

## ACCEPTED MANUSCRIPT

This is an early electronic version of an as-received manuscript that has been accepted for publication in the Journal of the Serbian Chemical Society but has not yet been subjected to the editing process and publishing procedure applied by the JSCS Editorial Office.

Please cite this article as: N. Jović, M. P. Calatayud, B. Sanz, A. Montone, G. F. Goya, *J. Serb. Chem. Soc.* (2014), doi: 10.2298/JSC131121019J

This “raw” version of the manuscript is being provided to the authors and readers for their technical service. It must be stressed that the manuscript still has to be subjected to copyediting, typesetting, English grammar and syntax corrections, professional editing and authors’ review of the galley proof before it is published in its final form. Please note that during these publishing processes, many errors may emerge which could affect the final content of the manuscript and all legal disclaimers applied according to the policies of the Journal.



## ***Ex situ* integration of iron oxide nanoparticles onto the exfoliated expanded graphite flakes in water suspension**

NATAŠA JOVIĆ<sup>1\*</sup>, MARIA P. CALATAYUD<sup>2</sup>, BEATRIZ SANZ<sup>2</sup>, AMELIA MONTONE<sup>3</sup>  
and GERARDO F. GOYA<sup>2</sup>

<sup>1</sup>Vinča Institute of Nuclear Sciences (020), University of Belgrade, P.O. Box 522, 11000 Belgrade, Serbia, <sup>2</sup>Aragón Institute of Nanoscience and Department of Physics of Condensed Matter, University of Zaragoza, Zaragoza, Spain and <sup>3</sup>ENEA, Technical Unit Materials Technology, Research Centre of Casaccia, Via Anguillarese 301, 00123 Rome, Italy

(Received 21 November 2013, revised 3 March 2014)

**Abstract:** Hybrid structures composed of exfoliated expanded graphite (EG) and iron oxide nanocrystals have been produced by an *ex situ* process. The iron oxide nanoparticles coated with *meso*-2,3-dimercaptosuccinic acid (DMSA), or poly(acrylic) acid (PAA) were integrated onto the exfoliated EG flakes by mixing their aqueous suspensions at room temperature under support of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS). EG flakes have been used both, naked and functionalized with branched polyethylenimine (PEI). Complete integration of two constituents has been achieved and maintained stable for more than 12 months. No preferential spatial distribution of anchoring sites for attachment of iron oxide nanoparticles has been observed, regardless EG flakes have been used naked or functionalized with PEI molecules. The structural and physico-chemical characteristics of the exfoliated expanded graphite and its hybrids nanostructures has been investigated by SEM, TEM, FTIR and Raman techniques.

**Keywords:** nanocomposites; TEM; Raman spectroscopy.

### INTRODUCTION

Due to its outstanding properties, graphene is widely investigated material. Recently, decoration of graphene platelets with different nanoparticles (quantum dots<sup>1</sup>, magnetic<sup>2</sup>, or noble metal nanoparticles<sup>3–5</sup>) has attracted a great attention. Such graphene-based hybrid structures combine the properties of both constituents. Depending on a kind of used nanoparticles, multifunctional hybrids can express magnetic, optically-active, conducting, catalytic and electrochemically-active properties, simultaneously keeping good characteristics

---

\* Corresponding author. E-mail: natasaj@vinca.rs  
doi: 10.2298/JSC131121019J

of graphene sheets related to its stiffness, electrical conductivity and optical transparency. For example, graphene platelets decorated with transition metal or metal oxide nanoparticles have been shown as good candidates for anode material in lithium-ion batteries<sup>2,6</sup>, or as an effective adsorbent for removing organic molecules and heavy metal ions from waste water.<sup>7-9</sup> The properties of such hybrid structures are additionally dependent on the thickness of graphene platelets<sup>10</sup> (mono- or few-layer graphene), the structural defects inside the basal graphene plane, and/or the amount of oxygen-containing functional groups on a surface.<sup>11,12</sup> Another important factor in defining performances of hybrids can be related to interfacial adhesion between anchoring entities and graphene support.<sup>6</sup>

The production of graphene platelets as substrate for hybrid structures, are usually based on two basically different methods. The most common method to produce graphene platelets is the reduction of graphite oxide (GO) prepared from graphite according to the Hummers method.<sup>13</sup> However, this process involves the use of strong and harmful reducing reactants such as hydrazine. At the same time, the restacking of graphene sheets usually brings: *i*) corrugated sheets structure with damages in a basal plane and *ii*) the surface enriched with oxygen residues. Another method to produce graphene platelets is based on the exfoliation of graphite by means of ultrasonic treatment.<sup>14-16</sup>

A hybrid structure with graphene-based material as support matrix can be produced by distinguished synthesis procedures such as: thermal decomposition of metal salts in the presence of graphene or graphene oxide sheets<sup>17-19</sup>, hydrothermal/solvothermal method<sup>20,21</sup> or simple mixing of solutions.<sup>22</sup> Methods based on *in situ* approach (the synthesis of nanoparticles occurs in the presence of graphene or graphene oxide sheets) are commonly in use. Only few works followed an *ex situ* approach in which previously synthesized and functionalized nanoparticles are used to anchor the graphene sheets.<sup>8,22</sup> Table I presents an overview of the literature data with the emphases on the synthesis method, type of carbon-based matrix as support for nanoparticles, type of bonding between constituents and possible application of graphene-based hybrid structures. Graphene-based hybrids can be further used as a filler in various polymer matrix<sup>23,24</sup>, for production of thin films<sup>1</sup>, or as colloids.<sup>25</sup>

