SURFACE MORPHOLOGY AND RAMAN STUDY OF GRAPHENE/$CuGaO_2$ AEROGELS

Cristina Mosoarca[1], Radu Banica[1], Florina Stefania Rus[1], Petrica-Andrei Linul[1,2], Daniel Ursu[1], Cosmin Pascariu[1]

[1]National Institute of Research and Development for Electrochemistry and Condensed Matter, 144 Aurel Paunescu-Podeanu, RO-300569 Timisoara, Romania
[2]Politehnica University Timisoara, 2 Piata Victoriei Sq., RO-300006 Timisoara, Romania
e-mail: radu.banica@yahoo.com, mosoarca.c@gmail.com

Introduction

Graphene aerogel [1], obtained after a series of steps of cooling and heating under high pressure (supercritical drying) or vacuum (lyophilization), is considered to be the least dense solid in existence, possessing very good elasticity and thus preserving its original form after compression. Due to its low density it also exhibits good absorption properties, finding applications in oil spills and other environmental clean-ups. Hybrid materials like $CuGaO_2$/graphene aerogels [2] could find applications for a wide range of technologies, from storage and transfer of energy [3] to advanced electrodes and dye-sensitized solar cells.

This paper reports the synthesis of graphene and graphene/$CuGaO_2$ materials. The samples underwent lyophilization, followed by thermal treatment in vacuum. An aerogel containing a homogenous distribution of $CuGaO_2$ was obtained by mixing the aqueous solution of graphene oxide and reduced graphene with $CuGaO_2$, followed by freezing.

The resulting samples were characterized by Scanning Electron Microscopy (SEM), 3D Laser Measuring Microscopy (LSCM) and Raman spectroscopy.

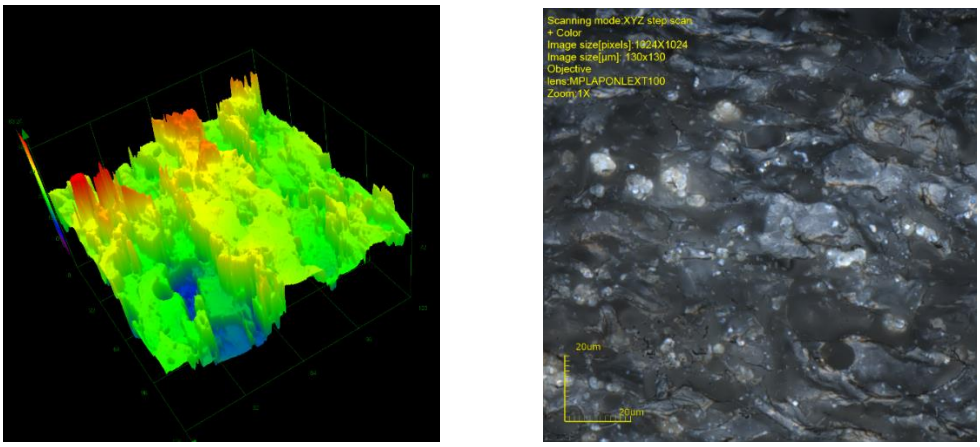
Experimental

The graphene aerogel was obtained from a mixture of graphene oxide (conc. 0.9 mg/mL), prepared by using a modified Hummers method, and graphene Quattro-Type (conc. 1.4 mg/mL) purchased from NanoIntegris. Additionally, the suspension was freeze dried and thermally treated in a GSL-1500X Vacuum furnace (MTI Corporation) at a pressure < 1 Torr and a temperature rise rate of –5 °C/minute, resulting in graphene aerogel samples.

$CuGaO_2$ was obtained using metal nitrates as precursors under hydrothermal conditions at 250 ºC. $CuGaO_2$ was added to graphene aqueous solution, following the protocol described above, resulting in $CuGaO_2$/graphene aerogel samples.

