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MECHANICAL EXFOLIATION OF GRAPHITE TO GRAPHENE IN POLYVINYLPIRROLIDONE AQUEOUS SOLUTION

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In presented work we have reported that polyvinylpyrrolidone (PVP) is suitable organic solvent for mechanical exfoliation of crystalline graphite to graphene in aqueous solution through kitchen blender technique. Morphological, structural and optical, properties of graphene samples were characterized by scanning electron microscopy, Raman scattering and UV-Visible spectroscopy. Scanning electron microscopy demonstrates folded morphology of graphene flakes with ~4 nm thickness. Raman scattering was revealed the high-quality graphene with low levels of defects after the exfoliation process of graphite/PVP dispersions. The G band at ~1582 cm⁻¹ on Raman spectra is related with stretching vibrations of carbon atoms. The broadening of the G band is not observed, that indicated on absence of the basal plane defects in the graphene structure, which can be introduced during exfoliation by the kitchen blender. The ratio of the intensity of 2D and G bands equal to 1.66 ($I_{2D}/I_G > 1$) and the value of 2D band full width at half maximum is 79.88 cm⁻¹, indicated a few-layer graphene (FLG) structure. The defects quantity identified by the intensity ratio of the D and G bands, I_D/I_G is 0.18, significantly lower than that reported for graphene oxide with basal plane defects (> 1) and for sonication dispersed graphene (~0.6). The graphene dispersions were characterized by UV-Vis spectroscopy, minimum transmittance observed at around 270 nm is attributed to the $\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds in graphene. The optical transmittance minimum and the overall high transmittance decreasing values observed between 270 and 800 nm strongly suggest the presence of two-dimensional material in the dispersion, thus confirming the successful exfoliation of graphite to graphene by blending.

We demonstrate the simple and nontoxic method to product high-quality FLG sheets, free from defects, using a kitchen blender and eco-friendly polyvinylpyrrolidone as an organic exfoliant.

Keywords: crystalline graphite, few-layer graphene sheet, polyvinylpyrrolidone, scanning electron microscopy, Raman scattering, optical transmittance

INTRODUCTION

In recent years, graphene is one of the most investigating 2D-structured materials. Due to its unique electrical, mechanical, thermal properties, optical transmittance, graphene is prospective material to use in transparent conducting electrodes, solar cells, photodetectors, and other electronic devices [1, 2]. But graphene is still very expensive due to its difficulty for industrially scalable production. Therefore, it's necessary to develop simple and inexpensive method to obtain high-quality graphene. Mechanical exfoliation of graphite to graphene in organic solvents using a kitchen blender is simple and low cost method for synthesis of graphene. The shear-assisted liquid exfoliation method is done by using the shear force in a rotor-stator mixer allows one to produce

the graphene with low oxidative defects and high concentration [3]. In paper [4] the preparation was demonstrated of large, quantities of defect-free multilayered graphene using a kitchen blender or rotating-blade mixer in concentrated water/acetone mixtures for several hours. It was shown in [5] that shear-exfoliation of graphite to graphene can be industrially scalable method for producing graphene. The kitchen blender can generate enough shear force for delamination of the graphene flakes. However, without proper approach for the stabilization of the released nanosheets, graphene flakes will restack and the efficiency of exfoliation will be low [6, 7]. For successful exfoliation solvent plays a paramount role because the energy required to exfoliate graphene is balanced by the solvent-graphene interaction for solvents whose surface energies

match that of graphene [8]. Application of some organic solvents can achieve high-quality graphene dispersions. The organic amine-based solvents N-methyl pyrrolidone (NMP), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) have been proved to be good solvents for the exfoliation of graphene in previous experimental studies [9, 10] but some of them are toxic. To improve the dispersion of carbon nanotubes and their orientation in aqueous solutions, a polyvinylpyrrolidone (PVP) was used as dispersant in works [11, 12]. Polyvinylpyrrolidone (PVP), $(C_6H_9NO)_n$ is a water-soluble synthetic polymer with good solubility in water, strong complexing ability with both hydrophilic and hydrophobic substances, and nontoxic character [12]. It's used by a wide variety of industries, such as pharmaceutical, medicine, food, cosmetic, *etc.* Stabilization of few-layer graphene with the use of PVP in aqueous medium also was utilized in [13]. PVP has long chain molecules with lengths greater than the attraction range of the van der Waals force. Therefore, when PVP is adsorbed onto the surface of graphene sheets, it forms a coating with several tails extending from the surface that creates a repulsive force between graphene sheets, and the long molecule chains also prevent the particles from getting close enough to each other for the van der Waals force to be effective. This prevents re-aggregation of graphene sheets and thus supports a stable dispersion [13].

