Materials science communication

Production of graphene composite by direct graphite exfoliation with chitosan

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HIGHLIGHTS

- We report on direct graphite exfoliation with chitosan allowing to obtain graphene composite.
- We show that different chitosan solvents strongly influence properties of graphene flakes.
- Method gives graphene with low amount of defects.
- Electrical resistance of the chitosan-graphene composite can be tuned by factor of 2.

ARTICLE INFO

ABSTRACT

We propose a technique of direct exfoliation of graphite with chitosan (CS) allowing to obtain graphene flakes in a polymer matrix. During the process chitosan macromolecules were converted into soluble forms by the addition of the acetic acid (Ac) and the asparagine acid (Asp). The acid selection was proven to have an influence on the electrical and the morphological properties of graphene-chitosan composites. The electrical resistance is changing by factor 2 depending on used acid. Graphene sheets obtained in both processes were shown to have low amount of defects. The new composite may have wide range of potential applications, e.g. for conducting composites, optoelectronic, and in biological or medical research.

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1. Introduction

Among many methods of production of graphene, the direct graphite exfoliation in liquids seems to be very promising for obtaining good quality and highly conductive graphene composites on a large scale, which have been confirmed by a number of studies. There are many reports about obtaining graphene composites and almost all of them refers to reduced graphene oxide called simply graphene. In some cases composites are used to improve electrical parameters of electrically insulating polymers. For example cellulose acetate propionate (CAP) has a resistivity c.a. 10^{15} Ωcm [1], but with 10 wt. % of graphene in CAP matrix resistivity decreases to 10^6 Ωcm, which is enough for some applications. Composites of polystyrene with graphene (precisely reduced graphene oxide) are reaching the conductivity up to 1 S/m. This value is much more above an antistatic criterion [2]. For similar materials like PET/graphene composites (i.e. PET/rGO) the highest value of electrical conductivity was obtained for sample with 3 vol. % of graphene −2.11 S/m [3]. Some studies were made for composites consisted of graphite powder or graphite nanoplatelets [4–6]. Composite of HDPE containing 40 wt. % expanded graphite exhibits the electrical conductivity of 2.08 S/cm. The electrical conductivity of PMMA/nanographite film reached 10^{-3} S/cm at a graphite content of about 2.0 vol. %. Similar value of the conductivity was reached for polypropylene/xGnP (exfoliated graphite nanoplatelets) composite, but for much higher values of graphite content (c.a 30%). Recent studies on graphene/graphite/polymer composites shows that there are two main fabrication methods. The former one consists of polymer matrix and reduced graphene oxide and the latter of polymer matrix and graphite flakes. In both cases graphene/graphite is only additive for improving the electrical conductivity, mainly for antistatic applications.

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To the best of our knowledge, the studies of direct exfoliation of graphite in chitosan solutions has not been reported until now. So far, it has been studied as-prepared graphene oxide (GO) and reduced GO mixed with chitosan [7,8], with focus on the mechanical and the biological properties of these composites. Graphene oxide (GO) and reduced graphene oxide were mixed with chitosan in different ways to produce biocompatible materials. GO/chitosan was applied to load a water-insoluble anticancer drug-camptothecin [7]. Ibuprofen and 5-fluorouracil were loaded successfully to graphene oxide sheets functionalized with chitosan and the controlled release behaviour of these species was investigated [9]. Graphene/chitosan composites was investigated as biosensors, e.g. for glucose detection [10,11]. Such composite is also proved to be a material with enhanced mechanical strength. Preparation of graphene/chitosan films was described in [8]. The authors used graphene sheets previously prepared by direct-current arc-discharge method, which were dispersed in acetic acid solution by ultrasonication and then chitosan were dissolved in this graphene suspension.