In the present work, we used an *ex situ* process to decorate exfoliated expanded graphite (EG) sheets with *meso*-2,3-dimercaptosuccinic acid (DMSA)- or poly(acrylic) acid (PAA)-coated iron oxide nanoparticles (IONs). The aqueous suspensions of two constituents were mixed at room temperature. This is the one of rare attempts where exfoliated expanded graphite<sup>27</sup> was used as the support instead of graphene sheets obtained by reduction of graphene oxide. The starting material is a commercially available expanded graphite which has been subjected to sonication in ethanol. The graphite flakes obtained in such way were used naked or grafted with PEI molecules and then were decorated with DMSA-

or PAA-coated IONs in the presence of 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS). The morphology and structural properties of exfoliated expanded graphite sheets and its hybrid structures with IONs were studied by SEM, TEM, FTIR and Raman techniques.

## EXPERIMENTAL

### *Materials*

A commercial, highly expanded graphite (supplied by Carbone Lorraine group, France), iron(III) acetylacetonate ( $\text{Fe}(\text{acac})_3$ , Aldrich,  $\geq 97\%$ ; IUPAC name: tris(acetylacetonato)iron (III)), iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), oleic acid (90% pure; IUPAC name: (9Z)-octadec-9-enoic acid), oleylamine (70% pure; IUPAC name: (Z)-Octa-9-decenylamine), 1,2-dodecandiol (90% pure), 1-octadecene, hexane, toluene (IUPAC name: methylbenzene), *meso*-2,3-dimercaptosuccinic acid (DMSA, Sigma Aldrich,  $\sim 98\%$  pure), poly(acrylic acid) (PAA, 450 kDa), dimethyl sulfoxide (DMSO, Sigma Aldrich, 99.9% pure), triethylamine (PANREAC, 99.5% pure), branched polyethylenimine (PEI, 25 kDa; IUPAC name: poly(iminoethylene)), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC; IUPAC name: 3-(ethyliminomethyleneamino)-*N,N*-dimethylpropan-1-amine)), *N*-hydroxysuccinimide (NHS, Fluka,  $>97\%$ ; IUPAC name: 1-hydroxy-2,5-pyrrolidinedione), absolute ethanol, potassium nitrate ( $\text{KNO}_3$ ), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were used as purchased.

### *Exfoliated expanded graphite (EG) flakes and its surface modified nanosheets (PEI-EG)*

0.2 g of commercial expanded graphite (EG) in 50 ml of absolute ethanol was placed into an ultrasonic bath for 10 h. A certain amount of such obtained exfoliated EG flakes in absolute ethanol (concentration  $\sim 4$  mg/ml) were mixed with branched polyethylenimine (PEI, 25 kDa), previously dissolved in a mixture of milli-Q-water and dimethyl sulfoxide (DMSO) (1:4, v/v). The mass ratio of EG flake and PEI was 10:1. The mixture was agitated for two days in a rotatory mixer at room temperature. After mixing and rinsing with water, the surface-modified EG flakes were dispersed in milli-Q-water. The suspension of EG flakes we labeled as PEI-EG *aq.* (concentration  $\sim 1$  mg of EG per ml of  $\text{H}_2\text{O}$ ). For the sake of comparison, a suspension of EG flakes in absolute ethanol was only rinsed several times with milli-Q-water and finally redispersed in water (naked EG flakes).

### *Synthesis and surface modification of iron oxide nanocrystals*

Two types of iron oxide nanocrystals (IONs) were used to decorate exfoliated expanded graphite flakes. One type of IONs were produced by thermal decomposition of iron(III) acetylacetonate salt in the presence of oleic acid and oleylamine in organic solvent.<sup>28</sup> Second type of IONs was synthesized directly through an oxidative hydrolysis method.

### *Synthesis of iron oxide nanocrystals (IONs) by the thermal decomposition method and its surface modification by DMSA*

The iron oxide nanocrystals were synthesized by the well studied thermal decomposition method, starting from iron(III) acetylacetonate ( $\text{Fe}(\text{acac})_3$ ).<sup>28</sup> In brief, 2.825 g of  $\text{Fe}(\text{acac})_3$ , 12.554 g of oleic acid, 15.286 g of oleylamine, and 8.992 g of 1,2-dodecandiol (mole ratio of 1:5:5:5) were added into in a three neck flask, previously filled with 80 ml of 1-octadecene. The solution was mechanically stirred at room temperature for 30 min under the bubbling by nitrogen. Then, the mixture was heated to 200 °C, kept at that temperature for 2 h, further heated up to 290 °C under reflux conditions, aged at 290 °C for 30 min, and slowly cooled

down to room temperature. The black precipitate was collected by a magnet and washed several times by ethanol and hexane. Finally, the precipitate was dissolved in toluene (the so-called stock solution). The concentration of IONs in the stock solution was determined by UV-vis spectroscopic approach<sup>29</sup> and was found to be ~ 9.53 mg/ml.

