Graphene oxide and reduced graphene oxide used as counter electrode in flexible DSSC devices

Mikel Hurtado-Morales[a,b], Sonia Castarlenas[a], Eduard Romero[b], Gerardo Gordillo[b], Carlos Téllez[a], Joaquín Coronas[a,*]

[a]Department of Chemical and Environmental Engineering and Nanoscience Institute of Aragon (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain

[b]Grupo de Materiales Semiconductores y Energía Solar, Universidad Nacional de Colombia, Carrera 30 45-03, Bogotá, Colombia

*Corresponding author email: coronas@unizar.es. Tel: +34 976 762471

Abstract

Graphene oxide (GO) and reduced graphene oxide (RGO) were synthesized from commercial graphite using an oxidation/reduction exfoliation method and characterized by SEM, TEM, XRD, Raman spectroscopy and UV-VIS absorption. Films of these materials were deposited on polyethylene terephthalate (PET) and soda lime glass flexible supports allowing the measurement of the sheet resistance. This was lower for GO (0.028-0.160 $k\Omega sq^{-1}$) than for RGO (0.391-0.413 $k\Omega sq^{-1}$) coatings, regardless of the support used. Based on these results, GO and RGO films were used to prepare dye sensitized solar cells (DSSC) with a Ru complex as dye, TiO_2 as semiconducting electrode, ITO as counter electrode material and I_3^-/I^- as the redox pair. The highest efficiencies were obtained on PET-based DSSC devices.

Keywords: Graphene, Graphene oxide, Reduced graphene oxide, DSSC, Grätzel cell.

1 Introduction

Graphene is a material consisting of a 2D layer of sp^2 hybridized carbon atoms arranged in a hexagonal geometry [1]. Graphene constitutes the basic structure of other carbon allotropes given that the stacking of several sheets of graphene leads to graphite, wrapping graphene into a sphere produces fullerenes, and rolling it up gives rise to nanotubes. Since it was first isolated in 2004 [2], it has proved to be a very promising material due to its outstanding properties including high electron mobility [3], large mean-free path [2], theoretical surface area close to 2600 m^2g^{-1} [4], better thermal conductivity than most crystals $(5.3 \pm 0.5)\cdot 10^3$ $Wm^{-1}K^{-1}$ [5], Young modulus of 1.0 TPa, ten times greater than steel and with a breaking strength of 40 Nm^{-1} reaching the theoretical limit [6], and an optical transparency of 97.7% [7]. These properties make this material suitable for a large number of applications in electronics [8], photo-chemical cancer treatment [9], biological [10] and physical [11] devices, micro-mechanics [12] and dye sensitized solar cells (DSSC) [13], among others.

Various synthetic routes for graphene production can be found in the literature. a) Mechanical exfoliation from highly oriented pyrolytic graphite by the process known as Scotch tape peeling is based on the method reported by Novoselov et al. in 2004 [2]. This method yields almost perfect graphene sheets which can be used in scientific research. Even though this Scotch tape peeling method is not appropriate for industrial purposes, other mechanical processes such as milling are commercially promising for modifying carbon structures [14]. b) Thermal decomposition of SiC wafers under ultrahigh vacuum conditions yields non-uniform materials [15]; however, these materials may not be suitable for certain applications. c) Epitaxial growth by chemical vapor deposition (CVD) on different metallic substrates is a method for obtaining graphene with very good electronic

properties, but it is very expensive [16]. d) Exfoliation of graphite in different solvents allows obtaining large amounts of graphene-derived materials in a cheaper way but without achieving one sheet material [17, 18]. e) Preparation of graphene by oxidation (Hummers method) [19] and subsequent reduction with hydrazine [18, 20] is the method chosen in this work.

During recent years, research into graphene has been focused on its application in plastic electronics, especially in flexible devices [21, 22]. Nowadays, technologies based on thin film solar cells provide several options for reducing module costs, increasing flexibility and reducing the use of toxic materials such as Cd, Te, Se and In, which are the base of Cu(In,Ga)(Se,S)(CIGSSe) compounds [23-25]. Graphene and its derivatives can be used with different functions in solar cell devices, for example as a hole transporting layer [26, 27] in quantum dot-sensitized solar cells (QDSSCs) based on TiO_2 film photoanodes [28], as a super capacitor electrode [29], as a counter electrode [30, 31], and as a transparent electrode [32]. This last function remains a challenge since the most common materials used as counter electrodes are Sn-doped In_2O_3 (ITO) and F-doped SnO_2 (FTO). However, these materials have low transparency and flexibility [33, 34] and such limitations make graphene a possible alternative material for replacing ITO and FTO.