This work is devoted at the development of an efficient, safety and an inexpensive method for producing of the high-quality graphene in PVP aqueous solution through kitchen blender technique and the exploring of its properties.

EXPERIMENTAL DETAILS

Sample preparation. Crystalline graphite (GL-1 analogue, GOST 17022-81) was used as an initial material for the graphene production. Graphite powder consists of main particles (80 %) with developed form and sizes of 20–60 μm ; near 10 % of particles characterized by dimensions 8–20 μm and ~ 2 % of individual particles with a size of 4–8 μm ; at the same time, there are ~ 8 % large particles with a size of 70–90 μm . Graphene was synthesized using a kitchen blender and polyvinylpyrrolidone (PVP) K-30. The experimental method was adapted from the works [5, 6]. Graphite powder was dispersed in PVP aqueous solution with concentration of 3 mg/mL

to form 500 mL graphite dispersions (15 mg/ml). A “Tefal Perfectmix+” kitchen blender (model BL811D38) has been utilized for facile producing graphene dispersions. This kitchen blender was equipped with a six-blade 1200 W motor (rotational speed of 28 000 rpm) and 1.5 L glass jug.

The graphite/PVP aqueous solution was subjected to blending at 150 min in a kitchen blender at 8500–9000 rpm. Aliquots (10 mL) of the sample dispersions were taken every 10 min interval from blender flask. Before collecting the aliquots of graphene dispersions out of the kitchen blender, it was stopped during 30 min for separate large unexfoliated graphite particles, which fall down on the bottom of the flask. After mixing in blender during some time the liquid turns into a black color due to dispersing the graphite (Fig.1). This black graphene dispersion is stable for a long time at room temperature. Then, graphene dispersion were centrifuged (Micromed CM-3) for 5 min at 5000 rpm to remove unexfoliated graphite flakes. Graphene was studied as in a form of thin films deposited on substrates. The powders of graphene were obtained after centrifugation of dispersions and dried at 50–70 $^{\circ}\text{C}$ for further experiments. Graphene thin films were deposited through spraying technique over a glass and silicon substrates at 250 $^{\circ}\text{C}$. Before deposition process, the substrates were cleaned multiple times with distilled water, acetone and isopropanol.



Fig. 1. Scheme of the production of graphene in a kitchen blender using PVP aqueous solution

Characterization. The surface morphologies of the graphene were analyzed by field emission scanning electron microscopy (SEM). A scanning electron microscope (SEM), Tescan Mira 3 LMU SEM with a primary beam acceleration potential of 20 kV, was used to investigate the morphology of obtained graphene features. Additionally, installed energy dispersion X-ray (EDX) spectrometer accessories give us a possibility to determine the local elemental composition. The Raman and measurement of initial graphite powder and exfoliated few-layer graphene were carried in backscattering configuration using a Horiba Jobin-Yvon T64000 triple spectrometer with integrated Olympus BX41 microscope. The Raman spectra were excited with the help of radiation emitted by an Excelsior solid state laser with a wavelength of the 532 nm. The laser beam was focused on the sample surface into the spot of about 0.5 μm in diameter. The laser power on the sample surface was always kept below 2 mW to avoid laser-induced damage. The optical

transmittance of graphene dispersions was recorded using a spectrophotometer SF-2000 in the spectral range of the study from 0.2 to 1.1 μm .

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM). SEM images of graphene flakes after 150-min mechanical exfoliation in the PVP solution, centrifuged and dried are shown in Fig. 2 *a, b*. SEM analyses indicated that graphene flakes are ~ 4 nm thick. The images indicate that the exfoliated graphene has low layer thickness. It was found that the sheets have a folded or crumpled morphology. SEM analyses confirmed that the powders contain a large number of few-layer graphene (FLG) sheets. We have chosen the several stacked flakes (Fig. 2 *b*), to show that lateral exfoliation take place. Shear, turbulence, and collisions in the liquid result in a gentle lateral force-dominated way for graphite self-exfoliation through its lateral self-lubricating ability [6].