In the next step, iron oxide nanocrystals (from the stock solution) were subjected to a surface exchange process in which the hydrophobic oleic acid molecules were replaced by a hydrophilic *meso*-2,3-dimercaptosuccinic acid (DMSA). The exchange process occurred in dimethyl sulfoxide (DMSO). 10 mg of IONs, taken from the stock solution in toluene, were added into a DMSO solution of DMSA (20 mg/ml). Then, 50 µl of triethylamine was added, and the mixture was stirred at 60 °C for 17 h. The obtained black precipitate was collected by pipette, transferred into microcentrifuge tubes, redispersed in an absolute ethanol and centrifuged several times at 13000 rpm for 10 min in order to remove free oleic acid molecules. Finally, the precipitated nanoparticles were redispersed in milli-Q-water. The obtained suspension was labeled as DMSA-ION.

#### *Synthesis of PAA-ION nanocrystals by a modified oxidative hydrolysis method*

The synthesis protocol used was based on the well-known oxidative hydrolysis method which consists of the precipitation of an iron salt (FeSO<sub>4</sub>) in basic media (NaOH) with a mild oxidant. In a typical synthesis, a mixture of 1.364 g of KNO<sub>3</sub> and 0.486 g of NaOH was dissolved in 135 ml of distilled water in a three-necked flask bubbled with N<sub>2</sub>. Then 15 ml of 0.01 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.3 g of FeSO<sub>4</sub>·7H<sub>2</sub>O and 0.30 g of poly(acrylic acid) (PAA, 450 kDa) (previously bubbled with N<sub>2</sub> for 2 h) was added dropwise under constant stirring. When the precipitation was completed, nitrogen was allowed to pass for another 5 min and the suspension with the black precipitate was held at 90 °C for 24 h under N<sub>2</sub>. Afterwards, the solution was cooled down to room temperature with an ice bath, and the solid was separated by a magnet, washed several times with distilled water and redispersed in milli-Q-water. The obtained suspension was labeled as PAA-ION. The concentration of iron oxide nanoparticles in the suspension was found to be ~0.5 mg/mL (from UV-vis spectra).

#### *Preparation of iron oxide nanocrystals/expanded graphite hybrids*

The four iron oxide/exfoliated expanded graphite hybrids has been prepared by mixing of aqueous suspensions of exfoliated EG flakes with DMSA- and PAA-coated IONs. Exfoliated graphite flakes have been used naked (EG), or functionalized with branched polyethylenimine (PEI-EG *aq.*). The aqueous suspensions were mixed at room temperature in the presence of EDC and NHS. Details about production of the DMSA-ION/PEI-EG-2 nanohybrid structures are given below.

*Sample DMSA-ION/PEI-EG-2.* 0.5 mg of graphite flakes functionalized with PEI molecules (PEI-EG *aq.*) was added in 1 ml of milli-Q-water, followed by addition of 5 mg of EDC and 5 mg of NHS. Then, 1 mg of iron oxide nanoparticles coated with DMSA and suspended in milli-Q-water (DMSA-ION), was added by dropwise into the mixture and stirred for two days at room temperature. The concentration of IONs in the solution was determined by UV-vis spectroscopic approach.<sup>29</sup> The mixture was then collected, transferred into plastic tubes and washed in access of milli-Q-water three times (centrifuged at 4000 rpm for 10 min). The obtained sample is labeled as DMSA-ION/PEI-EG-2. The number at the end of sample's name represents the mass ratio between the loaded IONs and EG flakes in the sample.

In the next three samples, EG flakes were decorated with PAA-coated IONs (PAA-ION) by the same procedure. In order to study possible influence of the PEI molecules on the attachment strength of PAA-IONs, naked EG flakes were used instead of PEI-grafted

ones (sample PAA-ION/naked-EG-0.1). The mass amounts of all ingredients mixed together, relative to EG, are given in Table II. The hybrids are labeled according to the type of IONs used and EG flakes, and their relative mass amounts.

#### *Characterization and measurements*

The structural features of expanded graphite (EG) flakes were investigated by X-ray diffraction (Bruker D8 Advance diffractometer, in glaze angle ( $2^\circ$ ) incident geometry;  $\lambda = 1.5406$  nm,  $I = 30$  mA;  $V = 38$  kV). Scanning electron microscopy (SEM, Cambridge, Stereoscan 250 Mk3) was used to observe morphological features of EG and exfoliated EG flakes. The hybrid structures built of naked or PEI-grafted EG flakes, and DMSA- or PAA-coated iron oxide nanoparticles were studied by transmission electron microscopy (TEM, FEI TECNAI T20, 200 kV), attenuated total reflectance infrared (ATR-FTIR, Bruker, Vertex 70) and Raman spectroscopy (Thermo Scientific DXR microRaman). ATR-FTIR spectra were acquired in the  $400\text{--}4000$   $\text{cm}^{-1}$  region with a resolution of  $4$   $\text{cm}^{-1}$ , by accumulating 40 scans. The Raman spectra were collected in the spectral range of  $60$  to  $3100$   $\text{cm}^{-1}$  using a HeNe  $532$  nm gas laser with laser power  $9.8$  or  $2$  mW. The samples were previously casted onto a glass holder and dried at  $40$   $^\circ\text{C}$  for  $3$  h to eliminate water.

### RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of pristine expanded graphite before sonication in ethanol revealed the presence of diffraction peak at  $26.5^\circ$  which belongs to the (002) reflection of a hexagonal graphite structure (see inset in the Fig. 1a). The average crystallite thickness along the [001] direction of the pristine expanded graphite,  $L_c$ , was estimated using the Scherrer equation:  $L_c = K\lambda/\beta_{002} \cos\theta$ , and the integral width of (002) reflection,  $\beta_{002}$ , and it was found to be around  $20$  nm ( $K=0.9$ ). Keeping in mind that for ideal graphite the interlayer distance along  $c$  axis,  $d_{002}$ , is  $0.335$  nm, it means that the accordion-like pristine graphite (Fig. 1(a,b)) is built of bundles of expanded graphite sheets composed of approximately  $60$  graphene layer. SEM images of the exfoliated expanded graphite (EG) flakes obtained after sonication in absolute ethanol for  $10$  h (Fig. 1(c,d)) reveal that, under ultrasonic treatment, thin and transparent nanosheets with high aspect ratio have been produced. The lateral dimensions of EG flakes range from  $2$  to  $20$   $\mu\text{m}$ . Based on the SEM micrographs, we can notice that additional cleavage of EG flakes occurs under ultrasonic irradiation, giving rise to foliation and production of EG flakes tinner than those found in pristine expanded graphite. Such a statement is additionally corroborated by the Raman spectroscopy as follows.

The Raman spectra of pristine and exfoliated EG flakes (after ultrasonic treatment) are shown in Fig. 2a. In the Raman spectrum of pristine EG flakes, a weak D band at  $\sim 1360$   $\text{cm}^{-1}$ , a G band at  $\sim 1585$   $\text{cm}^{-1}$  and an asymmetric 2D band were detected. The 2D band was deconvoluted into two Lorentzian peaks: the one at  $\sim 2725$   $\text{cm}^{-1}$  with a full width at half maximum, FWHM of  $38$   $\text{cm}^{-1}$ , and another at  $\sim 2688$   $\text{cm}^{-1}$  with a FWHM =  $59$   $\text{cm}^{-1}$  (Fig. 2b). A split 2D band which can be fitted by two peaks is characteristic of a 3-dimensional graphitic

materials.<sup>27,30</sup> Low intensity of the D band pointed out the large lateral dimension of EG sheets. Upon sonication in ethanol for 10 h, intensity of the D-band (at  $\sim 1350\text{ cm}^{-1}$ ) increases which can be assigned to the involvement of defects and disordering in the hexagonal graphitic layers upon ultrasound treatment. Simultaneously the G-band at  $\sim 1579\text{ cm}^{-1}$  becomes broader. The 2D-band of exfoliated EG flakes was also fitted by two Lorentzian peaks with maxima at  $2717\text{ cm}^{-1}$  (FWHM =  $38\text{ cm}^{-1}$ ) and  $2685\text{ cm}^{-1}$  (FWHM =  $75\text{ cm}^{-1}$ ) (Fig. 2c). The relative intensities of these two Lorentzian components changed upon sonication which indicates different degrees of stacking order along the *c* direction.<sup>30</sup>

The ATR-FTIR spectra of naked and PEI-grafted EG flakes, and the PAA-ION/PEI-EG-0.5 hybrid show very similar, almost featureless characteristics (Fig. 3). Such behavior is probably caused by dark gray color of exfoliated EG flakes. Closer inspection of these spectra (inset of Fig. 3) pointed out on the presence of a weak transmittance peaks at  $870\text{ cm}^{-1}$  in all three samples, which can be assigned to the asymmetric ring stretching.<sup>31</sup> Additional broad peak centered at *c.a.*  $\sim 1100\text{ cm}^{-1}$  observed in the FTIR spectrum of PEI-grafted EG flakes can be assign to C-N stretching vibration peak for primary amines<sup>32</sup> ( $1130\text{ cm}^{-1}$ ), and/or the presence of C-O groups<sup>33</sup> ( $1060\text{ cm}^{-1}$ ). A transmittance band at *c.a.*  $\sim 660\text{ cm}^{-1}$  in the FTIR spectrum of PAA-Fe<sub>3</sub>O<sub>4</sub>/PEI-EG-0.5 hybrid can be attributed to the Fe-O bonds. Due to nearly featureless nature of FTIR spectra, it is difficult to recognize presence/absence of functional groups at the surface of EG flakes. Nevertheless, the PEI-grafted EG flakes have shown better dispersion in water in comparison with naked EG flakes. In addition, we also observed that if aqueous suspensions of both kinds of EG flakes were subjected to centrifugation under the same conditions, the PEI-grafted EG flakes precipitate while the naked EG flakes still floats, which clearly indicates the difference in density of these two types of EG flakes. It is likely that positively charged PEI molecules attached to the surface of EG sheets produce a surface charge changes, thus causing the weakening of hydrophobicity and improving the stability of dispersion of PEI-grafted EG flakes in water.