Here we report a novel method of producing composites with low-defect graphene sheets by direct chemical exfoliation of graphite in chitosan solution (CS-Ac) and in chitosan derivative (CS-Asp). We propose obtaining composites with graphene in a single step processing, but the main component is exfoliated graphite and polymer is an additive one. Chitosan macromolecules were used as an exfoliating and stabilizing compound. Long chains of chitosan enable to separate graphene layers and prevent them from re-agglomeration after exfoliation of graphite. In acidic solutions the amino groups with free electron pair on nitrogen atom in CS are protonated creating positive charge ($-NH^{3+}$) and making CS a perfect cation exchanger. Protonated CS chains interact with atoms of graphene-electron donors. SC in acidic solution adsorbs on the surface of graphene sheets and acts as cationic surfactant. In addition, polymeric chains, because of the positively charged N atoms, repulse each other and facilitate distribution of graphene flakes in the solution [12]. Dipole moment in exfoliated graphite can occur on defects, especially on the damaged edges, analogously to carbon nanotubes. Thus, the electrostatic interaction plays a partial role in stabilization effect. Adsorption of the polymer on graphene flakes is supposed to have an entropy character, as it was calculated for non-functionalized carbon nanotubes [13].

The exfoliated graphene sheets are in the form of firmly stable suspensions. Asparagine and acetic acids act as a regulator of acidity and transform chitosan into its water-soluble forms. The acetic acid was selected as a typical, widely used in chitosan dissolution. The asparagine acid was selected as a biocompatible compound, which is an endogenic amino acid present in human body. Asparagine acid plays an important role mediating metabolic processes in neurons. The use of this acid in exfoliation of graphite is justified by a potential future medicine and other biological applications of as prepared graphene composites.

2. Materials and methods

Used materials: acid-washed graphite flakes, chitosan (low molecular weight), acetic acid (99.5%), L (+)- asparagine acid (98%), deionized water.

The method of preparation of graphene-chitosan composites solution consists of the following steps. In case of the first solution, acid-washed (intercalated) graphite flakes were inserted into a furnace and expanded at 1050 °C in ambient to obtain expanded graphite. The beaker with graphite was inserted to previously heated chamber and left for 2.5 min.

0.1 g of chitosan (of low molecular weight) was dissolved in 2.5% acetic acid solution. 0.1 g of graphite was added to the chitosan and

stirred on magnetic stirrer with simultaneous heating at 70 °C. The mixture was then sonicated for 1 h of an effective probe work with pulses 1 s on/1 s off, with an amplitude of 60%. The maximum power enable to reach on the used ultrasound system is 500 W. The beaker with material was placed in ice-water bath during the sonication. After this treatment a stable dispersion of carbon material was obtained. Graphene/chitosan composite prepared in this way was dried in freeze dryer. Second composite was prepared by dissolving 0.1 g of chitosan in 2.5×10^{-3} M asparagine acid solution with subsequent addition of 0.1 g of expanded graphite. Then, the solution was stirred, heated and sonicated in the same way as the first solution, and finally dried in freeze dryer. For structural characterization the graphene/chitosan composite was applied to a silica wafer or dried in freeze dryer. The schematic structure of graphene/chitosan composite is shown in Fig. 1.

The graphene/chitosan composite was applied to a silica wafer or dried in freeze dryer and the structural characterization was conducted: SEM, Raman and AFM measurements. Morphological properties were investigated with scanning electron microscopy (SEM), using Auriga CrossBeam Workstation (Carl Zeiss). AFM was acquired in tapping mode using Veeco Nanoman V microscope with Bruker MPP-11100-10 silica probe. The microstructure was characterized by Raman spectroscopy (Dilor XY-800 spectrometer), using 514 nm wavelength of an argon-ion laser with the low laser power of 1 mW. After drying, the composites were pressed under the pressure 136 bars to obtain thin (with the thickness of 0.03 mm) tablets to investigate electrical conductivity of the sample. Three silver electrodes were sputtered to the surface of tablet. Electrical resistance was measured using a transmission line method (TLM). Current-voltage characteristics were collected for each pair of electrodes. On this basis we calculated electrical resistance as well as contact resistance of electrodes. For FTIR measurements the samples were prepared in the following manner: chitosan dissolved in proper acid (acetic, asparagine) was dropped onto silica plate to form a layer. Then it was dried at 70 °C.

