon oxidation of pristine graphite (Fig. 5, curve 1) the 002 reflection peak shifts to the lower angle ( $2\theta = 10.8^\circ$ ,  $d$ -spacing = 0.822 nm). The increase in  $d$ -spacing is due to the intercalation of water molecules and the formation of oxygen-containing functional groups between the layers of the graphite. The XRD of RGOGT and

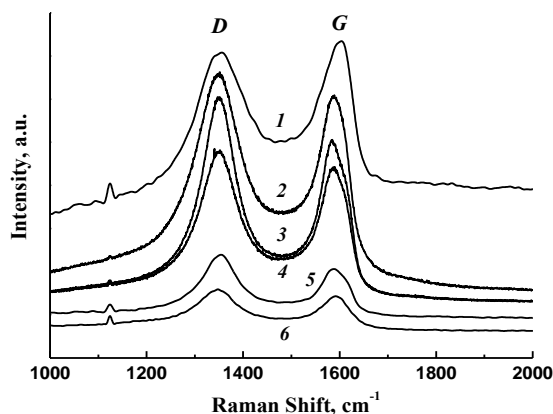


Fig. 4 – Raman spectra of GO (1), RGOB (2), RGOA (3), RGOS (4), RGOGT (5) and TRGO (6)

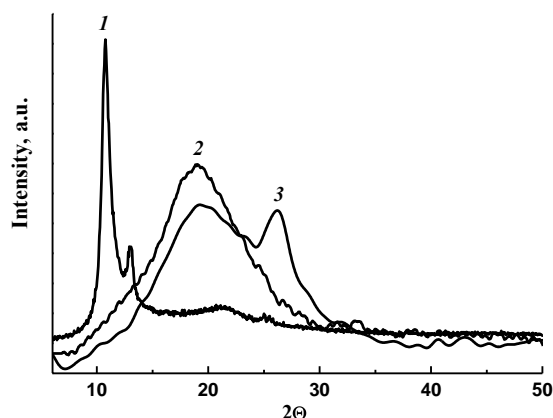


Fig. 5 – XRD pattern of GO (1), TRGO (2) and RGOGT (3)

TRGO show the appearance of a broad band centered at 19.3 and 19.0° (d-spacing = 0.470 and 0.462, respectively) corresponding to the stacking of graphene layers. The disappearance of reflection peak of graphite oxide and appearance of a broad band in the RGOGT and TRGO indicate the formation of few-layer graphene sheets. Along with a broad band at  $2\theta = 19.3^\circ$  in the RGOGT also was observed broad band at  $2\theta = 26.3^\circ$  (d-spacing = 0.339 nm). Thus in RGOGT along with few-layer graphene sheets there is also multi-layered graphite.

#### 4. CONCLUSION

The graphene sheets may find use in a variety of applications such as hydrogen storage and as an electrically conductive filler material in composites. Therefore the important problem is looking up of synthesis methods of graphene that can deliver large quantities of the material at low cost. This method may be the reduction of GO. In our work a comparison of the deoxygenation efficiency of graphene oxide suspensions by different reductants has been made, revealing that the highest degree of reduction was achieved using hydrazine hydrate and hydroxylammonium chloride. However, in the samples was observed the presence of nitrogen in their composition, which is not removed even after heating at 900 °C. On the other hand the use of thermal reduction of GO also there is a high degree of reduction, but weight loss has compounded about 60 wt%.

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