



24th COBEM - 2017



24th ABCM International Congress of Mechanical Engineering
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-1901

TRANSPARENT AND CONDUCTIVE FILMS OF REDUCED GRAPHENE OXIDE: SPRAY DEPOSITION AND CHARACTERIZATION

Andreza Menezes Lima
Géssica Seara Faria
Rodrigo Amaral de Medeiro
Leila Rosa de Oliveira Cruz
Wagner Anacleto Pinheiro

Instituto Militar de Engenharia, Department of Mechanical and Materials Engineering, Praça General Tibúrcio, 80 – Urca, Rio de Janeiro - RJ

andrezamenezeslima@gmail.com

gessica.seara.faria@gmail.com

digfisc@gmail.com

leilacruz@ime.eb.br

anacleto@ime.eb.br

Abstract. *Dispersions of graphene oxide (GO) and reduced graphene oxides (rGO) were used to produce thin films by spray coating method. Deposition parameters were varied to optimize the procedure. The films were characterized in relation to thickness, morphology, composition, transmittance and resistivity. The method was efficient in producing uniform layers with nanometric thicknesses, transparency and sheet resistance are close to those required for the application as a transparent and conductive film in electronic devices.*

Keywords: *graphene, spray, transparent and conductive film.*

1. INTRODUCTION

The foundation of transparent and conductive films (TCFs) is to have high transmittance and low electrical resistance. Wassei and Kaner (2010) defined good TCFs as films with optical transparency in visible and infrared regions, high electrical conductivity, low sheet resistance, chemical stability, low production cost, and favourable work-function.

These TCFs can be applied in many different areas in electronic field. According to Wang et al. (2010), Zheng et al. (2011) e Zheng et al. (2011), these films are applied to various photoelectronic devices such as liquid crystal displays, sensors, lasers, organic light emitting diodes, optical communication devices, solid-state lighting and solar cells.

The dominant materials in these applications are indium tin oxide (ITO) and fluorine doped tin oxide (FTO), which present disadvantages such as high cost and low flexibility. A viable alternative would be the application of materials from carbon in substitution of these traditional ones (Lee et al., 2013).

Graphene is defined as an atomic carbon monolayer with sp^2 hybridization in a two-dimensional hexagonal structure (Geim and Novoselov, 2007). In relation to the electronic properties, graphene is considered a bandgap zero semiconductor, that is, it exhibits an ambipolar electric field effect and charge carriers can be adjusted continuously between electrons and holes in high concentrations (10^{13}cm^{-2}). Thus, the mobility can be as high as $15000 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, at room temperature (Zhu et al., 2010). Because it is a thin layer of atoms, the optical transmittance in the visible range is considered extremely high, about 97.7%, with absorbance of the material being reported around 2.3%. These properties are associated with the number of layers that graphene presents linearly: the less number of layers, the larger is the transmittance (Zhu et al., 2010).

In addition to exhibiting high transmittance and low sheet resistance values for those applications, graphene also exhibits excellent flexibility, large-scale production capability, and non-toxicity. All these properties together with the abundance of raw material resources make this material a potential candidate for application as TCF (Lee et al., 2013).

Graphene layers can be deposited by several techniques. The spray method is widely used in industry, easily adaptable for large-scale productions, able to cover various substrates, in various shapes and with large variability of parameters. According to Tong et al. (2013) it is considered a simple and low cost procedure.

Several authors have studied graphene films produced by the spray coating technique for application as TCF. Pham et al. (2010) deposited chemically converted graphene films by spray coating method, achieving 84% transparency at 550 nm and 2.2 K Ω / \square of sheet resistance. Already Shi et al. (2015) reported spray-reduced graphene oxide films with transmittance of 68.69% at 550 nm and sheet resistance of 58 K Ω / \square .

In this work, dispersions of graphene oxide (GO) and reduced graphene oxide (rGO) were used to produce thin films by spray coating method for applications as TCFs.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The following materials were used in constitution of this research: graphite Graflake 99550 +50 mesh, from Nacional de Grafite; sulfuric acid 98% (H₂SO₄), from B Herzog; sodium nitrate (NaNO₃), from Vetec; potassium permanganate 99.3% (KMnO₄), from Vetec; hydrogen peroxide 32% (H₂O₂), from Vetec; deionized water; ammonium hydroxide 29% (NH₄OH), from Vetec; ascorbic acid 99% (C₆H₈O₆), from Synth; poly (sodium 4-styrenesulfonate) solution 30% (PSS), from Aldrich, and soda lime glass.

