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Structural analysis of reduced graphene oxide by transmission electron microscopy

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Graphene has attracted scientific interest in recent years due to its unique properties. Reduced graphene oxide (RGO) was prepared by chemical oxidation of purified natural graphite to obtain graphite oxide then the material was exfoliated to reduced graphene nanosheets by ultrasonication and reduction process using sodium borohydride ($NaBH_4$). The transmission electron microscopy (TEM) investigations were performed on a TEM JEOL 2100 instrument at an accelerating voltage of 200 KV. The measurements of lattice-fringe spacing recorded in High Resolution Transmission Electron Microscopy (HRTEM) micrographs were made using digital image analysis of reciprocal space parameters. The analysis was carried out by the Digital Micrograph software. The obtained selected area electron diffraction (SAED) data show unambiguously that the sample RGO is different from Graphite 2H PDF 75-1621 and has typical interplanar distance d_{002} from 3.586 Å up to 4.016 Å. Lattice fringes obtained by HRTEM method also give additional information about interplanar distance d_{002} for RGO materials where the value is 3.850 Å. It was established that the main phase is RGO but some impurities of Graphite is also found.

Key words: Reduced Graphene Oxide, Structural analysis, TEM analysis.

INTRODUCTION

Reduced graphene oxide (RGO) is one of the exciting topics in many research fields especially in the field of nanotechnology during the last few years. It has different names such as chemically modified graphene, functionalized graphene, chemically converted graphene, or simply graphene. RGO has excellent electrical, thermal and mechanical properties [1, 2]. It is a very promising material for many applications, such as in the development of energy-storage capacitors [3–5], field-effect transistors [6], energy-related materials [7], sensors [8], heavy metal removal [9], drug delivery [10] and biomedical applications [11]. Generally graphene can be produced by top-down or bottom-up approaches. The common methods include mechanical or chemical exfoliation of graphite, epitaxial growth on SiC and chemical vapor deposition on metal surfaces [12–15]. These methods can produce graphene with a relatively perfect structure and excellent properties. The most popular method which considered a promising route to achieve mass production with low cost is the chemical method for producing graphene sheets from natural graphite [16]. Graphite is available in large quantities from natural sources and consists of a stack of flat graphene sheets held together by weak van der Waals forces [17]. By using highly oxidizing reagents these stack sheets of graphite exfoliated to be graphite oxide. The carbon atoms plane in graphite oxide is heavily decorated by oxygen-containing groups, which expand the interlayer distance and make the atomic-thick layers hydrophilic [18]. These oxidized layers can be exfoliated in water under moderate ultrasonication. Reduction of graphene oxide sheets using reductive reagents such as sodium borohydride [19, 20] removes the oxygen-containing groups to produce

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graphene-like sheets named reduced graphene oxide. There is a general consensus that it is very difficult to remove all the oxygen-containing groups from the graphene oxide layers by chemical reduction. Obviously, the electrical performance of RGO depends on the strength of the reducing agents and the amount of residual functional groups remaining after reduction. The conductivity of graphene oxide can be increased more than 4 orders of magnitude after reduction [21–22]. Generally, a detailed study of the atomic structure of RGO is considered as an important step to understand the properties of this material. The specific atomic scale features in chemically derived graphene monolayers has been already studied in details by Gomez-Navarro [23]. They contribute to the better understanding of effects of the defects which has to be taken into account for any comprehensive study of the RGO properties. There are a few papers concerning the structural analysis of RGO obtained by different methods such as chemical graphitization using a novel reducing agent system hydriodic acid with acetic acid [24], hot pressing [25], thermocatalytic decomposition of methane [26]. Up to now, there is no sufficient data on the structural analysis with lattice-fringe spacing measurements made by HRTEM of chemically derived RGO. This motivates our study.

Recently, we studied the thermal stability of RGO and RGO/SiO_2 nanocomposite prepared by sol-gel technique [20]. This paper is a continuation of our previous investigations and an attempt to present a structural analysis of chemically derived RGO using HRTEM and Powder X-ray Diffraction (XRD) is made.

EXPERIMENTAL

RGO nanosheets are obtained from purified natural graphite powder 99.9% (Alfa Aesar Co.) by different chemical treatments. First step comprises oxidation of graphite powder to graphite oxide by using a modified Hummer's method [27, 28]. In the next step, the graphite oxide is ultrasonicated in order to obtain graphene oxide which is subsequently reduced by using sodium borohydride 98% (Alfa Aesar Co.) to reduced graphene oxide (RGO). A detailed scheme describing each step of the synthesis method is given in our previous paper [20].