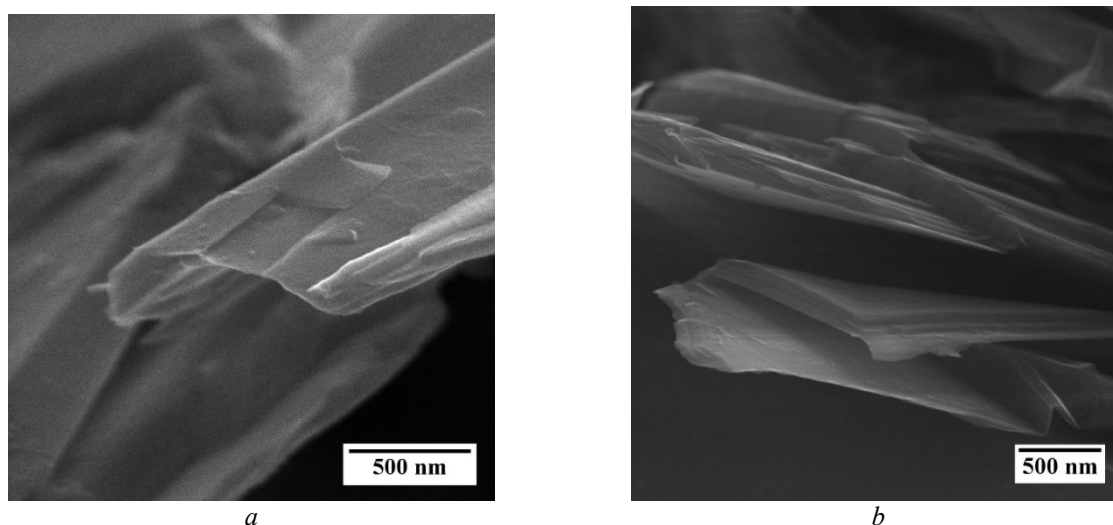


Fig. 2. SEM images of grapheme powders prepared after 150 min mechanical exfoliation in PVP solution

Raman spectroscopy. Quality of graphene was examined by Raman spectroscopy. Raman spectra of initial crystalline graphite GL-1 and exfoliated graphene are presented in Fig. 3. As known, graphene has four prominent Raman peaks at ~ 1350 , ~ 1580 , 1620 and ~ 2700 cm^{-1} , corresponding to the *D*, *G*, *D'* and *2D* bands, respectively [14]. *G* band (at 1582 cm^{-1}) is related to the doubly degenerate symmetry mode E_{2g} of the Brillouin zone center and is a

manifestation of stretching vibrations of all pairs of carbon atoms that are sp^2 -hybridized and are located in benzene rings. The appearance of *D* (at 1350 cm^{-1}) and *D'* (at 1620 cm^{-1}) bands indicated on defects in carbon structures. The *D* band is a manifestation of A_{1g} breathing mode at point *K* at the boundary of the Brillouin zone of sp^2 -hybridized carbon atoms in the benzene rings, it apparent, consistent with edge effects. The *G* and *2D* are the main graphene bands and

are always present, whereas the D band intensity depends on the quality of graphene and increases with the defect level of the material. The $2D$ band is the second-order two-phonon process of the D band and does not require defects to be activated and is always prominent even in the absence of the D band. The shape of the $2D$ band can be used to identify the number of graphene layers [15]. Single-layered graphene is characterized by the intense symmetric $2D$ band. If the number of graphene layers increases to two or more, the $2D$ band becomes a superposition of four bands with different intensities, but its shape is qualitatively different from the $2D$ mode shape of graphite, as shown in Fig. 3. The $2D$ band in the spectra is also broader than what is expected from single graphene sheets [16], suggesting that the dispersions consist of few-layer graphene. It has also been shown that the $2D$ maximum shifts to the lower value as the number of layers is reduced [15].

In the case of single-layer graphene, the Raman $2D$ band is symmetrical and is fitted with only one Lorentzian maximum which shows one π -electron valence band and π^* conduction band structure that indicate that one Raman scattering cycle is excited at the K and K' points [13]. It was found that quantitative indication of graphene layers number is the full width at half maximum (FWHM) value of the $2D$ band. The $2D$ FWHM for single graphene sheets is $\sim 30 \text{ cm}^{-1}$. The FWHM of graphene increases with an increase in the number of layers. In few-layer graphene the electronic bands split into dispersive configurations and, therefore, the more resonant phonons with different frequencies contribute to the widening and lower intensity of the $2D$ bands. The value of FWHM for the $2D$ band of FLG was found to be 79.88 cm^{-1} , which is in the range for literature data [15, 17].