2.2 Preparation of graphene oxide and chemical reduction of graphene oxide

GO dispersion was produced by a modified Hummers method (Rourke et al., 2011), from graphite flakes, according the following steps: intercalation (addition of NaNO₃ and H₂SO₄), oxidation (KMnO₄) and exfoliation (washing/centrifugation steps).

rGO dispersion was produced from GO dispersion, by adding PSS, ascorbic acid, and NH₄OH, while heating at 80°C for 3 days. The mixture was washed to eliminate the excess of reagents.

2.3 Films preparation

The films were prepared on soda-lime glass substrates. For better adherence, the substrates were firstly cleaned in ultrasonic bath with deionized water and neutral soap for 10 minutes, then acetone for 20 minutes and at last immersed in a H₂O-H₂O₂-NH₄OH solution in a ratio of 5:1:1, at 80°C for 10 minutes (Roh et al., 2014). This procedure ensures a good hydrophilization of substrate and more chances for obtaining uniform and continuous films.

For spray deposition, a Steula BC 66-08 airbrush with nozzle of 0.8 mm was used. The following deposition parameters were varied: N₂ pressure, substrate-nozzle distance, and number of layers. For better accuracy and reproducibility of results, an automatic homemade activation system for the airbrush was prepared based on a solenoid, an electric circuit and a computer program in C++ language, as seen in Fig. 1. This automatic system made the production of films easier and faster, being capable of producing high quality layers.

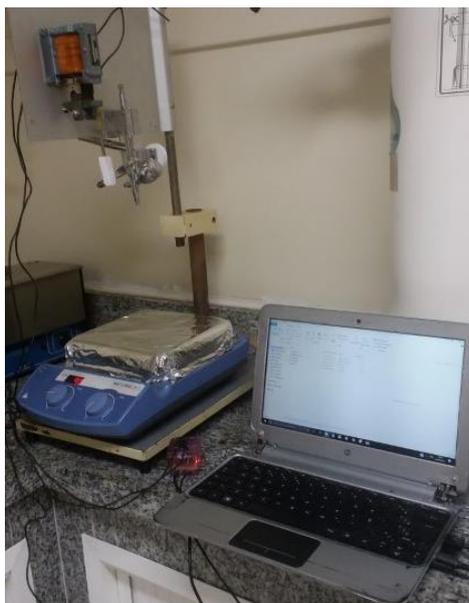


Figure 1 – Homemade spray deposition system.

Four samples were chosen as the best films for the desired application. They were prepared from GO and rGO solutions with a concentration of 1.0 mg/ml. For the spray deposition, the substrate was placed on a hot plate at 90°C. The drying time between depositions was fixed in 30 s. Other deposition parameters are shown in Tab. 1.

Table 1. Spray deposition parameters of GO and rGO films.

Sample	Gas pressure	Distance	Deposition time	Number of layers
trGO ^A	10 psi	20 cm	1s	5
trGO ^B	20 psi	20 cm	0,5s	5
rGO ^C	20 psi	5 cm	1s	5
rGO ^D	20 psi	20 cm	1s	4

After deposition, the GO and rGO layers were submitted to thermal treatment in a tubular furnace, from NBD Nobody, model NBD-O1200, at 550°C for 30 min in an Argon atmosphere. This procedure promotes reduction of GO layers, resulting in thermally reduced graphene oxide films (trGO) and improves the conductivity of rGO films, by the elimination of the remaining PSS used in the production of the rGO dispersion.