In this work, the device chosen was a flexible DSSC type cell [35]. We show the results obtained when using a commercial graphite to produce graphene oxide and reduced graphene oxide. These materials were then applied as counter electrodes, demonstrating how the relationship between their photovoltaic properties and different sheet resistances affect the DSSC device performance.

2 Experimental

2.1 Graphite exfoliation

Graphite exfoliation was carried out following a variation of Hummers method [36]. For the oxidation step, raw graphite (0.5 g) with an average size of 5 μm (RANCO 9904, kindly supplied by Richard Anton KG) was mixed slowly with $NaNO_3$ (Acros Organics, 99.0%) (0.375 g) in an acidic solution made of sulfuric acid 5 wt% (Sigma-Aldrich, 95.0-98.0%) (37.5 mL). The mixture was kept refrigerated by means of an ice bath. Afterwards, $KMnO_4$ (Acros Organics, 99.0%) (2.25 g) was slowly added for 30 min, and the resulting suspension was maintained at 369 K under stirring for 2 h. At the end of this time and decreasing the temperature to 333 K, 6 mL of an aqueous solution of H_2O_2 30 wt% (Sigma-Aldrich, 35 wt% in water) was poured into the previous mixture and maintained under stirring for another 2 h.

To remove both ions and impurities coming from the oxidation process, the resulting material was washed with 200 mL of H_2SO_4 3 wt% and H_2O_2 0.5 wt% and placed in an ultrasound bath for 15 min. The suspension was then filtered and the washing was repeated using 200 mL of deionized water. The resulting graphene oxide product (named GO) was dried at 323 K during12 h.

The next step in the graphene production was the reduction of the GO. This process was carried according to a method described in the literature [20]. First of all, NH_3 (Panreac, 25%) was poured into the previously described suspension to maintain the basic media at pH 10.4. Then, 1μL of N_2H_4 hydrate (Sigma-Aldrich, 99.99%) for each 3 mg of GO was added to the GO suspension and stirred at 363 K for 2 h. The GO suspension was

electrostatically stabilized because of the dissociation of carboxyl groups from GO in basic media [37]. Finally, to obtain a powder material, the resulting suspension was filtered, washed with water and dried at 323 K for 6 h, giving rise to reduced graphene oxide (RGO).

2.2 GO and RGO coatings

Aqueous dispersions of 6 mg/mL of GO in water were prepared and stirred for 2 h at room temperature, yielding stable suspensions. Different solvents such as ethanol, methanol, acetone, toluene and hexane were checked, but deionized water appeared to be the best for the purpose of the study.

The coating process of GO and RGO was carried out by adding a controlled amount of the previous water suspensions (1 mL) on soda lime glass (SLG) and polyethylene terephthalate (PET) 2x2 cm^2 substrates, and letting the solvent evaporate at room temperature. At first sight, more homogeneous and consistent distributions of the dispersed RGO and GO materials were achieved on the SLG than on the PET substrates. ITO/PET substrates were acquired from Sigma-Aldrich (150 mm x 150 mm x 0.2 mm and $\leq$10 Ωsq^{-1}), while ITO/SLG substrates (80 mm x 20 mm x 1.0 mm and 30-60 Ωsq^{-1}) were home-made by spray pyrolysis [38].

2.3 Building the DSSC

As seen above, ITO/SLG or ITO/PET were the substrates used for building up the dye sensitized solar cell (DSSC) devices. TiO_2 (rutile, Sigma-Aldrich, 99.99%) was used as semiconducting electrode. A slurry was produced by mixing TiO_2 (1.0 g) with water (10

mL) in an ultrasound bath during 30 min, while for GO and RGO coatings the above described 6 mg/mL suspensions were used. Home-made doctor blade equipment with a micrometric screw system was used to obtain homogeneous and continuous TiO_2 (5 μm), GO (2 μm) and RGO (2 μm) coatings.

