1. Introduction

Graphite is a well-known allotrope of carbon, which is constructed by stacked sheets of two-dimensional hexagonal carbon structures. A single sheet of these structure is known as graphene, which has been the research focus of many area in physics, chemistry and material sciences during recent years. This interest is due to the countless exciting properties of this material. Graphene has unique electronic properties: as the ballistic transport of electrons with a mobility which can be exceed 100,000 cm² V⁻¹ s⁻¹, and a quantum Hall effect (QHE) that can be measured at room temperature [1]. These properties make them suitable for many electronic applications. Beside that, graphene was found to have superial thermal conductivity: even 5,300 W mK⁻¹ [2]. Moreover, it has remarkable mechanical properties. Named as the strongest materials ever measured, with Young’s modulus of E = 1 TPa and with intrinsic strength of σ₁₆ = 130 GPa, [3] is indicated as an excellent reinforcements for ceramic materials.

Numerous methods have been investigated for preparation of graphene. The typical methods are the mechanical exfoliation of graphite, the different epitaxial growths and the various chemical fabrications. These methods include chemical reduction of graphite oxide using different reductants as hydrazine [4-6], solvothermal synthesis followed by sonication [7], liquid-phase exfoliation of graphite in organic solvents [8,9] and the method based on the intercalation of graphite followed by rapid thermal heating [9-15].

The preparation of tailored carbon nano-materials has been widely investigated, reveling the mechanical milling in a ball milling device as the most common method. The ball milling method is a type of mechanical exfoliation because the shear component of the applied stress is dominant [16]. Usually low-energy planetary and vibratory mills are used as ball milling equipments, however there are examples for high-energy nanoporous carbon production too [17-18]. In this study we have used high efficient attritor mill because it possibly encourages the intercalation or expansion of graphite. Hereby, we tried to combine two method (micromechanical and intercalation based exfoliation of graphite) to realize a simple and efficient process, which can lead us to the mass production of graphene-based materials.

2. Experimental Procedure

The starting materials used in experiments were as follows: 10 g of synthetic graphite powder (from Aldrich) and deionized water or ethanol (from Reanal)
Preparation and examination of multilayer graphene nanosheets by exfoliation of graphite in high efficient attritor mill without further purification. The graphite was milled in high efficient attritor mill (Union Process, type 01-HD/HDDM) equipped with zirconia discs and grinding media (diameter of 1 mm) in a 750 mL silicon nitride tank. The ball milling was run with different rotation speed (mild: 600 or intensive: 4000 rpm) until different times (5, 6 or 10 h) as revealed in Table 1.

There were detailed measurements with the sample milled until 10 h in presence of ethanol with 4000 rpm. In brief 10 g of the graphite was added into the tank with 70 g ethanol. During the milling another 70 g ethanol was added into the solution and there were sample collections every 2 hour. Finally the substance was dried and sieved with a filter with mesh size of 100 μm. Morphology and microstructure of the materials were studied by scanning electron microscope (Zeiss-SMT LEO 1540 XB and Jeol JSM-25-SIII). Phase compositions were determined by X-ray diffractometer (Bruker AXS D8).

3. Results and Discussion

For comparison the starting graphite material is shown in Fig. 1 with an average particle size of 10-20 μm. Samples with mild milling (600 rpm) are presented in Figs. 1b and 1c, while materials made by intensive milling (4000 rpm) are shown in Figs. 1d, 1e and 1f. First, we tried dry milling techniques (Figs. 1b and 1d). But milling in air atmosphere did not cause a major change in the microstructure of the starting material especially with mild milling (Fig. 1b). Differences can be seen in Fig. 1d (dry, intensive milling), some ~20 μm wide but too thick sheets were formed. Samples made by wet milling are presented in Figs. 1c, 1e, and 1f. Thin sheets can be observed in each micrographs. Thicker and greater layers can be noticed in the case of mild milling in water (Fig. 1c) rather than the one made by intensive milling (Fig. 1e). However in case of intensive milling in ethanol (Fig. 1f) a lighter structure of graphite layers, as well as the edges of sheets, can be observed well. As a result of exfoliation the graphite layers separated. The results proved that intensive milling in ethanol could be the most efficient way to separate the graphite layers.

X-ray diffraction pattern of the starting graphite material with the marked Miller indices can be seen in Fig. 2a. The XRD profiles of the samples milled by different dispersion media are presented in Figs. 2b and 2c. The decrease of intensity of (002), (004) and (006) peaks was observed in both cases, but especially in case of water (Figs. 2b, 2c). However the decrease of the intensity of (100) and (101) peaks was also observed (Fig. 2c). These two peaks are preserved only in case of ethanol but are characterised by low intensity values. These results implicate that the hexagonal crystal structure in plane is damaged, but is not disappeared completely. The position of the (002) and (100) peaks (2θ_{002} = 26.4° and 2θ_{100} = 42.4°) were used