2.4. Characterization methods

The films were characterized by the following techniques: contact profilometry, in a Dektak 150 equipment from Veeco, in Hills & Valleys mode, scanning length 1000 µm, duration of 60 s, force of 1 mg and measure range of 6.5 µm; scanning electron microscopy, in a QUANTA FEG (FEI) SEM equipment, with Energy Dispersive X-ray Spectroscopy (EDS) accessory, with 500×, 2000× and 10000× magnifications, voltage of 20 kV, spot size 5 and working distance of approximately 9.0 mm; atomic force microscopy (AFM), in a Park Systems equipment, model XE7, in tapping mode, scan size of 30 µm and scan rate of 1 Hz; UV-visible spectrophotometry, in a CARY 5000, from VARIAN, for wavelengths from 400 nm to 800 nm; and four-point probe method, following the Van der Pauw technique, in Hall HL 5500, from BIO-RAD.

3. RESULTS AND DISCUSSION

3.1. Contact Profilometry

Table 2 presents the values of thicknesses and roughness of samples trGO^A, trGO^B, rGO^C and rGO^D. The measurements were performed in two different regions of the films, in the center of samples, in order to analyze the uniformity of layers. AT and AR represent the mean values and standard deviation for the measurements of thickness and roughness respectively.

Table 2. Thickness and roughness of sprayed GO and rGO films.

	trGO ^A	trGO ^B	rGO ^C	rGO ^D
AT (nm)	39,34 ± 2,602153	43,135 ± 7,827672	49,715 ± 11,41977	29,665 ± 4,475986
AR (nm)	32,905 ± 14,82803	86,885 ± 5,678067	35,005 ± 38,45954	52,94 ± 40,92734

From these results, it is possible to observe that the films have nanometric thicknesses, ideal for the desired application. In trGO^A it is possible to observe uniformity in relation to thickness, with only 6.6% of standard deviation, indicating that the method of deposition chosen is capable of producing uniform films throughout its length.

In respect to roughness, samples obtained by spraying rGO dispersions have proved to be more susceptible to large roughness differences in distinct regions, which indicates that films obtained with GO dispersions and thermally reduced may be more promising for application as TCF.

Shi et al. (2015) evaluated thickness of rGO films produced by spray coating and obtained values of approximately 14 nm, close to the values obtained in this study. However, Soltani-kordshuli et al. (2016) studied films produced by PEDOT:PSS nanocomposite spray-doped graphene, obtaining thicknesses of 200 to 280 nm and roughness ranging from 5.1 to 8.5 nm, values that are different from those obtained in this work, possibly due to the presence of large amounts of polymer.

3.2. Scanning Electron Microscopy

Figure 2 shows the SEM images of samples trGO^A, trGO^B, rGO^C, and rGO^D with magnitude of 500×. It is possible to observe that the substrate was completely covered by graphene flakes. It is also possible to notice that the films are uniform in all their extension.

All samples have lighter regions, with the appearance of wrinkles or needles, which are believed to be characteristic of inflection of flakes during heat treatment at high temperature.