3. Results and discussion

The morphological properties of graphene-chitosan composites were first investigated using scanning electron microscopy. Graphene flakes obtained from CS-Ac solution create a compact structure (see Fig. 2A and C). Graphite flakes exfoliated in chitosan dissolved in CS-Asp solution are shown in Fig. 2B and D, where graphene sheets form not tightly agglomerated powder. This shows different morphology of graphene flakes obtained in these two ways.

In order to study the interactions between chitosan and used acids, and to assess the impact of the sonication on the polymers structure, we conducted standard FTIR measurements (see Fig. 3). The mechanism of dissolving chitosan in both acids is different. While acetic acid dissolves chitosan only by the protonation of the amine groups [14], asparagine acid additionally creates new covalent bonds with chitosan. FTIR spectra of chitosan dissolved in acetic acid (Fig. 3A) is typical for chitosan structure [15,16]. FTIR measurements indicate existing of stretching vibrations v_{as} and v_s (C–O–C) bonds at 1068 and 1036 cm^{-1}, respectively, which are the most intensive peaks for both samples. Chemical bindings associated with amine and amide groups are localized in the range from about 1650 cm^{-1} to 1100 cm^{-1}. They are clearly seen in Fig. 3A, where 1581 cm^{-1} corresponds to the vibrations of the N–H amine groups and 1648 is related to the vibrations of carbonyl bonds (C=O) of the amide group CONHR in secondary amide. Bending vibrations of methylene and methyl groups were also visible at 1375 cm^{-1} and 1411 cm^{-1}, respectively. The band at 1261 cm^{-1} is related to v(C–O–H) vibrations and peak at 1152 cm^{-1} is related to
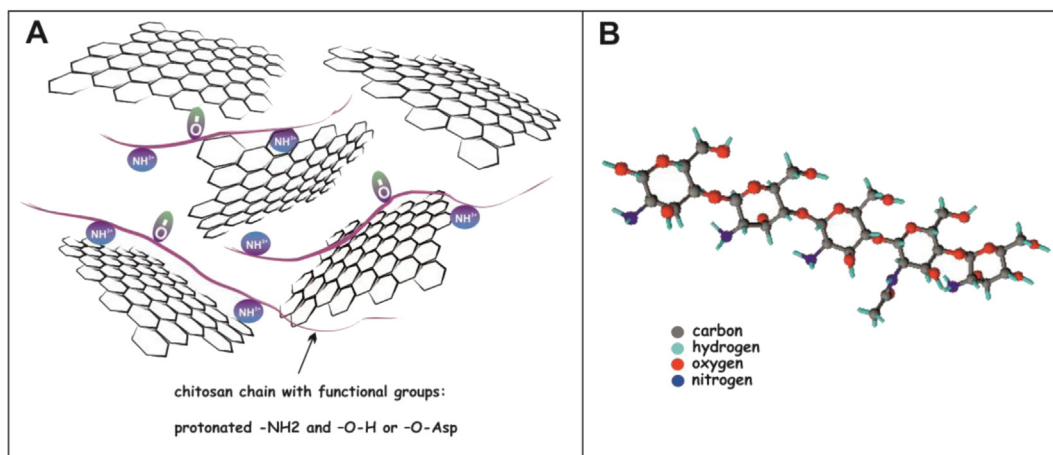
Fig. 1. A: The schematic structure of graphene/chitosan composite-chitosan chains between graphene sheets contain amine groups (protonated) and oxygen linked with proton or a part of asparagine acid molecules (while CS is dissolved in Asp)) and therefore O atom is symbolically signed with electron pair(O−). B: A fragment of chitosan chain.

asymmetric vibrations of CO in the oxygen bridge. An important peak is situated close to 900 cm^{-1}, which corresponds to β-(1,4)-glycosidic linkages, that occur for both samples and are due to the bond between rings in chitosan macromolecules [17].