The selected dye was tris(2,2'-bipyridyl)dichlororuthenium(II)hexahydrate (TBDR, Sigma-Aldrich, 99.9%) [39]. TBDR (0.0115 g) was dissolved in ethanol (Scharlau, absolute) (2 mL). In addition, iodine crystals (Sigma-Aldrich, 99.8%) (0.127 g) and potassium iodide (Sigma-Aldrich, 99.0%) (0.130 g) were dispersed in ethylene glycol (Sigma-Aldrich, 99%) (10 mL) to produce the liquid media redox pair (I_3^-/I^-). Figure 1a shows a scheme of the described system. The TBDR ethanol solution (2 mL) was spread by means of a syringe on the TiO_2 thin film and dried at 323 K for 10 min. This process is named one TDBR coating. Two different DSSC devices were prepared using GO and RGO as counter electrodes and two different substrates (ITO/PET and ITO/SLG). Each DSSC was built with one and three TDBR coatings to study the influence of the dye molecule excess.

The photovoltaic parameter in the DSSC devices was determined by means of an ISM 490 ISO-TECH photovoltaic solar cell analyzer. A halogen lamp was used to illuminate the cell at a distance of 10 cm in standard illumination conditions: irradiance 1000 Wm^{-2}, spectral distribution AM 1.5 and normal incidence. The open-circuit voltage (V_{OC}) is the maximum voltage available from a solar cell, and this occurs at zero current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current. The short-circuit current

($\mathbf{I_{SC}}$) is the current through the solar cell when the voltage across it is zero (i.e., when the solar cell is short-circuited).

The efficiency is the most commonly used parameter to compare the performance of one solar cell to another. It is defined as the ratio of energy output from the solar cell to input energy from the sun or a solar simulator. In addition to reflecting the performance of the solar cell itself, the efficiency depends on the spectrum and intensity of the incident sunlight and the temperature of the solar cell. The efficiency (η) of a solar cell is determined as the fraction of incident power which is converted to electricity and is calculated by means of equations (1) and (2):

$$P_{max} = V_{OC} \cdot I_{SC} \cdot FF \quad (1)$$

$$\eta = (P_{max}/P_{in}) \cdot 100 \quad (2)$$

where the fill factor (**FF)** is a parameter which in conjunction with $\mathbf{V_{OC}}$ and $\mathbf{I_{SC}}$ determines the maximum power ($\mathbf{P_{max}}$) from a solar cell. Equation (2) shows the relation between the photovoltaic parameters to determine the efficiency (η), $\mathbf{P_{in}}$ being the power of the incident source.

2.4 Characterization

GO and RGO materials were characterized by scanning electron microscopy (SEM) to observe the morphology of the particles and the homogeneous dispersion of the materials on the substrates and composite coatings. The samples were previously covered by a gold thin film since they must be conductive. A JEOL JSM 6400 microscope was used.

Transmission electron microscopy (TEM, with a JEOL-2000 FXII microscope) was used to observe the thin delaminated particles produced. Also, a selected area electron diffraction (SAED) probe was used to determine the crystalline properties of the materials.

Powder X-ray diffraction (XRD) was carried out to characterize raw graphite and RGO phases using a D-Max Rigaku X-ray diffractometer with a copper anode and a graphite monochromator to select CuKα radiation (λ= 1.5418 Å). The measurement was carried out in the 2.5-40º 2 theta range, with a step of 0.03º/s.

Raman spectra were collected at room temperature with a WITEC microRaman spectrometer connected to a confocal microscope and a 532 nm laser. A 20x objective was used and an integration time of 1.5 s. Extreme care was taken to avoid sample damage or laser induced heating, and under these conditions the maximum laser intensity was used. The powder samples were supported on a glass substrate.

UV-VIS spectra were carried out in a V-670 Jasco spectrophotometer from Analytical Instruments using a double-beam, single monochromator design covering a wavelength range from 190 to 2700 nm. This was provided with a photomultiplier detector.

Finally, the sheet resistance was measured using a Fluke multimeter in resistance mode with two fine tips (Figure 1b). The separation between the tips was 1 cm and 5 measurements for each GO or RGO coating were used to calculate an average value.

3 Results and discussion

3.1 Graphite, GO and RGO materials

Comparing to the precursor graphite (Figure 2a), GO samples exhibit finer particles (Figure 2b). As shown by the TEM images (Figure 3b), this material is highly crystalline.

In addition, the SEM images of RGO suggest a relatively high efficiency exfoliation process (Figure 2c).

Figure 3a shows the selected area electron diffraction (SAED) pattern for a GO sample. Rings with six equidistant bright points describing a hexagonal structure are clearly observed. Large area particles composed of superimposed single layers of GO are evidenced in Figure 3b. From this TEM characterization, it can be inferred that the commercial graphite precursor used here was appropriate for obtaining graphene-based ordered structures by the so-called Hummers method.