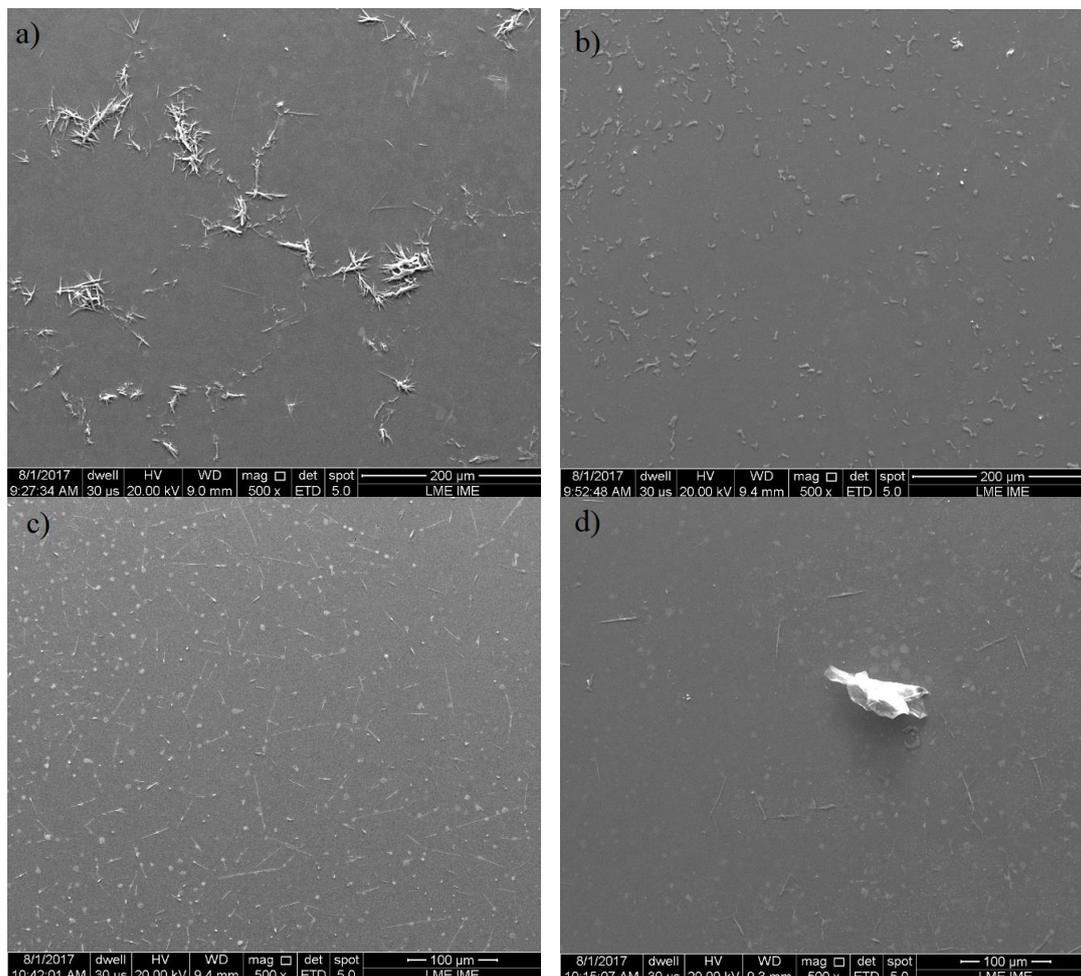


Figure 2. SEM images of sprayed GO and rGO films: (a) trGO^{A} , (b) trGO^{B} , (c) rGO^{C} and (d) rGO^{D} .

In Fig. 3 it is possible to observe SEM images in higher magnification ($2000\times$ and $10000\times$) for sample trGO^{A} , indicating that these observed needles are related to folding of flakes.

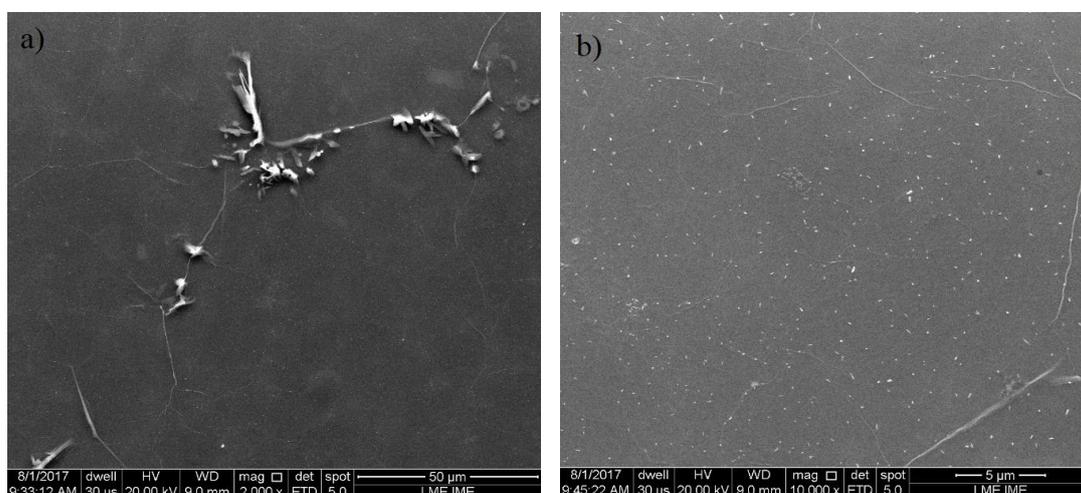


Figure 3. SEM images of trGO^{A} sample: (a) $2000\times$ and (b) $10000\times$ magnification.