The phase formation was studied by XRD technique (Bruker D8 Advance, Cu Kα radiation) while the microstructure and morphology of the as-obtained products were observed by Scanning Electron Microscopy (SEM, Philips 525M). TEM investigations were performed on a JEOL JEM 2100 instrument at an accelerating voltage of 200 kV. The specimens were prepared by grinding and dispersing them in ethanol by ultrasonic treatment for 6 min. The suspensions were dripped on standard carbon/Cu grids. The measurements of lattice-fringe spacing recorded in HRTEM micrographs were made using digital image analysis of reciprocal space parameters. The analysis was carried out by the Digital Micrograph software.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of graphite, graphite oxide (GO) and reduced graphene oxide (RGO). Pristine graphite exhibits a basal reflection (002) sharp peak at 2θ = 26.37 degree corresponding to d spacing of 3.370 Å which is compatible with the literature data (JCPDS 75-2078, 3.347 Å). Upon oxidation of pristine graphite, the (002) reflection peak shifts to the lower angle at 2θ = 12.43 degree (d spacing = 7.110 Å) and a small peak remains closed to the position 2θ = 26.26 degree (d spacing = 3.390 Å). 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 [29]. In contrast to GO, all RGO have a broad peak centered at 2θ = 26.29 degree corresponding to d spacing of 3.380 Å which might be attributed to very thin RGO layers due to high degree of exfoliation. The close d-spacing of RGO to pristine graphite and disappearance of peak at 2θ = 12.43 degree indicate that the oxygen containing group of graphite oxide have been efficiently removed. There are published data which report that the graphene nanosheets are exfoliated into a monolayer or few-layers and it results in new lattice structure, which is significantly different from the pristine graphite flakes and graphite oxide

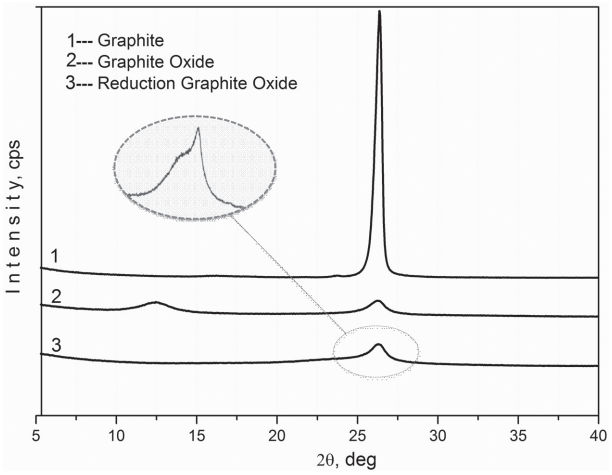

Fig. 1. XRD patterns of graphite, graphite oxide and reduced graphene oxide

sheets [30, 31]. As it is seen on Figure 1 a presence of amorphous halo at 2θ = 23−25 degree is observed. According to S. Huh [30] this is amorphous-like carbon which comprises many defects, folding structures, impurities, sp^1, sp^2, and sp^3 hybridization structures.

Figure 2 presents SEM image of RGO sheets which appeared as similar thin sheets randomly aggregated, with distinct edges, wrinkled surfaces, and folding. The mean sheets dimension was about 10 x 20 μm.

The TEM investigations at lower resolutions are shown on Figure 3 and the obtained data exhibit that RGO sheets consist of few layers (n < 6) stacked each other with less wrinkles and folding. Figure 4 represents a HRTEM micrograph of RGO sheets and it clearly shows the lattice fringes of graphene. This gives additional information about the interplanar distance d_{002} for RGO material which value is 3.850 Å. The crystallographic structure of the graphene sheets was characterized by SAED method. The previous studies mentioned that most of the graphene sheets exhibited a single set of hexagonal diffraction pattern with sharp and clear diffraction spots [32]. Figure 5 shows SAED pattern of reduced graphene oxide. The obtained SAED data show unambiguously that the sample RGO differs from Graphite 2H PDF 75-1621 and has typical interplanar distance d_{002} from 3.586 Å up to 4.016 Å for three different RGO samples. For comparison, the