During formation of hybrid structures between the PEI-grafted EG flakes and DMSA- and PAA-coated IONs, the amino groups ( $-\text{NH}_2$ ) of PEI molecules can react with free carboxyl ( $-\text{COOH}$ ) and thiol ( $-\text{SH}$ ) groups of DMSA molecules, as well as with  $-\text{COOH}$  groups of PAA molecules. The role of EDC molecules is to activate carboxylic groups for direct conjugation to primary amines and thus facilitate the attachment of iron oxide nanoparticles onto EG flakes. Complete integration of IONs onto the exfoliated expanded graphite flakes in the PAA-ION/PEI-EG-0.5 hybrid has been verified by its attraction by strong permanent magnet (see inset of Fig. 3), while the naked EG flakes have not been attracted. The microstructure of the DMSA-ION/PEI-EG-2 and



PAA-ION/PEI-EG-0.5 hybrids, shown in Fig. 4, indicate that iron oxide nanoparticles are randomly distributed on a basal plane of PEI-grafted EG flakes; they are agglomerated or form clusters of nanoparticles. Any preferential site for attachment of IONs onto exfoliated EG sheets has not been noticed. On the contrary, Zhang *et al.*, achieved a preferential periphery decoration of the graphene oxide sheets by magnetic nanoparticles caused by a difference in the spatial distribution of oxygen-containing groups attached onto GO sheets (the carboxylic groups are located on the edge, while epoxy and hydroxyl groups are usually located on basal plane of GO sheets).<sup>22</sup>

To check if there is any influence of PEI molecules to the assembling process of coated magnetic nanoparticles with EG flakes, we produced two hybrids with the same nanoparticle loading (10 wt% of PAA-IONs), using PEI-grafted and naked EG flakes as a substrate (PAA-ION/PEI-EG-0.1 and PAA-ION/naked-EG-0.1 samples, respectively). In both cases, the integration of iron oxide nanoparticles with EG flakes has been achieved. The TEM micrographs of these two hybrids are shown in Fig. 5. Dark spots, observed only in the TEM micrograph of PAA-ION/naked-EG-0.1 hybrid, can be an indication of the presence of water droplets on a surface of naked EG flakes. This can be explained by the difference in a macroscopic wetting behavior of water droplets on naked and PEI-grafted EG sheets due to a difference in a binding energy (given by the Lennard-Jones potential) between a water monomer on one side, and naked or PEI-grafted EG flakes on the other side.<sup>34</sup>

The Raman spectra of these two nanohybrids, PAA-ION/PEI-EG-0.1 and PAA-ION/naked-EG-0.1, are shown in Fig. 5c. In order to avoid the degradation of PAA, the spectra were recorded with lower laser power. The intensity of Raman bands, characteristic for exfoliated EG structure, decreases. The Raman modes at 227, 294 and 411  $\text{cm}^{-1}$  found in the spectrum of PAA-ION/naked-EG-0.1 sample inevitably correspond to hematite phase (inset of Fig. 5c). In the sample PAA-ION/PEI-EG-0.1, the characteristic Raman modes for hematite are shifted to 216, 277 and 388  $\text{cm}^{-1}$ , respectively. The appearance of  $\alpha\text{-Fe}_2\text{O}_3$  (instead of expected magnetite) phase can result from a laser treatment on IONs during Raman spectrum collection.

As we can see, the IONs are attached on the surface of exfoliated EG flakes, either naked or PEI-grafted, without any preferential sites along EG sheets for attachment of nanoparticles. It can be an indication that either the PEI molecules are not preferentially anchored along the border of EG flakes, or it might be also that epoxy groups, or some structural defects inside the honeycomb graphene lattice serve as anchoring sites.

## CONCLUSION

In summary, successful decoration of exfoliated expanded graphite (EG) flakes with DMSA- or PAA-coated iron oxide nanoparticles has been achieved by an *ex situ* process through mixing of aqueous suspensions of two constituents at room temperature. The integration of EG flakes and iron oxide nanoparticles has been supported by EDC and NHS molecules. The bonds between the hybrid constituents has been stable for more than 12 months. No preferential spatial distribution of anchoring sites for attachment of iron oxide nanoparticles has been observed, regardless EG flakes have been used naked or functionalized with PEI molecules. This can indicate that other oxygen-containing functional groups (epoxy and/or hydroxyl) or structural defects inside graphene plane might serve as anchoring sites.

*Acknowledgements.* This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia through the project No. 45015. N. J. would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for the Postdoctoral fellowship at the Institute of Nanoscience of Aragon, University of Zaragoza, Spain (2010/2011). We thank Dr. Danica Bajuk-Bogdanović for performing Raman measurements.

## ИЗВОД

EX SITU УГРАЂИВАЊЕ НАНОЧЕСТИЦА ГВОЖЂЕ ОКСИДА НА ЛИСТИЋЕ  
ЕКСПАНДИРАНОГ ГРАФИТА У ВОДЕНОЈ СУСПЕНЗИЈИ

НАТАША ЈОВИЋ<sup>1</sup>, MARIA P. CALATAYUD<sup>2</sup>, BEATRIZ SANZ<sup>2</sup>, AMELIA MONTONE<sup>3</sup> и GERARDO F. GOYA<sup>2</sup>

<sup>1</sup>Институт за нуклеарне науке Винча (020), Универзитет у Београду, и.бр. 522, 11001 Београд, Србија, <sup>2</sup>Aragón Institute of Nanoscience and Department of Physics of Condensed Matter, University of Zaragoza, Zaragoza, Spain и <sup>3</sup>ENEA, Technical Unit Materials Technology, Research Centre of Casaccia, Via Anguillarese 301, 00123 Rome, Italy

Хибридне наноструктуре изграђене од наночестица оксида гвожђа и листића експандираног графита добијене су *ex situ* поступком. Водене суспензије наночестица оксида гвожђа, претходно обложених DMSA, односно PAA молекулима, и листића експандираног графита мешане су на собној температури уз додатак EDC и NHS супстанци. Коришћени су чисти и полиетиленимином (PEI) функционизовани листићи графита. Постигнуто је комплетно сједињавање две компоненте, а разградња хибридних структура није уочена ни након годину дана. Одсуство преферентне просторне расподеле места на графитним листићима за која се каче наночестице оксида гвожђа такође није уочена, без обзира на то да ли су коришћени чисти или функционизовани листићи графита. Структурна и физичко-хемијска својства листића експандираног графита и хибридних структура испитивана су применом скенирајуће и трансмисионе електронке микроскопије и инфрацрвене и Раманове спектроскопије.