EDS was also carried out together with SEM in order to evaluate composition in distinct regions of the trGO^A sample. The following elements were identified: carbon, oxygen, sodium, magnesium, aluminum, silicon, sulfur and calcium in very similar compositions for all regions, including the observed needles.

This analysis proves that the method of deposition did not generate contamination in the films, since all the elements identified are constituents of GO and rGO dispersions or soda lime glass substrate. It is also observed that the composition remains regular in distinct regions analyzed, indicating uniformity of the process.

3.3. Atomic Force Microscopy

Figure 4 shows AFM 2D image and the thickness profile for region 1 of sample trGO^A . It is observed that flakes cover the entire surface of the substrate. Also, the flakes folds are more clearly noticed, even in the thickness profile (Fig. 4 (b)), where the difference in height in this fold region is evident. This fact corroborates to the assertion that the wrinkles observed in SEM images come from the inflection of flakes.

The 2D image (Fig. 4 (a)) presents characteristics close to the image obtained by Shi et al. (2015), who produced RGO films by the same technique of this work.

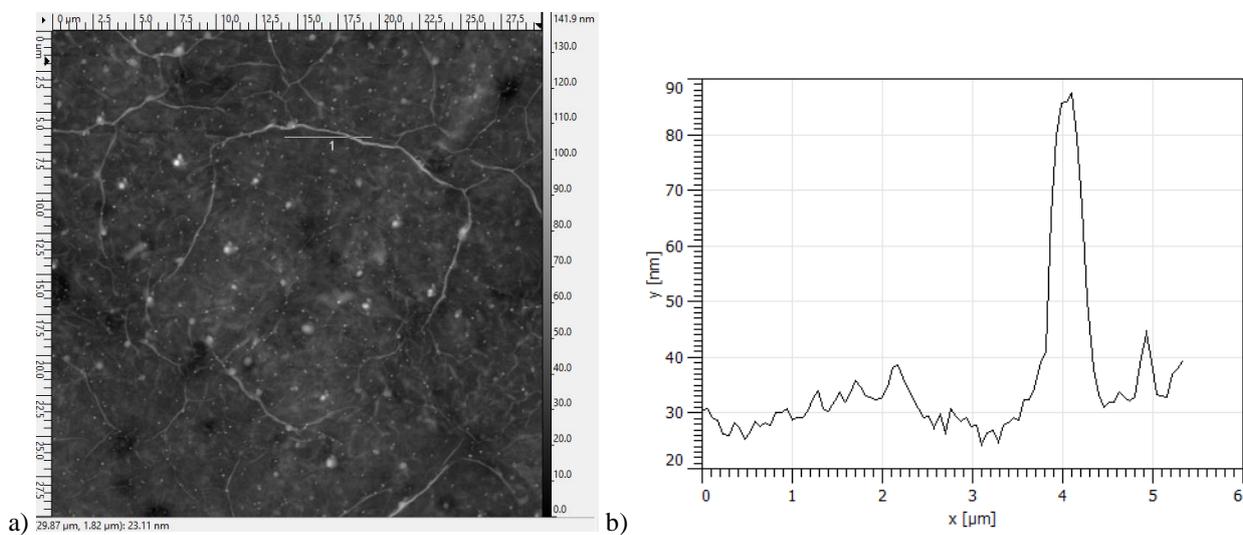


Figure 4. AFM image for sample trGO^A : (a) 2D image and (b) thickness profile.

3.4. Spectrophotometry

Figure 5 shows the transmittance of studied samples. For wavelengths of 550 nm, transmittance values range from 74.50%, for rGO^A , to 64.86%, for rGO^D . These results are somewhat below the transmittance range of other materials used as TCF, such as ITO (~85%) and FTO (~84%), according to Irvine et al. (2011).