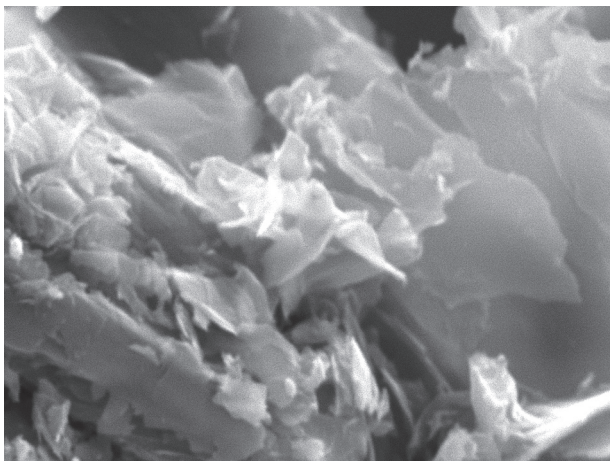

Fig. 2. SEM image of reduced graphene oxide sheets

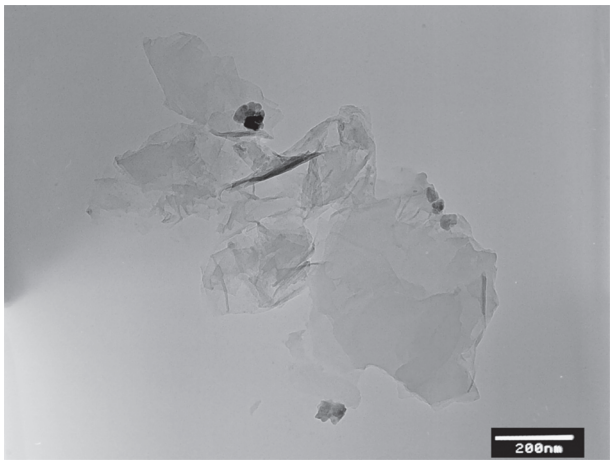

Fig. 3. TEM image of reduced graphene oxide sheets

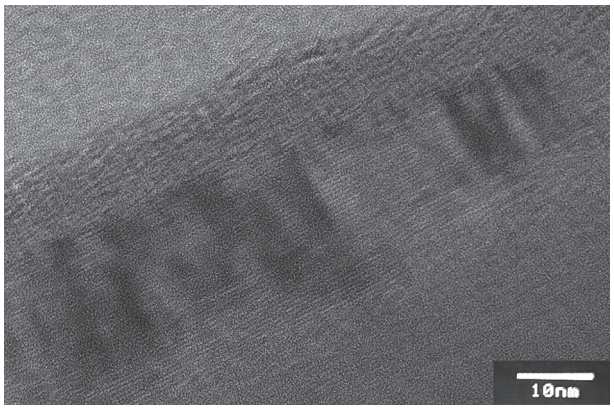

Fig. 4. HRTEM micrograph of reduced graphene oxide sheets

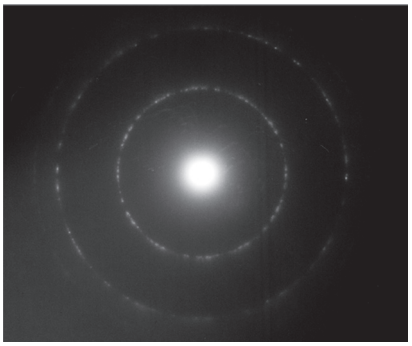

Fig. 5. SAED of reduced graphene oxide

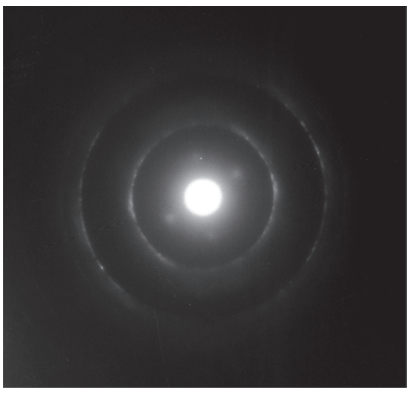

Fig. 6. SAED of graphite flaks

interplanar distance d_{002} of the graphite layers was measured to be about 3.400 Å as shown in Figure 6 and this data are in good accordance with the literature data [33].

CONCLUSIONS

The electron diffraction data established that the chemically derived RGO has interplanar distance d_{002} from 3.586 Å to 4.016 Å. Lattice fringes obtained by HRTEM method also give additional information about interplanar distance d_{002} where the value of RGO material was 3.850 Å.

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СТРУКТУРЕН АНАЛИЗ НА РЕДУЦИРАН ГРАФЕНОВ ОКСИД ЧРЕЗ ТРАНСМИСИОННА ЕЛЕКТРОННА МИКРОСКОПИЯ

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(Резюме)

През последните години графенът е интересен обект за научни изследвания преди всичко заради специфичните си свойства. В настоящата работа редуцираният графенов оксид (РГО) е синтезиран чрез химична реакция от графит и последваща ексфолиация до редуцирани графенови наноплоскости чрез ултразвуков метод и редукция чрез натриев борен хидирид ($NaBH_4$). Изследванията с трансмисионна електронна микроскопия (TEM) са извършени с апарат TEM JEOL 2100 и ускоряващо напрежение 200 kV. Структурните измервания са записани на HRTEM микрографии, използвайки дигитален анализ на реципрочните пространствени параметри. Анализът е направен чрез “Digital Micrograph” софтуер. Получените данни за избрани области на електрона дифракция (SAED) ясно показаха, че образецът РГО се различава от графита 2H PDF 75-1621 и има характерно междуплоскостно разстояние d_{002} от 3.586 Å до 4.016 Å. Допълнителната информация, получена чрез HRTEM метода, също показа, че междуплоскостното разстояние d_{002} за РГО има стойност 3.850 Å. Установено бе, че основната фаза е РГО, но малки замърсявания от графит също бяха регистрирани.