Table 1. Different samples made by milling in attritor

| Samples | Dispersion media | Milling frequency (rpm) | Milling time (h) |
|---------|------------------|-------------------------|-----------------|
| MA      | air              | 600                     | 5               |
| MW      | water            | 600                     | 5               |
| IA      | air              | 4000                    | 5               |
| IW      | water            | 4000                    | 6               |
| IE2     | ethanol          | 4000                    | 2               |
| IE4     | ethanol          | 4000                    | 4               |
| IE6     | ethanol          | 4000                    | 6               |
| IE8     | ethanol          | 4000                    | 8               |
| IE10    | ethanol          | 4000                    | 10              |

Table 2. Crystalline parameter of different samples (IW – intensive milling in water, IE2 – intensive milling in ethanol after 2 h, IE4 – after 4 h, IE6 – after 6 h, IE8 – after 8 h, and IE10 – after 10 h of milling)

| Sample | Lc(nm) |
|--------|--------|
| graphite | 17.66 |
| IW     | 15.51  |
| IE2    | 17.18  |
| IE4    | 16.33  |
| IE6    | 15.07  |
| IE8    | 13.92  |
| IE10   | 13.76  |
to calculate the layer-to-layer (inter-plane) distance and the interatomic (in-plane) distance between neighbouring carbon atoms in graphene planes. The results are $d_{002} = 0.337$ nm and $d_{100} = 0.213$ nm using Bragg’s law ($n\lambda = 2d \sin(\theta)$). Similar X-ray spectrum and similar results were shown by Malasevic et al. [19]. Thus, there cannot be observed any shift of the angular position which can be implicated that the preparation techniques presented here could not exfoliate or separate the graphite layers completely. The average sticking height of crystallite ($L_c$) in the direction of c axis (the average thickness of one multilayer) was determined from (002) peak using Scherrer equation ($L_c = 0.9\lambda/\beta\cos(\theta)$), where $\lambda$ is the wavelength of the X-rays (1.5406), $\beta$ is the full width at half maximum (FWHM) of the peak in radians and $\theta$ is the Bragg angle. The results are showed in Table 2. Decrease of the $L_c$ value can be observed which means that thickness of sticked layers decreased. The X-ray results seem to be well corresponded with SEM micrographs, proving that intensive milling in ethanol could be the most efficient way to separate the graphite layers.

The graphite was milled by high efficient attritor mill for 10 hours in ethanol. Evolution of graphite morphology from starting graphite (Fig. 3a) to debonded graphite layers is shown by scanning micrographs. Exfoliation and separation of graphene multilayers can be observed. The transformation started from the beginning after 2 h milling (Fig. 3b) and is ended in 10 h (Fig. 3f). In the insert of Fig. 3b similar morphology to freestanding few layer graphene (FLG) it is shown, as found by Malasevic et al. [19]. After 8 h (Fig. 3e) the separation process was very efficient, dozen of separated graphene multilayers
Preparation and examination of multilayer graphene nanosheets by exfoliation of graphite in high efficient attritor mill can be seen. The multilayers were still sticking together after 6h of milling (Fig. 3d) however the distance between multilayers increases considerably after 8h of milling. The distance between multilayers was approximately 500 nm at this stage, but at the end of the milling process, distance between multilayers can exceed one micrometres as revealed in Fig. 3f.

It is revealed by XRD that the intensity of (002) peaks continually decreased except the case of 4h where the highest intensity was evolved (Fig. 4a). The lowest intensity was obtained after 10 hours of milling. The sharp (002) diffraction peak indicates a highly graphitic ordered structure of graphene multilayers in good agreement with Shao et al. [20]. The lowest intensity for lower graphite content can be attributed to the lower number of graphite layers in the produced multilayer graphene. However, the decrease of intensity can also be caused by lattice defects such as stacking disorder [14]. The (100) and (110) peaks presented the hexagonal order in plane were still preserved in XRD patterns but at low intensity values, as revealed in Fig. 4b. The decrease of intensity of these peaks was only detectable for the first 2 hours of milling. This result indicates that after a short milling time the main effect of the procedure was exfoliation of graphite on (001) planes. However, the further crystal reduction in plane can be neglected. Similar values were previously found by Antisari et al. [16]. The position of the (002) and (100) peaks (d-spacing) was not changed. The average sticking height of crystallite ($L_C$) was calculated from (002) peak using Scherrer equation. The results are showed in Table 2. Continuous decrease of the $L_C$ value can be observed, meaning that thickness of stucked layers decreased. The lowest value of $L_C$ (13.76 nm) can be seen after 10h milling. Similar values were previously calculated by Chen et al. [21]. Thus, the results in accordance with SEM micrographs proved that the 10 hours milling could be the most efficient procedure.

4. Conclusions

To conclude, it was demonstrated that the high efficient milling is a succesful tool for producing graphene multilayers. The results showed that intensive milling in ethanol is the enhanced way to separate the graphite layers, rather than in water or in air. The 10h milling showed the largest distance between separated adhering multilayers (can exceed 1 μm) proving the highest degree of exfoliation. The average thickness of graphene multilayers was $L_C = 13.76$ nm according to XRD measurement. This results implicates that the graphene multilayers were composed of approximately 40 graphene layers on average.

Acknowledgements

We would like to thank L. Illés for performing the SEM measurements and we are thankful to Z. E. Horváth for X-ray measurements. This work was supported by the OTKA Foundation (No. 76181 and 63609).
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