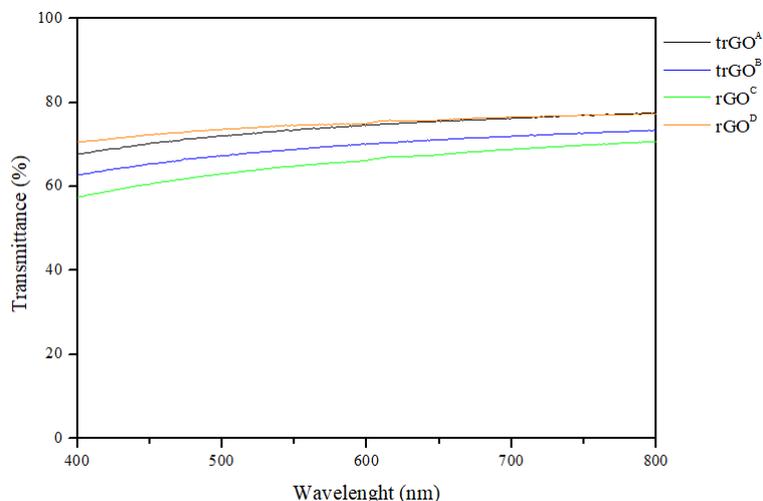


Figure 5. Transmittance of sprayed GO and rGO films.

It can be observed that rGO^A film presented a transmittance 10% lower than that observed for ITO and FTO in the same range, being 74.50% for the first and 85% (Irvine et al., 2011) for the second. These results are also in agreement with those obtained by Shi et al. (2015), which reached 68.69% at 550 nm, and Pham et al. (2010), which achieved 84% at the same wavelength both for rGO films produced by spray.

3.5. Sheet Resistance

Figure 6 shows sheet resistance and transmittance results at 550 nm for samples produced in this study and also for ITO and FTO (Irvine et al., 2011). It is observed that trGO and rGO films show promising results for replacement of the traditional materials. trGO^A and rGO^C are the samples that better combines the two properties of interest, sheet resistance and transmittance, the first one with 13.2 k Ω / \square and 73.39%, and second one with 13.30 k Ω / \square and 74.50%.

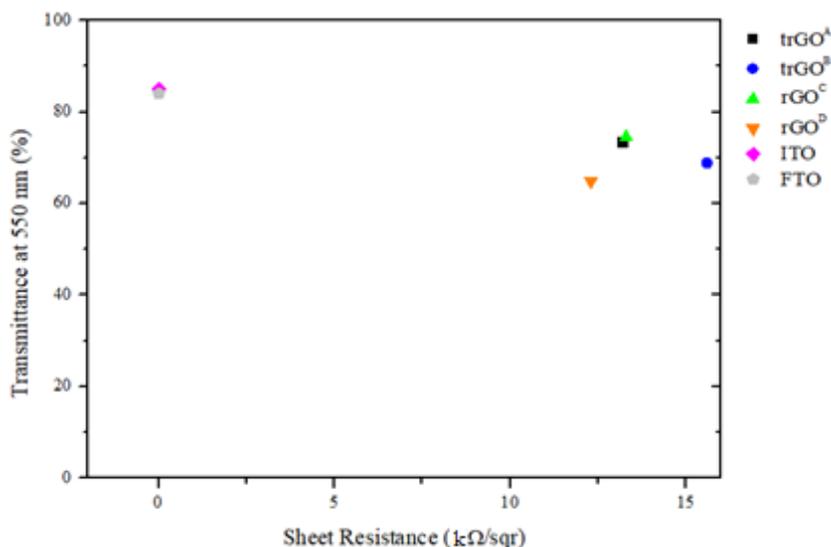


Figure 6. Relation between sheet resistance and transmittance at 550 nm of sprayed GO and rGO films and materials traditionally used as TCF.

The results obtained in this study surpass those reported by Shi et al. (2015), which reached 58 k Ω / \square and 68.69% at 550 nm, and are close to those obtained by Becerril et al. (2008), Yamaguchi et al. (2010) and Pham et al. (2010). All these studies have in common the use of one single deposition by spin or spray coating technique, while in this present research it is used layer by layer deposition.

4. CONCLUSIONS

Spray coating using GO and rGO dispersions proved to be an efficient method to produce transparent and conductive films, in a simple and low-cost procedure.

The trGO and rGO films produced in this research presented nanometric thickness and uniformity. SEM and AFM analyses demonstrated that those films were continuous, with flakes covering the entire substrate and without any contamination. Sheet resistance and transmittance results are near the range to be used in different electronic devices.

5. ACKNOWLEDGEMENTS

The authors thank Anderson Menezes Lima for the help in the assembly of the spray deposition system. This work was supported by CAPES and FAPERJ.

