Selective band gap manipulation of graphene oxide by its reduction with mild reagents

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ABSTRACT

Graphene oxide (GO) can be used as an electron acceptor for polymeric solar cells but still band gap matching for electron donor and acceptor demands more study. The generation of the exciton in such materials is intimately related to the optical band gap. However, exciton dissociation is related to transport band gap that controls the device performance, particularly the open circuit voltage and short circuit current. Therefore, the modulation of the optical gap is useful because it results into tuning of the transport gap. The interest of the present work is to study the reduction of graphene oxide (GO) at room temperature, using environmental friendly reagents like glucose, fructose and ascorbic acid for the modulation of a band gap. It has been found that glucose and fructose function effectively only in presence of NH_4OH. Although ascorbic acid can reduce GO alone, NH_4OH speeds up the reaction. The optical band gap of GO can be reduced and tuned effectively from 2.7 eV to 1.15 eV.

1. Introduction

In the last ten years, polymer solar cells (PSCs) based on solution process have attracted much attention because of their mechanical flexibility, low-cost, light weight and the ability of large-area and high throughput manufacturing. The most efficient PSCs are based on a mixture of electron donor and acceptor substances at the nanometer (nm) scale to form a bulk heterojunction (BHJ) structure with maximum donor/acceptor interfaces. The donor polymers have been well developed but the only successful acceptor is based on fullerene derivatives. Further improvement in power conversion efficiency (PCE) is anticipated by developing new acceptor materials.

Graphene with a 2D structure has become the hottest research topic in the world due to its outstanding mechanical, electrical, thermal, chemical and optical properties as well as its large specific surface area [1]. Its high carrier transport mobility makes it a promising alternative as an acceptor material. The use of functionalized graphene oxide (GO) [2,3] and quantum dots [4] as acceptor material has been demonstrated in polymer solar cells (PSCs). However, reported power conversion efficiencies (PCE) are low (<1.5%). It is therefore essential to explore the possibilities

to improve the PCE of this type of solar cells and to investigate the relevant mechanism. Density function calculations [5,6] indicate that semiconducting carbon nanotube (CNT) can be used to form P3HT:CNT polymer solar cells, while metallic CNT with zero bandgap (E_g) is detrimental to photovoltaic performance. Xiang et al. [7] proposed an ideal electronic structure of inorganic acceptor with a E_g of ~1.5 eV and a highest occupied molecular orbital (HOMO) level offset of 0.3 eV to allow both a significant absorption as well as a large open circuit voltage. Interestingly, theoretical calculation showed that the bandgap of hydrogenated graphene can be continuously tuned from 0 to 4.66 eV by different H coverage [8]. These results provide a new perspective to the application of graphene-based materials as the acceptor in the polymer solar cells field. The match of energy levels of polymer:graphene derivatives is the key to determine the efficiency. This can be achieved by functionalization through controlled oxidation and reduction processes from natural graphite. It is believed that graphene derivatives can make a great impact on PSC devices and offer the possibilities to accomplish high PCE. A tunable band gap in the intermediate energy range (e.g., 1–3 eV) is highly desirable here.

Graphene oxide (GO) is a heavily oxygenated monolayer material consisting of a variety of oxygen bearing functional groups, such as hydroxyl, epoxy, carbonyl and carboxyl groups. Conventionally, reduction of graphene oxide can be achieved by thermal reduction [9], chemical reduction [10,11] and UV irradiation reduction [12,13]. Mathkar et al. [18] reported a controlled and stepwise reduction of GO using a gas-based hydrazine method at room temperature, allowing a progressive tuning of the optical gap from 3.5 eV down to 1 eV. The reduction of GO by using hydrazine monohydrate to control the band gap of GO from 2.00 eV to 0.02 eV has been reported [14]. An alternative agent reported for chemical reduction is sodium borohydride [11]. The mentioned reagents, hydrazine, hydrazine monohydrate and sodium borohydride are hazardous, toxic and difficult to handle. Some research works have proposed the use of green reducing reagents instead. The main objective of these reports is to achieve the highest possible reduction in graphene [15,16], omitting the intermediate oxidation states of partially reduced graphene oxide. Thus in this systems the modulation of the band gap is unexplored. Some of the reagents which are less toxic, cheaper and environmental friendly and have the potential to reduce graphene oxide includes: glucose, fructose, sucrose [17], and ascorbic acid [18,19], which are commonly heated at 90 °C for 1 h. There is also information regarding thermal reduction of graphene oxide in water using similar conditions without the presence of reduction agents [20]. In this case, heating GO contributes to reduction.