(Примљено 21. новембра 2013, ревидирано 3. марта 2014)

## REFERENCES

1. X. Geng, L. Niu, Z. Xing, R. Song, G. Liu, M. Sun, G. Cheng, H. Zhong, Z. Liu, Z. Zhang, L. Sun, H. Xu, L. Lu, L. Liu, *Adv. Mater.* **22** (2010) 638

2. Z. S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li, H. M. Cheng, *ACS Nano* **4** (2010) 3187
3. B. S. Kong, J. Geng, H. T. Jung, *Chem. Comm.* (2009) 2174
4. M. Liu, H. Zhao, S. Chen, H. Yu, X. Quan, *ACS Nano* **6** (2012) 3142
5. H. Wu, J. Wang, X. Kang, C. Wang, D. Wang, J. Liu, I. A. Aksay, Y. Lin, *Talanta* **80** (2009) 403
6. J. Zhou, H. Song, L. Ma, X. Chen, *RSC Adv.* **1** (2011) 782
7. P. Bhunia, G. Kim, C. Baik, H. Lee, *Chem. Comm.* **48** (2012) 9888
8. F. He, J. Fan, D. Ma, L. Zhang, C. Leung, H. Laiwa Chan, *Carbon* **48** (2010) 3139
9. Y. W. Liu, M. X. Guan, L. Feng, S. L. Deng, J. F. Bao, S. Y. Xie, Z. Chen, R. B. Huang, L. S. Zheng, *Nanotechnology* **24** (2013) 025604
10. J. Zhu, Z. Luo, S. Wu, N. Haldoarachchige, D. P. Young, S. Wei, Z. Guo, *J. Mater. Chem.* **22** (2012) 835
11. L. Ćirić, D. M. Djokić, J. Jaćimović, A. Sienkiewicz, A. Magrez, L. Forró, Ž. Šljivančanin, M. Lotya, J. N. Coleman, *Phys. Rev., B* **85** (2012) 205473
12. Q. Tang, Z. Zhou, Z. Chen, *Nanoscale* **5** (2013) 4541
13. W. S. Hummers Jr., R. E. Offeman, *J. Am. Chem. Soc.* **80** (1958) 1339
14. G. Chen, W. Weng, D. Wu, C. Wu, J. Lu, P. Wang, X. Chen, *Carbon* **42** (2004) 753
15. I. Zaman, H. C. Kuan, Q. Meng, A. Michelmoro, N. Kawashima, T. Pitt, L. Zhang, S. Gouda, L. Luong, J. Ma, *Adv. Funct. Mater.* **22** (2012) 2735
16. J. Malig, C. Romero-Nieto, N. Jux, D. M. Guldi, *Adv. Mater.* **24** (2010) 800
17. A. Prakash, S. Chanda, D. Bahadur, *Carbon* **50** (2012) 4209
18. H. P. Cong, J. J. He, Y. Lu, S. H. Yu, *Small* **6** (2010) 169
19. D. W. P. Pang, F. W. Yuan, Y. C. Chang, G. A. Li, H. Y. Tuan, *Nanoscale* **4** (2012) 4562
20. L. Ren, S. Huang, W. Fan, T. Liu, *Appl. Surf. Sci.* **258** (2011) 1132
21. K. Zhou, Y. Zhu, X. Yang, C. Li, *New J. Chem.* **34** (2010) 2950
22. Y. Zhang, B. Chen, L. Zhang, J. Huang, F. Chen, Z. Yang, J. Yao, Z. Zhang, *Nanoscale* **3** (2011) 1446
23. T. T. Tung, J. F. Feller, T. Y. Kim, H. Kim, W. S. Yang, K. S. Suh, *J. Polym. Sci., A* **50** (2012) 927
24. X. Xia, Q. Hao, W. Lei, W. Wang, D. Sun, X. Wang, *J. Mater. Chem.* **22** (2012) 16844
25. S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, R. S. Ruoff, *J. Mater. Chem.* **16** (2006) 155
26. X. Fan, G. Jiao, W. Zhao, P. Jin, X. Li, *Nanoscale* **5** (2013) 1143
27. G. Katsukis, J. Malig, C. Schulz-Drost, S. Leubner, N. Jux, D. M. Guldi, *ACS Nano* **6** (2012) 1915
28. S. Sun, H. Zeng, *J. Am. Chem. Soc.* **124** (2002) 8204
29. M. P. Calatayud, C. Riggio, V. Raffa, B. Sanz, T. E. Torres, M. R. Ibarra, C. Hoskins, A. Cuschieri, L. Wang, J. Pinkernelle, G. Keilhoff, G. F. Goya, *J. Mater. Chem., B* **1** (2013) 3607
30. M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cançado, A. Jorio, R. Saito, *Phys. Chem. Chem. Phys.* **9** (2007) 1276
31. M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. T. McGovern, G. S. Duesberg, J. N. Coleman, *J. Am. Chem. Soc.* **131** (2009) 3611
32. Z. Qian, M. A. Khan, S. Mikkelsen, P. Chen, *Langmuir* **26** (2010) 2176
33. Y. Si, E. T. Samulski, *Nano Lett.* **8** (2008) 1679

34. T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, P. Koumoutsakos, *J. Phys. Chem., B* **107** (2003) 1345.

Accepted Manuscript

## TABLE CAPTIONS

Table I Iron oxide/carbon-based hybrid structures: methods of synthesis, types of support matrix/iron oxide nanoparticles, types of bonding, and potential applications of hybrids.