6. REFERENCES

- Becerril, H.A., Mao, J., Liu, Z., Stoltenberg, R.M., Bao, Z. and Chen, Y., 2008. "Evaluation of solution-processed reduced graphene oxide films as transparent conductors". *ACS Nano*, Vol. 2, p. 463.
- Geim, A.K. and Novoselov, K.S., 2007. "The rise of graphene". *Nature Materials*, Vol. 6, p. 183.
- Irvine, S.J.C., Lamb, D.A., Barrioz, V., Clayton, A.J., Brooks, W.S.M., Rugen-Hankey, S. and Kartopu, G., 2011. "The role of transparent conducting oxides in metal organic chemical vapour deposition of CdTe/CdS photovoltaic solar cells". *Thin Solid Films*, Vol. 520, p. 1167.

- Lee, Y. and Anh J-H., 2013. "Graphene-based transparent conductive films". *Nano*, Vol. 8, p. 1330001.
- Pham, V.H., Cuong, T.V., Hur, S.H., Shin, E.W., Kim J.S., Chung, J.S. and Kim E. J., 2010. "Fast and simple fabrication of a large transparent chemically-converted graphene film by spray-coating". *Carbon*, Vol. 48, p. 1945.
- Roh, K.M., Jo, E.H., Chang, H., Han, T.H. and Jang, H.D., 2015. "High performande dye-sensitized solar cells using graphene modified fluorine-doped tin oxide glass by Langmuir-Blodgett technique". *Journal of Slid State Chemistry*, Vol. 224, p. 71.
- Rourke, J.P., Pandey, P.A., Moore, J.J., Bates, M, Kinloch, I.A., Young, R.J. and Wilson, N.R., 2011. "The real graphene oxide revealed: stripping the oxidative debris from the graphene-like sheets". *Angewandte Chemie*, Vol. 50, p. 3173.
- Shi, H.F., Wang, C., Sun, Z.P., Zhou, Y.L., Jin, K.J. and Yang, G.Z., 2015. "Transparent conductive reduced graphene oxide thin films produced by pray coating". *Science China Physics, Mechanics & Astronomy*, Vol. 58, p. 014202.
- Soltani-kordshuli, F., Zabihi, F. and Eslamian, M., 2016. "Graphene-doped PEDOT:PSS nanocomposite thin films fabricated by conventional and substrate vibration-assisted spray coating (SVASC)". *Engineering Science and technology, an international Journal*, Vol. 19, p. 1216.
- Tong, Y., Bohm, S. and Song, M., 2013. "Graphene based materials and their composites as coatings". *Austin Journal of Nanomedicine & Nanotechnology*, Vol. 1, p. 1003.
- Wang, S.J., Geng, Y., Zheng, Q. and Kim J., 2010. "Fabrication of highly conducting and transparent graphene filmes". *Carbon*, Vol. 48, p. 1815.
- Wassei, J.K. and Kaner, R.B., 2010. "Graphene, a promising transparent conductor". *Materials Today*, Vol. 13, p. 52.
- Yamaguchi, H., Eda, G., Mattevi, C., Kim, H. and Chhowalla, M., 2010. "Highly uniform 300 mm wafer-scale deposition od single and multilayered chemically derived graphene thin films". *ACS Nano*, Vol. 4, p. 524.
- Zheng, Q.B., Guzardi, M.M., Wang, S.J., Geng, Y., Li, Z. and Kim, J., 2011. "Improved electrical and optical characteristics of transparent graphene thin films produced by acid and doping treatments". *Carbon*, Vol. 49, p. 2905.
- Zheng, Q.B., Ip, W.H., Lin, X., Yousefi, N., Yeung, K.K., Li, Z. and Kim, J., 2011. "Transparent conductive films consisting of ultralarge graphene sheets produced by Langmuir-Blodgett assembly". *ACS Nano*, Vol. 5, p. 6039.
- Zhu, B.Y., Murali, S., Cai, W., Li, X., Suk, J.W., Potts, J.R. and Ruoff, R.S., 2010. "Graphene and graphene oxide: synthesis, properties, and applications". *Advanced Materials*, Vol. 22, p. 3906.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.