The SAED for the RGO material is shown in Figure 3c. The electron diffraction pattern on a single layer revealed well-defined bright points and an easily identifiable typical hexagonal pattern. The first bright ring has six differentiable points corresponding to a (100) reflection plane, while the second bright ring also has six points and corresponds to a (110) reflection plane. These two signals are clues suggesting a hexagonal and single layer graphene structure. However, the RGO samples did not show a well-defined SAED pattern when the analysis was carried out in a crystalline zone of multiple layers. TEM imaging of the RGO (Figure 3d) shows graphene-like particles with 1, 2 and 3 stacking layers.

Figure 4 depicts the XRD patterns for raw graphite and reduced graphene oxide (RGO). The XRD pattern of graphite exhibits a sharp peak at 26.6º corresponding to the typical interlayer spacing of 0.32 nm [40]. This XRD peak disappears as the sheets of graphite exfoliate into single layers. The very low intensity XRD peak observed for the RGO in Figure 4 suggests a high exfoliation yield but also the presence of remaining graphite. It is worth mentioning that neither of the diffractograms in Figure 4 were normalized, so that the area below the peak in the parent graphite sample was about 18

times larger than that in the RGO sample. Combining these results with those obtained from the TEM analysis gives an overall picture showing that while strictly speaking we did not produce a pure graphene (single layer) type material, highly exfoliated graphite was obtained in which a graphene hexagonal monolayer was evident in certain domains (Figure 3).

Figure 5 shows the Raman spectra of raw graphite, graphene oxide and reduced graphene oxide. All the materials present a first peak at 1340 cm^{-1} (D peak) corresponding to defects in the structure. Since the peak appears in the starting material, the defects present in the final material are attributable to both the oxidation process and to the defects already present in graphite. In any event, it is worth mentioning that this D peak is clearly larger for RGO than for GO, suggesting a more defective RGO sample. To characterize the exfoliation process, the ratios between the intensities of the G (1565 cm^{-1}) and 2D (2675 cm^{-1}) peaks were calculated. The G peak is due to the doubly degenerate zone center E_{2g} phonons, while the 2D is the second order of zone-boundary phonons [41, 42]. Those ratios were 3.8, 3.1 and 2.2 for graphite, RO and RGO, respectively. This is consistent with a more efficient exfoliation process in the RGO than in the GO sample. In agreement with the results above discussed, our exfoliation process was far from complete since the ratio between G and 2D intensities is about 0.7 in 6-layer materials [41].

Using UV absorption spectroscopy it was possible to identify some peaks corresponding to transitions of interest. Figure 6 shows the UV absorption spectra for GO and RGO suspensions (0.6 mg/mL in deionized water) between 200 and 340 nm. Water was used as blank. No spectrum was achieved for graphite because of the lack of stability of its corresponding suspension. At 230 nm, a shoulder appeared due to particles or nano-sheets of GO. This corresponds to the $\pi-\pi*$ aromatic interaction. In addition, the two

shoulders between 250 and 325 nm can be assigned to the C=O type bond. The UV spectrum for RGO did not show the peaks corresponding to the oxygenated groups, suggesting that the reduction process was carried out successfully. The almost total absence of the 230 nm signal corresponding to the aromatic system means that most of the sample remained as continued to have C-C type bonds, typical for a graphene-like structure.

3.2 Sheet resistance and PV parameters

The indirect measurement of the sheet resistance gives an idea of the surface conductivity of the materials. Figure 7 shows the values of sheet resistance for GO and RGO on ITO/PET and ITO/SLG glass substrates. The sheet resistances for GO films were 0.028 and 0.160 $k\Omega sq^{-1}$ on ITO/PET and ITO/SLG substrates, respectively, i.e. the resistance value was about 6 times larger when GO was dispersed on SLG glass than on PET. When RGO was used these results increased to 0.391 $k\Omega sq^{-1}$ on PET substrate and 0.413 $k\Omega sq^{-1}$ on glass, showing a weaker influence of the substrate in this case. Knowing that the conductivity is inversely proportional to the resistance, a higher conductivity on the polymer substrate of the order of one magnitude was expected. The better electrical properties of GO can be related to the obtaining of a partially delaminated RGO material with a higher concentration of defects, as discussed above. These results are corroborated below with the measurement of solar cell efficiency (η).