Table II The mass amount relative to exfoliated expanded graphite flakes (EG) of iron oxide nanoparticles (ION), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), and *N*-hydroxysuccinimide (NHS) used in preparation of hybrid structures.

Table I

Method of synthesis	Graphene-based support/IONs	Type of bonding	Potential application
In Situ			
Co-precipitation of iron salts in water	rGO <sup>a</sup> /Fe <sub>3</sub> O <sub>4</sub>	-	Electrochemical detection of chromium <sup>17</sup>
Thermal decomposition of iron precursor in organic solvents	Graphene or rGO/Fe <sub>3</sub> O <sub>4</sub>	-	Wave filters; superconductors <sup>10, 18</sup>
Hydrothermal method	Graphene/Fe <sub>3</sub> O <sub>4</sub>	Direct bonding (without molecular linkers)	In polymer matrix for optical devices; bioimaging <sup>20</sup>
Solvothermal reaction	Graphene/Fe <sub>3</sub> O <sub>4</sub> microspheres	-	Loading of doxorubicin hydrochloride <sup>21</sup>
Direct pyrolysis of Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Graphene/Fe <sub>3</sub> O <sub>4</sub>	Via Fe-O-C bond	In Li-ion batteries <sup>6</sup>
Ex Situ			
Ultrasonication	GO/Fe <sub>3</sub> O <sub>4</sub>	Covalent bonding/ assisted by EDC/NHS	For removing cationic dyes (methylene blue; neutral red) <sup>8</sup>
Mixing of aqueous solutions	PEI-grafted rGO/Fe <sub>3</sub> O <sub>4</sub>	Covalent bonding/ assisted by EDC/NHS	For removal of antibiotics or aromatic anticancer drugs <sup>22</sup>
Mixing of aqueous solutions	Graphene/Fe <sub>3</sub> O <sub>4</sub>	Covalent bonding assisted by EDC	For drug delivery (loading and release of 5-fluorouracil) <sup>26</sup>

<sup>a</sup>rGO – reduced graphene oxide

Table II

Sample	ION	EDC	NHS
DMSA-ION/PEI-EG-2	2	10	10
PAA-ION/PEI-EG-0.5	0.5	10	10
PAA-ION/PEI-EG-0.1	0.1	1	1
PAA-ION/naked-EG-0.1	0.1	1	1

Accepted Manuscript

## FIGURE CAPTIONS

Figure 1. SEM images of: a and b) expanded graphite (EG); c and d) exfoliated EG. Inset: the XRD profile of (002) reflection of EG.

Figure 2. a) Raman spectra, and the deconvoluted 2D peak of b) pristine and c) exfoliated expanded graphite.

Figure 3. ATR-FTIR spectra of exfoliated EG flakes (naked and PEI-grafted) and selected hybrid, PAA-ION/PEI-EG-0.5. Inset (left): Response of water suspensions of pure exfoliated EG flakes and PAA-ION/PEI-EG-0.5 hybrid to the presence of strong permanent magnet. Inset (right): Magnified ATR-FTIR spectra.

Figure 4. TEM images of a and b) DMSA-ION/PEI-EG-2 and c and d) PAA-ION/PEI-EG-0.5 hybrids.

Figure 5. TEM micrographs of a and b) PAA-ION/PEI-EG-0.1, c) PAA-ION/naked-EG-0.1 hybrids and d) the Raman spectra.