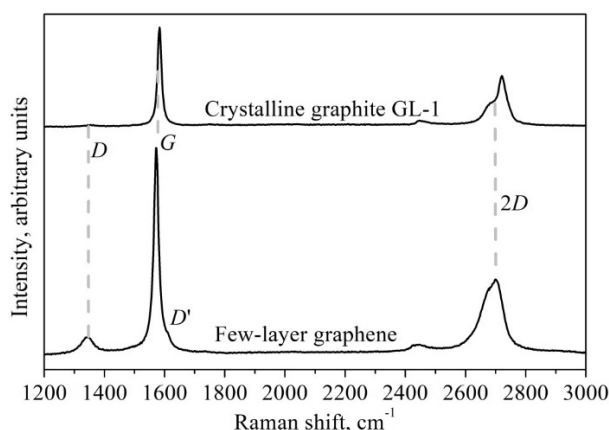


Fig. 3. Raman spectra of mechanical exfoliated graphene and crystalline graphite

The size diminishes of carbon crystallites reflect in the intensity ratio for the D and G bands grow. This is a consequence of the fact that a reduction of crystallite dimensions increases the number of surface defects, whereas the number of modes connected with stretching vibrations (they give a contribution to the G band) decreases, because the total number of atoms in crystallites becomes smaller [18]. The intensity of the D band is proportionate with the defect population in the sample. Defects apporportion into two major categories: basal plane defects (topological) and edge defects. Basal plane defects result in typically broadening the G band while the fragmentation effect cause to be

unavoidable existence of edge defects. If we see that the narrow G band does not become broadened, we can conclude that in samples, the edge defects are dominated instead of the basal plane defects. Therefore, Raman spectra indicate that absence of basal-plane defects which could have been introduced during exfoliation by the kitchen blender [3]. Curve 1 corresponds to initial casting graphite. In this spectrum, the D band has a low intensity and the D' band does not manifest itself at all, which testifies that initial graphite contains few defects. The intensity of the D band increases after the blundering process, indicating that exfoliation induces some defects into the graphene sheets.

The *D* band is narrow and less intense than the reported values for graphene oxide. This indicates that the defects induced by shear exfoliation are not basal plane defects. However, the introduction of the edge defects is inevitable because the size of the flakes is reduced by shearing and the total edge length increases with the reduction of flake sizes.

The quantity/content of defects can be identified by the intensity ratio of the *D* and *G* bands, I_D/I_G and equal 0.18, what is significantly lower than that reported for graphene oxide with basal plane defects (> 1) [19] and for sonication dispersed graphene (~ 0.6) [20].

The ratio of the intensity of *2D* peak and *G* peak (I_{2D}/I_G) allows evaluating the quality of graphene. In our case, this ratio equal to 1.66 ($I_{2D}/I_G > 1$), which demonstrates a FLG structure.

It worth to note that, for FLG sheets, the shape and position of this band is considerably different from that of graphite [21], as was observed in our spectra as well (curve 2).

UV-Vis spectroscopy. UV-Vis spectroscopy is a suitable method for indicating the quasi-two-dimensional materials in obtained dispersions. Graphene dispersions were characterized by UV-Vis spectroscopy in the wavelength range from 200 to 800 nm. Fig. 4 shows the optical transmittance loss of graphene dispersions

obtained by mechanical exfoliation technique from 10 to 150 min process. In the ultraviolet region a minimum transmittance observed at around 270 nm, that is attributed to the $\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds in graphene [22]. Also, as have been reported in the literature [6], the absorption peaks at near 270 nm corresponds no oxidation or defect content of the FLG flakes. The transmittance decreasing at 270 nm with mixing time indicates on the increasing content of graphene particles in the dispersion as a result of breaking down the thick graphene stacks into individual layers, thus increasing the final content of separated graphene sheets. The transmittance minimum and the overall high transmittance decreasing values observed between 270 and 800 nm strongly suggest the presence of two-dimensional material in the dispersion, thus confirming the successful exfoliation of graphite to graphene by blending [20]. These features are present in all the dispersion samples taken from process starting at 10 min.

The transmittances of graphene dispersions were measured at the wavelength of 660 nm at which the effects of PVP are negligible [13]. Increasing the time of mechanical exfoliation from 10 to 150 min, the optical transmittance at a wavelength 660 nm, decreased from 76 to 45 %.