Comparing the results shown in Table 1, it can be seen that V_{OC} is higher in PET devices than in SLG devices. This is consistent with the sheet resistance characterization. Besides, better results were achieved when PET was used as substrate and the GO was used as counter electrode with one TBDR coating. However, when TBDR was coated three

times both cells with RGO showed an increase of 26% in the $\mathbf{V_{OC}}$ for the SLG device and an increase of 9.2% for the PET device, while the GO devices showed a reduction of 33% for PET and 61% for SLG. Consequently, the highest efficiency ($\boldsymbol{\eta}$) was achieved by the PET/ITO/TiO_2/TBDR/($\mathbf{I_3^-/I^-}$)/GO/ITO/PET device with 0.25% (one TBDR coating) and by the PET/ITO/TiO_2/TBDR/($\mathbf{I_3^-/I^-}$)/RGO/ITO/PET device with 0.20% (three TDBR coatings). When the amount of dye exceeds the available area to be covered on TiO_2 particles, the dye molecules may aggregate. If solar radiation with enough energy ($h\nu$) can promote electrons from the HOMO to the LUMO level in the dye, they cannot escape immediately to the conduction band of TiO_2 without first overcoming several grain boundaries due to this aggregation process. Then the electron energy is loosened and the dye returns to the HUMO level. However, when the PET DSSC device contains RGO the recombination process seems to be faster with three TDBR coatings. In any event, the efficiencies are low compared with others published with grapheme as counter electrode [13]; however, these configurations and phenomena have not been previously studied in DSSC devices and require further research in the future.

4. Conclusions

Graphene oxide (GO) and reduced graphene oxide (RGO) has been synthesized from commercial graphite using an exfoliation method based on a process described in the literature. This basically consists of exhaustive oxidation with $KMnO_4$ in a strong acidic medium followed by reduction with hydrazine. The characterization carried out by TEM, XRD, Raman and UV-VIS absorption suggested that, strictly speaking, graphene (single

layer) was not obtained. However, highly exfoliated graphite was produced with domains where the presence of graphene in a few layers was evident.

In any event, sheet resistance measurements of GO and RGO films deposited on ITO/polyethylene terephthalate (PET) and ITO/glass supports indicated the suitability of these flexible supports for preparing dye sensitized solar cells (DSSC) with a Ru complex as dye, TiO_2 as a semiconducting electrode, ITO/(PET or glass) as counter electrode material and I_3^-/I^- as the redox pair. Consequently, GO or RGO materials were coated as counter electrodes on either ITO/PET or ITO/glass, giving rise to an enhancement of the DSSC device. In particular, the GO/ITO/PET counter electrode combination produced the highest efficiency observed in this work, even higher than that observed with RGO instead of GO, suggesting better electrical properties for GO than for RGO.

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References

[1] A. V. Rozhkov, G. Giavaras, Y. P. Bliokh, V. Freilikher, F. Nori, Phys. Rep. 503 (2011) 77.
[2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 306 (2004) 666.
[3] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H. L. Stormer, Solid State Commun. 146 (2008) 351.
[4] A. Peigney, C. Laurent, E. Flahaut, R. R. Bacsa, A. Rousset, Carbon 39 (2001) 507.
[5] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, Nano lett. 8 (2008) 902.
[6] C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 321 (2008) 385.