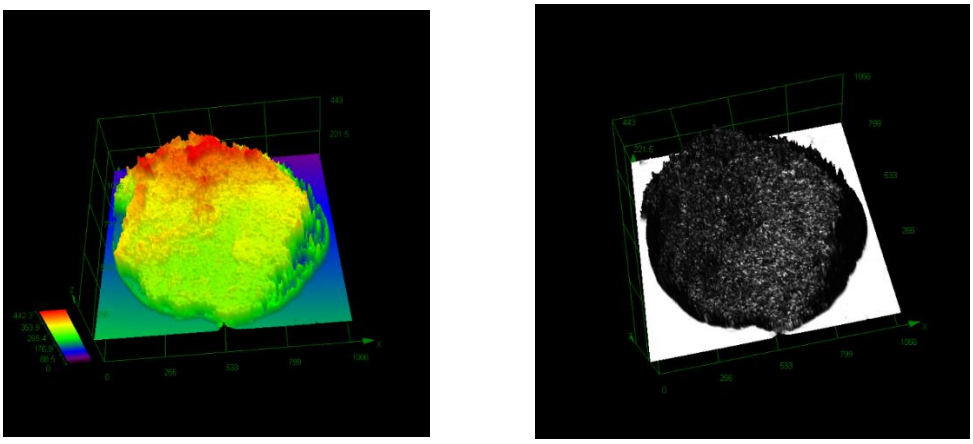
Results and discussion

The morphological investigations of topographic surfaces were performed on LEXT OLS4000 3D Laser Measuring Microscope designed for 3D measurement, nanometer level imaging and roughness analysis. The imaging generates a 3D representation of the surface height using LEXT software, by setting the lower and upper limits on the size of the features that are being characterized.



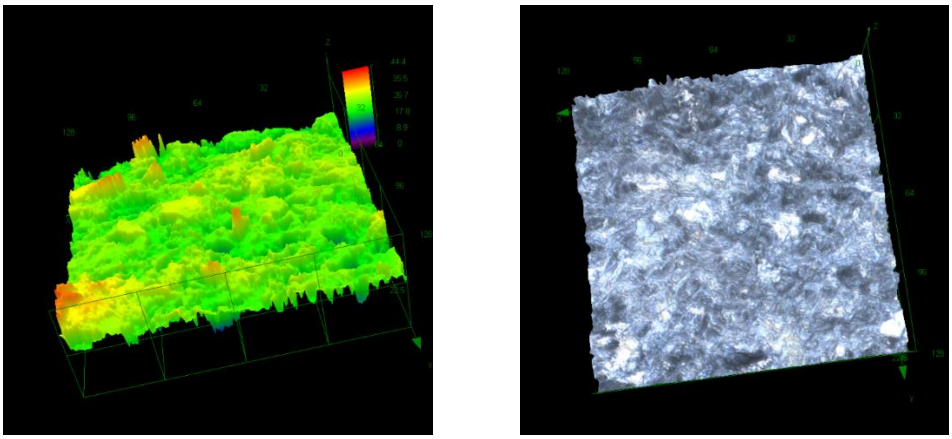
a) b)

Figure 1. Three-dimensional image taken with an LSCM of $CuGaO_2$/graphene aerogel, with 100x magnification: (a) in color, (b) black and white.



a) b)

Figure 2. Three-dimensional image taken with an LSCM of $CuGaO_2$/graphene aerogel, with 10x magnification: (a) in color, (b) black and white.

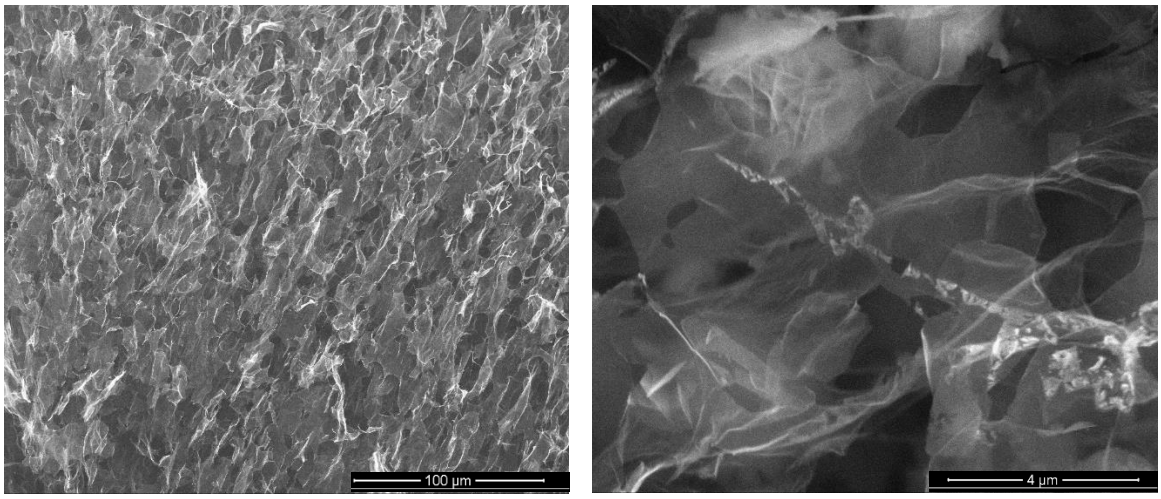


a) b)

Figure 3. Three-dimensional image taken with an LSCM of graphene aerogel, with 100x magnification: (a) in color, (b) black and white.