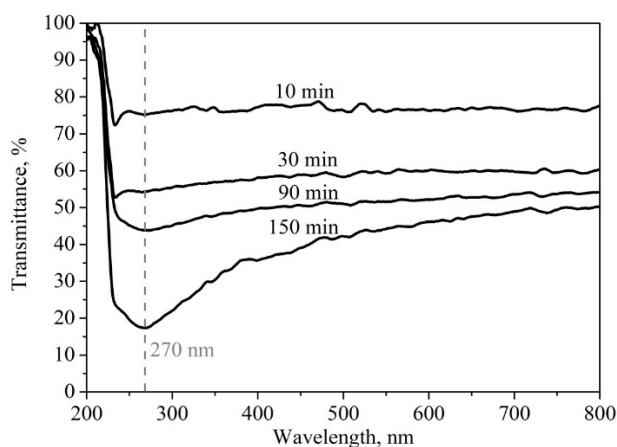


Fig. 4. UV-Vis spectra of the graphene/PVP dispersions after different time of mechanical exfoliation

CONCLUSIONS

In the present work, a facile, inexpensive and safe method has been reported for preparation of high-quality graphene by kitchen blender technique, suitable for large-scale production. Raman spectroscopy is an effective method for

monitoring the graphite transformation into graphene. Raman spectroscopy of dried powders indicated a few-layer graphene of very high quality and low levels of defects. By scanning electron microscopy the sheet-like morphology of the exfoliated graphene was detected. The graphene dispersion was characterized by

ultraviolet–visible (UV–Vis) spectra at the wavelength 660 nm. The results of UV-Vis spectrometry confirm the presence of graphene in the dispersion. It was found of that the optical transmittance of graphene dispersions is dependent on the time of exfoliation process.

The results obtained confirmed that graphite sheets have been successfully exfoliated after 150 min mechanical exfoliation in PVP aqueous media to give few layer graphene.

Механічне відлущування графіту до графену у водному розчині полівінілпіролідону

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У представленій роботі показано, що полівінілпіролідон (ПВП) є придатним органічним розчинником для механічного відлущування кристалічного графіту до графену у водному розчині з допомогою кухонного блендера. Морфологічні, структурні та оптичні властивості зразків графену охарактеризовано методами скануючої електронної мікроскопії, спектроскопії комбінаційного розсіювання світла (КРС) та оптичного пропускання. Скануюча електронна мікроскопія виявила складчасту морфологію графенових пластинок з товщиною ~4 нм. Результати дослідження зразків методом КРС, виявили високоякісний графен з низьким рівнем дефектів після процесу відлущування у водному розчині графіт/ПВП. Смуга G при ~1582 см⁻¹ на спектрах КРС пов'язана з валентними коливаннями атомів карбону. Розширення смуги G не спостерігається, що вказує на відсутність дефектів базальної площини в структурі графену, які можуть бути внесені під час розшарування графену шляхом механічного відлущування. Співвідношення інтенсивності 2D і G-смуг, що дорівнює 1.66 ($I_{2D}/I_G > 1$), значення повної ширини на половині максимуму 2D-смуги становить 79.88 см⁻¹, що вказує на структуру графену з невеликою кількістю шарів. Кількість дефектів характерних для базисної площини, ідентифікована за співвідношенням інтенсивності смуг D і G, I_D/I_G , становить 0.18, що значно нижче, ніж для оксиду графену (> 1) та диспергованого ультразвуком графену (~0.6). Водні дисперсії графену, досліджені за допомогою оптичного пропускання, характеризуються мінімумом пропускання при 270 нм, що пояснюється $\pi \rightarrow \pi^*$ переходами ароматичних зв'язків C–C у графені. Мінімум оптичного пропускання та загальні високі значення зменшення пропускання, що спостерігаються в діапазоні 270–800 нм, переконливо свідчать про наявність двовимірного матеріалу в дисперсії, таким чином підтверджуючи успішне розшарування графіту до графену в водному розчині ПВП.

Було показано простий та екологічно безпечний метод отримання високоякісного графену з використанням кухонного блендера і органічного розчинника полівінілпіролідону як нетоксичного диспергатора.

Ключові слова: кристалічний графіт, багатошаровий графеновий лист, полівінілпіролідон, скануюча електронна мікроскопія, комбінаційне розсіювання, оптичний коефіцієнт пропускання

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