[7] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, Science 320 (2008) 1308.
[8] L. Liao, X. Duan, Mater. Sci. Eng. R-Rep. 70 (2010) 354.
[9] K. Yang, J. Wan, S. Zhang, B. Tian, Y. Zhang, Z. Liu, Biomaterials 33 (2012) 2214.
[10] S. Gurunathan, J. W. Han, V. Eppakayala, J.-H. Kim, Colloid Surface B 102 (2012) 772.
[11] R. Verdejo, C. Saiz-Arroyo, J. Carretero-Gonzalez, F. Barroso-Bujans, M. A. Rodriguez-Perez, M. A. Lopez-Manchado, Eur. Polym. J. 44 (2008) 2790.
[12] M. P. Ariza, M. Ortiz, J. Mech. Phys. Solids 58 (2010) 710.
[13] H. Wang, Y.H. Hu, Energ. Environ. Sci. 5 (2012) 8182.
[14] V. Leon, M. Quintana, M. A. Herrero, J. L. G. Fierro, A. De La Hoz, M. Prato, E. Vazquez, Chem. Commun. 47 (2011) 10936.
[15] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. Mcchesney, T. Ohta, S. A. Reshanov, J. Rohrl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, T. Seyller, Nat. Mater. 8 (2009) 203.
[16] L. Zhao, K. T. Rim, H. Zhou, R. He, T. F. Heinz, A. Pinczuk, G. W. Flynn, A. N. Pasupathy, Solid State Commun. 151 (2011) 509.
[17] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. Mcgovern, B. Holland, M. Byrne, Y. K. Gun'ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, Nat. Nanotechnol. 3 (2008) 563.
[18] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, Adv. Mater. 22 (2010) 3906.
[19] W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 80 (1958) 1339.
[20] X. Gao, J. Jang, S. Nagase, J. Phys. Chem. C 114 (2009) 832.
[21] V. P. Verma, S. Das, I. Lahiri, W. Choi, Appl. Phys. Lett. 96 (2010) 173106.
[22] S. K. Lee, K. Rana, J. H. Ahn, J. Phys. Chem. Lett. 4 (2013) 831.
[23] A. Jager-Waldau, Sol. Energy Mater. Sol. Cells 95, 2011, 1509-1517.
[24] I. Lauermann, C. Loreck, A. Grimm, R. Klenk, Ouml, H. Nig, M. C. Lux-Steiner, C. H. Fischer, S. Visbeck, T. P. Niesen Thin Solid Films 515 (2007) 6015.
[25] D. B. Mitzi, O. Gunawan, T. K. Todorov, K. Wang, S. Guha, Sol. Energy Mater. Sol. Cells 95 (2011) 1421.
[26] Y.-J. Jeon, J.-M. Yun, D.-Y. Kim, S.-I. Na, S.-S. Kim, Sol. Energy Mater. Sol. Cells 105 (2012) 96.
[27] H. Yang, G. H. Guai, C. Guo, Q. Song, S. P. Jiang, Y. Wang, W. Zhang, C. M. Li, J. Phys. Chem. C 115 (2011) 12209.
[28] G. Zhu, T. Xu, T. Lv, L. Pan, Q. Zhao, Z. Sun, J. Electroanal. Chem. 650 (2011) 248.
[29] K. Zhang, L. L. Zhang, X. S. Zhao, J. Wu, Chem. Mater. 22 (2010) 1392.
[30] J.-P. Shim, M. Choe, S.-R. Jeon, D. Seo, T. Lee, D.-S. Lee, Appl. Phys. Express 4 (2011) 052302.
[31] L. Wan, S. Wang, X. Wang, B. Dong, Z. Xu, X. Zhang, B. Yang, S. Peng, J. Wang, C. Xu, Solid State Sci. 13 (2011) 468.
[32] Y. H. Hu, H. Wang, B. Hu, ChemSusChem 3 (2010) 782.
[33] S. I. Noh, H.-J. Ahn, D.-H. Riu, Ceram. Int. 38 (2012) 3735.
[34] C. Sima, C. Grigoriu, S. Antohe, Thin Solid Films 519 (2010) 595.
[35] S. Ito, T. N. Murakami P. Comte, P. Liska, C. Gratzel, M. K. Nazeeruddin, M. Gratzel, Thin Solid Films 519 (2010) 595.

[36] S. Donner, H.-W. Li, E. S. Yeung, M. D. Porter, Anal. Chem. 78 (2006) 2816.
[37] D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, Nat. Nanotechnol. 3 (2008) 101.
[38] R. Riveros, E. Romero, G. Gordillo, Braz. J. Phys. 36 (2006) 1042.
[39] H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, Y. Chen, ACS Nano 2 (2008) 463.
[40] S. D. Perera, R. G. Mariano, N. Nijem, Y. Chabal, J. P. Ferraris, K. J. Balkus Jr, J. Power Sources 215 (2012) 1.
[41] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, L. Wirtz, Nano Lett. 7 (2007) 238.
[42] A.C. Ferrari, J.C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K.S. Novoselov, S. Roth, A.K. Geim, Phys. Rev. Lett. 97 (2006) 187401.

Table and figure captions

Table 1.$\mathbf{V_{OC}}$, $\mathbf{J_{SC}}$ and $\boldsymbol{\eta}$ parameters as a function of TBDR number of coatings

Figure 1. DSSC system (left). Scheme of sheet resistance measurement (right): a) multimeter, b) tip, c) GO or RGO layer, and d) ITO/PET or ITO/SLG substrate.

Figure 2. SEM images for: a) raw graphite, b) GO and c) RGO.

Figure 3. SAED and TEM images of: a,b) GO; c,d) RGO.

Figure 4. XRD patterns of raw graphite and RGO.

Figure 5. Raman spectra of raw graphite, GO and RGO.

Figure 6. Normalized UV absorption spectra for GO and RGO suspensions.

Figure 7. Sheet resistances of GO and RGO on ITO/SLG and on ITO/PET.