The SEM images of $CuGaO_2$ show that the material is uniformly distributed in the volume of the graphene aerogel (Fig. 4a and 4b), confirming the relative homogenous

dispersion of the inorganic compound in the aerogel matrix. The aerogels have both high electrical conductivity and high polar molecule absorption capacity, the former being due to the reduced graphene, while the latter being due to the functional groups attached to the graphene oxide.



a) b)

Figure 4. SEM images of $CuGaO_2$/graphene aerogel: (a) 100 µm, (b) 4 µm magnification.

Raman spectroscopy represents a nondestructive and ambient probing tool which is very sensitive to the microstructure of nanocrystalline materials [4]. Graphene aerogels exhibit common features in the 800–3.250 cm^{-1} domain. The Raman spectrum, which was recorded using a Nanonics Imaging (Israel) - MultiProbe Imaging - MultiView 1000™ Platform (SPM), equipped with a 532 nm laser, was used in order to identify the vibrational states of the graphene aerogel and is being shown in Fig. 5.

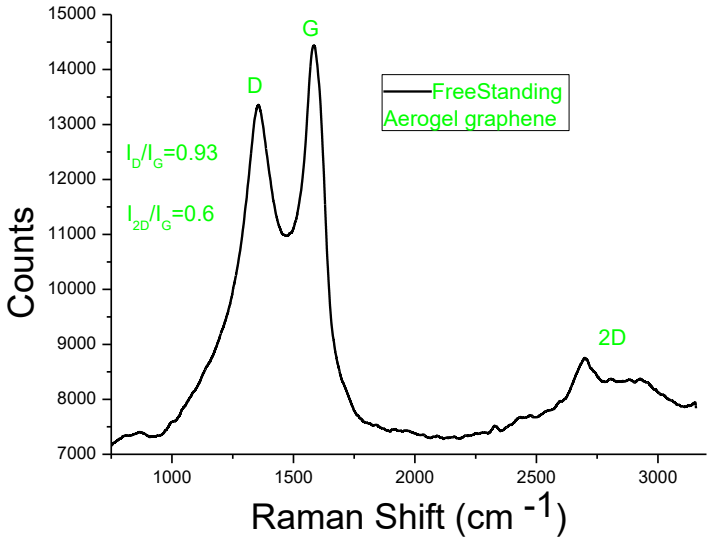


Figure 5. Raman spectrum of graphene aerogel.

Three major peaks are found at 1.596, 1.353, and 2.702 cm^{-1}, representing the G, D, and 2D bands, respectively. The obtained sample exhibits intense G and D bands, which

confirms the presence of defects in the graphene aerogel. The D-mode is caused by a disordered structure of graphene known as an attractive measure of quality. The G peak arises from the stretching of the C-C bonds in graphitic materials, and is common to all sp^2 carbon systems, while the 2D-band (corresponding to an overtone of the D band) is related to the stacking order of graphene layers [5]. Graphene aerogel spectrum exhibits intense D and G bands and a flat 2D region (2400 to 3250 cm^{-1}), with the D band being less intense than the G band (I_D/I_G = 0.93). Raman spectrum of a pristine graphene oxide normally shows an intensity ratio between the D and G bands around 0.9 [6], indicating the presence of defects in the crystal lattice which is comparable with as obtained aerogel intensity ratio. We can conclude that the quality of freestanding graphene aerogel is high with low disordered structure.

Conclusion

Graphene and graphene/$CuGaO_2$ based aerogels, with various possible nanotechnology applications, were obtained by lyophilization followed by thermal treatment in vacuum. The graphene oxide obtained from precursors is partially reduced, during the thermal treatment, while due to condensation and decarboxylation reactions some hydrophilic bonds are lost, leading to a change in the pore sizes after water adsorption. An aerogel with a homogenous distribution of the semiconductor within it was obtained by mixing the aqueous solution containing reduced graphene and graphene oxide with the $CuGaO_2$ semiconductor, prior to freezing.

Acknowledgements

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References

[1] G. Gorgolis, C. Galiotis, 2D Materials 7 (2017) 032001.
[2] D. Ursu, M. Miclau, R. Banica, N. Vaszilcsin, Mat. Lett. 143 (2015) 91-93.
[3] C. Zamfirescu, I. Dincer, G.F. Naterer, R. Banica, Chem. Eng. Sci. 97 (2013) 235-255.
[4] E. D. Dikio, F. T. Thema, A. M. Farah, et al., Mater Sci-Pol 31 (2013) 59.
[5] M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cancado, A. Jorio, R. Saito, Phys. Chem. Chem. Phys. 9 (2007) 1276–1291.
[6] C. Cavallo, M. Agostini, J. P. Genders, M. E. Abdelhamid, A. Matic, J.of Power Sources, 416 (2019) 111-117.