On the spectra for CS-Asp (Fig. 3B) is the prominence peak at 1707 cm^{-1} that derived from v_{as} C=O ketone groups. For CS-Asp the intensity of bonds corresponding to amine and amide groups is very high, slightly less than C−O−C bond intensity, in contrast to CS dissolved in acetic acid. It is in agreement with asparagine acid structure, that contains one amine group per one molecule. The molecules are grafted to the chitosan by the carboxyl groups and replace hydroxyl groups, which are indirectly linked with cyclic part of the chitosan macromolecules.

For CS-Ac, the ratio of the intensity of C−O−C peak to the peaks in the range of 1650−1100 cm^{-1} increased after sonication and the peak of glycosidic bond at 900 cm^{-1} decreased (Fig. 3A). This suggests, that the macromolecules of chitosan dissolved in acetic

acid were partially fragmented during the sonication. We have measured the peak ratios for (C−O−C)/(peaks from 1650 to 1100 cm^{-1}) that is 0.51 before and 0.34 after sonication, for (β-(1,4)-glycosidic linkages)/(peaks from 1650 to 1100 cm^{-1}) that is 0.11 before and 0.07 after sonication. The peaks corresponding to C−O−C and β-(1,4)-glycosidic linkages are responsible for the stable structure of chitosan chains and are of the highest intensity before sonication. The decrease of the ratios for polymer after sonication leads to the conclusion, that this process destroys these linkages resulting in degradation of chitosan. The spectra for CS-Asp structure shows no differences after sonication, which indicates that there was no degradation nor fragmentation of the polymer during this process (Fig. 3B).

Further, the quality of graphene sheets was verified using Raman spectroscopy. Results of the Raman measurements on graphene flakes in CS-Ac and in CS-Asp are presented in Fig. 4A. Apart from the main G mode (1582 cm^{-1}) there is the 2D mode split into
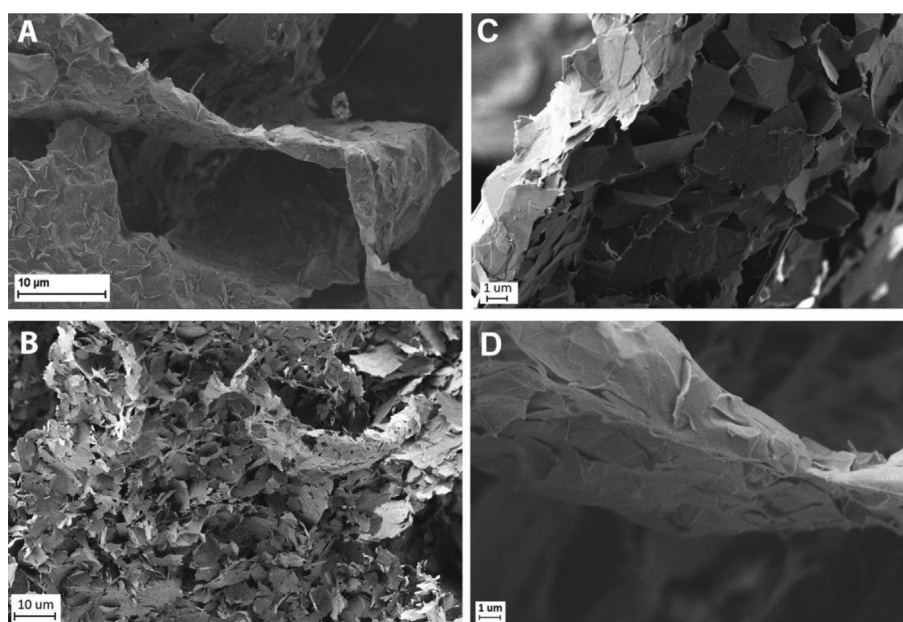