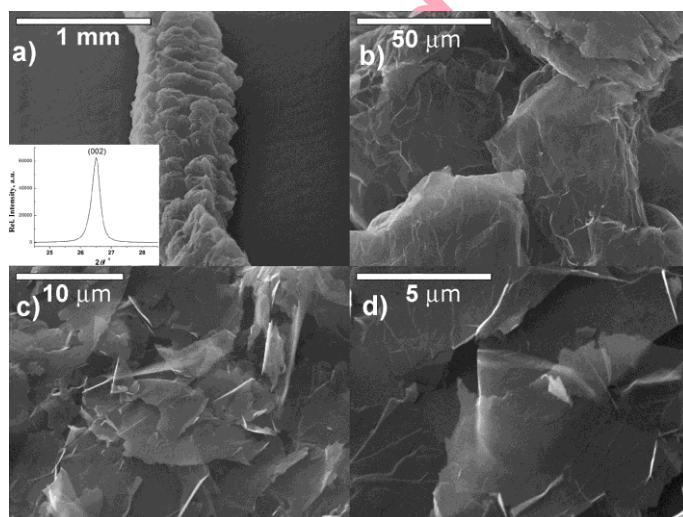


Fig. 1

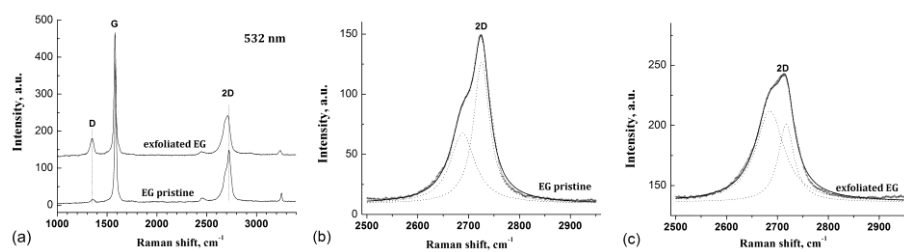


Fig. 2

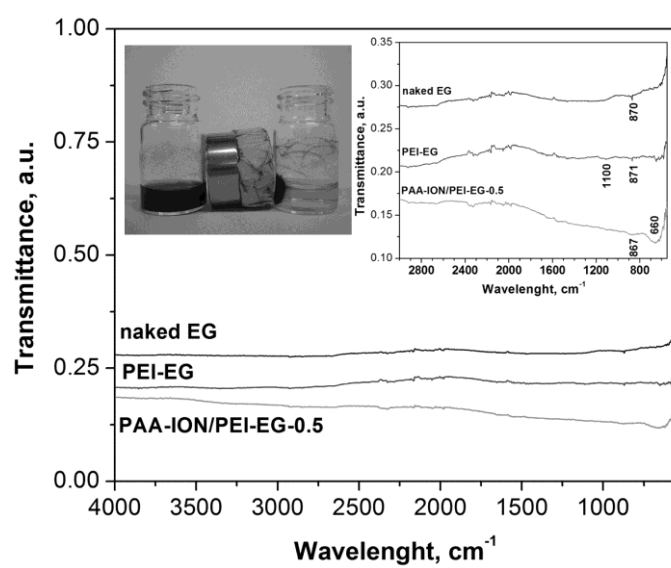


Fig. 3



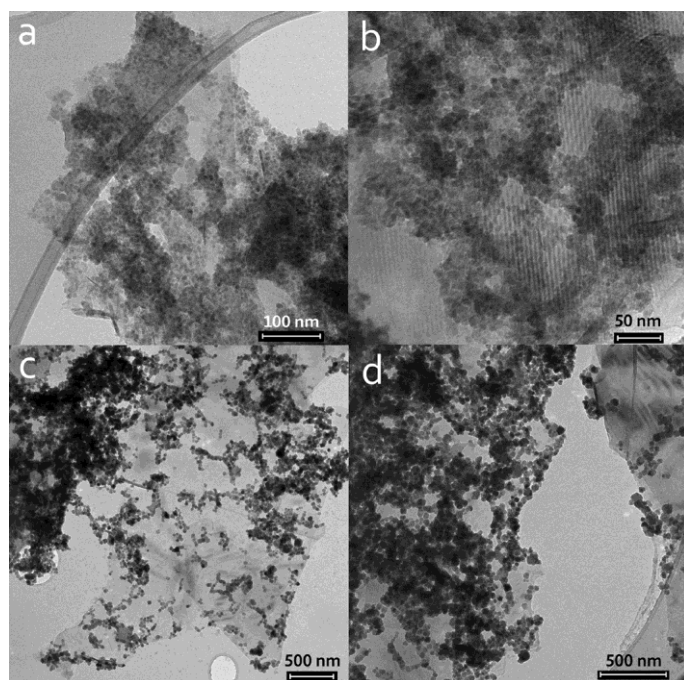


Fig. 4

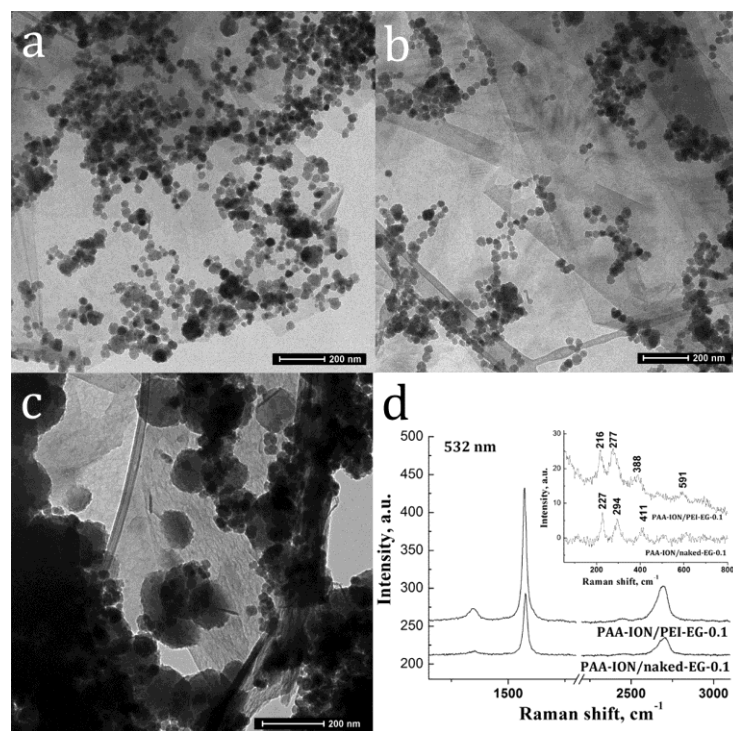


Fig. 5