Fig. 2. A) and C) SEM image of graphite flakes exfoliated with chitosan dissolved in acetic acid and B) and D) SEM image of graphite flakes exfoliated with chitosan dissolved in asparagine acid. Both dried in freeze dryer.
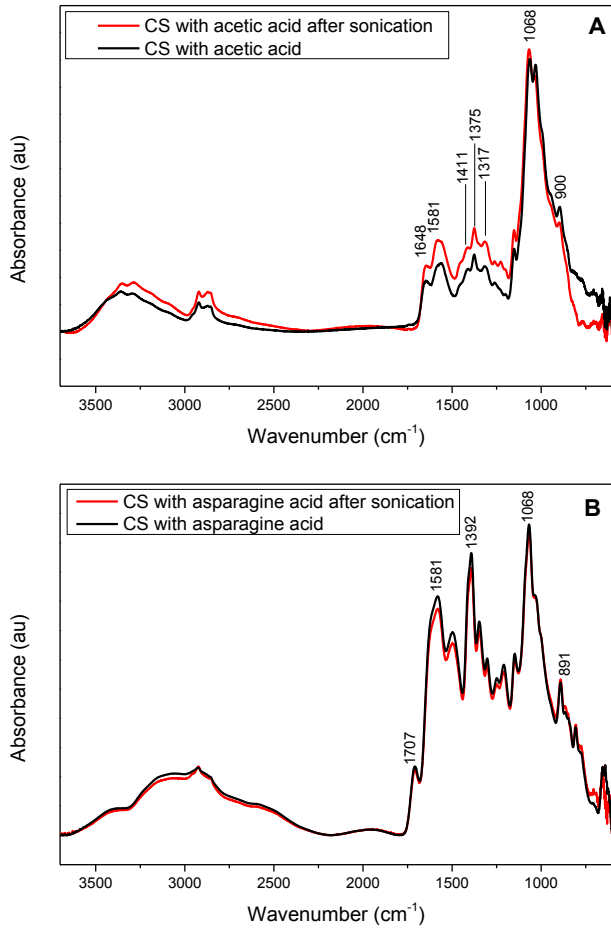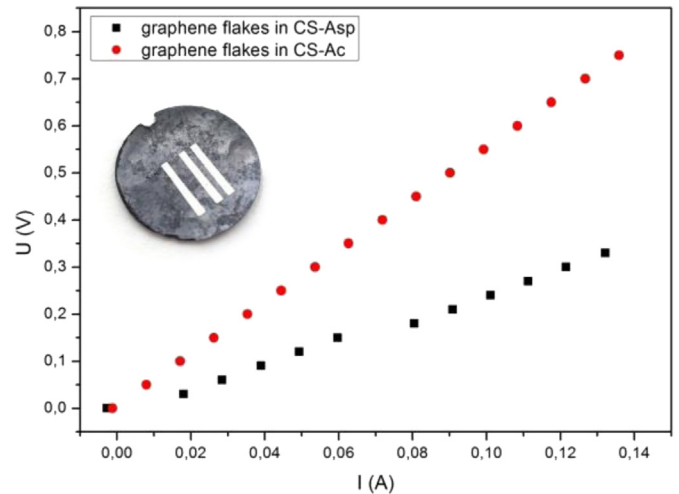
Fig. 5. Example of U(I) characterisation (in plane) of graphene/chitosan tablet determined for two most distant electrodes. Inside the graph the picture of the tablet is placed.

Fig. 3. A) FTIR spectra of chitosan in acetic acid solution and B) asparagine acid solution before and after the sonication.

two peaks ($\sim$2700 cm^{-1}). The shape and the intensity of the 2D suggest that studied flakes are few-layer structures rather than single-layer graphene. Importantly, the D peak remains low at any stage of the processing. To prove this we include the Raman spectra of the row material we used for further processing. For in CS-Ac/graphene sample a higher I$_G$/I$_{2D}$ and I$_G$/I$_D$ is observed suggesting that graphene sheets are less defected and thinner than in case of CS-Acs/graphene sample.

The few layer graphene structure of the composites is further confirmed by atomic force microscopy (AFM) measurements. Fig. 4B shows an example of few layer graphene flakes with $\sim$3 nm thickness. We note that samples dedicated for AFM study has been strongly diluted and dispersed on the sample surface in order to allow measurements of individual flakes.

Finally, we turn our attention to the electrical properties of the graphene composites. First, dried composite was pressed to obtain thin tablet and then three silver electrodes were sputtered on the surface of tablet (see inset of Fig. 5). The electrical resistance was measured by using two probe method from current–voltage characteristics (see Fig. 5) and a transmission line method [18]. The content of CS in graphene/chitosan tablets was 30%. Sample obtained by graphite exfoliation in CS-Asp solution has a sheet resistance about 0.03 Ω cm (3350 S/m). The second sample of graphene sheets obtained by the exfoliation with CS-Ac has 0.06 Ω cm (1580 S/m). Note that, these values are obtained for graphene composites, not for pristine graphene sheets. Importantly, the amount of chitosan in both samples were the same and the only variance was the used acid, which suggests the major role of the acids in the sheet resistance difference. Its indirect influence is to create changes in the structure of chitosan chains. Increased
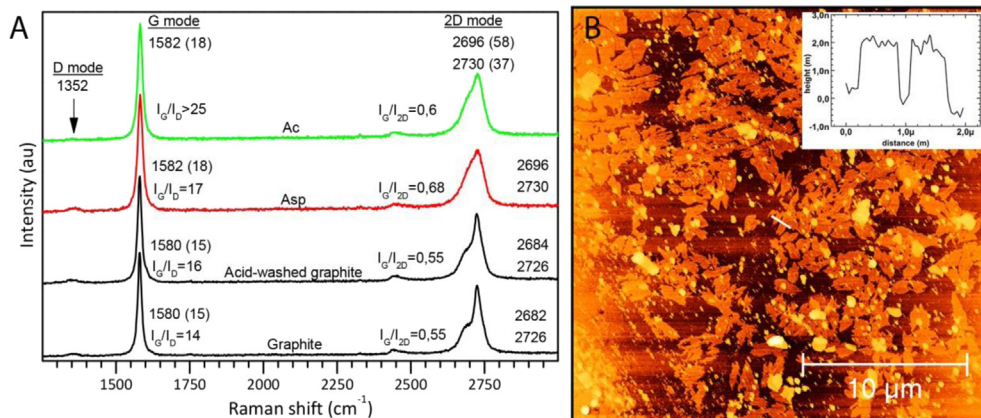

Fig. 4. A) Typical Raman spectra from graphene flakes prepared in CS-Ac solution (top) and in CS-Asp solution (bottom). The numbers in brackets indicate the FWHM (in cm) of the peaks. B) AFM image of few layer graphene sheets. The inset shows AFM cross-section with 2 nm thickness of CS-AS/graphene sample.

electrical conductivity of graphene obtained in chitosan-asparagine acid solution can be related to the fact, that not degraded, long chains of CS-Asp separate graphene flakes during graphite exfoliation better than CS-Ac molecules. The macromolecules of chitosan derivative (CS-Asp), that were not fragmented during sonication act as a binder soldering adjacent graphene sheets, and thus improving electrical contacts between them.

The yield of exfoliation of graphite was calculated to be about 25% in both samples, with months lasting stability.

4. Conclusions

In conclusion, we present the new method of graphite exfoliation using chitosan dissolved in acetic acid or in asparagine acid — compounds which are non-toxic and biocompatible. The method allows to obtain highly conductive graphene-chitosan composites with low defect graphene flakes. A slightly better parameters of graphene sheets are observed after exfoliation in CS-Ac solution: higher I_G/I_{2D} and higher I_G/I_D suggest graphene sheets are less defected and thinner. All in all, depending on application, if composite of better electrical conductivity is desired, graphene/CS-Asp will be more interesting and if non-defected graphene sheets is the main determinant, graphene/CS-Ac should be used.

The acid selection was proven to have significant influence on graphene/chitosan composites properties. The graphene sheets with chitosan solutions are in the form of stable water suspension which can be further processed into free-standing films, graphene paper and loose powder. This variety of forms makes the range of its potential application wider: from conducting composites to saturable absorbers in ultrafast lasers. Moreover, due to the biocompatibility of chitosan, obtained graphene composites may have potential applications in medicine and in biological research.

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