In this work, the effect of reducing agents without the influence of thermal treatment is studied. Graphene oxide is synthesized through a modified Hummers method using oxidants. Then, solutions of glucose, fructose and ascorbic acid are used for reduction. The effect of these reagents on GO reduction and band gap tuning will be compared, allowing future studies and comprehension for band gap matching in

composites of semiconductor polymers, GO and reduced graphene oxide (rGO).

2. Experimental

2.1. Materials

Graphite nanoplatelets from the Superior graphite Co. were used. The $KMnO_4$ powder and KNO_3 were purchased from CTR scientific. Glucose and fructose were purchased from Sigma–Aldrich and ascorbic acid from Mallinckrodt chemicals. All the chemicals were used without further treatment.

2.2. Graphene oxide synthesis

The GO was prepared via a modified Hummers method. In this process 0.5 g of graphite nanoplatelets were added to a solution consisting of 30 ml concentrated H_2SO_4 and 0.295 g of KNO_3. Afterwards 3 g of $KMnO_4$ was added slowly to the mixture to avoid extra temperature rise in a water bath at 14 °C. Then, the mixture was kept in the temperature bath at room temperature for 6 h. Subsequently, centrifugation at 3500 rpm for 10 min was used to separate the compound. The supernatant was discarded and the precipitate was then washed with 10% HCl for 2 times followed by deionized water until the resultant pH was around 3–4. The resulting gel was dispersed with deionized water in an ultrasonic bath for 30 min. This compound will be called herein GO6hOx with a concentration of 4.8 mg/ml.

2.3. Graphene oxide reduction

For the reduction experiments a 1 mg/ml GO6hOx solution was prepared and mixed with an equal volume of a solution with 20 mg/ml of glucose, fructose or ascorbic acid (pH 10 on NH_4OH). Samples were taken with variable intervals of 10 min, 2 days, and 6 days. The 10% HCl was added in order to precipitate the GÓs. The samples were centrifuged and the supernatant was discarded. The solids were suspended in water with the aid of ultrasonic bath, and then diluted to 10 ml on a volumetric flask in order to handle the same concentrations. For UV–Vis analysis, a portion of the diluted samples was taken. For XPS analysis, a portion of the liquid samples was mixed with ethanol, and dried at 60 °C.

2.4. Characterization

Scanning electron microscopy images of the reduced graphene oxides were taken with a field emission scattering electron microscope FEI Nova NanoSEM 200 at high vacuum conditions. For the optical characterization, a VARIAN Cary 5000 UV–Vis–NIR spectrophotometer was used. Band gaps were calculated with the aid of Tauc plot analysis from UV–Vis absorption spectra by assuming indirect band gap, as described elsewhere[21]. Here wavelengths of 200–800 nm were used. For X-ray photoelectron spectroscopy measurements, a Thermo Scientific Escalab 250Xi

spectrometer with monochromatized Al Kα radiation (1486.6 eV) was used.

3. Results and discussion

3.1. Optical properties of reduced graphene oxide (rGO)

Fig. 1 shows UV–Vis spectra for GO6hOx and some of the reduced graphene oxide conditions. In the GO6hOx UV–Vis spectrum (Fig. 1a) a maximum absorption peak arises at a wavelength of 230 nm, which is associated with π–π* transitions originating from sp^2 domains. A "shoulder" at a wavelength of 303 nm is also present, indicating n → π* electron transitions in carbonyl and carboxyl functional groups [22]. For the reduced graphene oxide conditions (Fig. 1b–e) redshift is observed. This is an indication of a reduction reaction taking place on the GO for the 4 reagents. Glucose and fructose act effectively only in the presence of NH$_4$OH [17]. Ascorbic acid reduction (Fig. 1e) has an effect for shifting the maximum absorption spectra from 230 nm (for GO6hOx) to 268 nm, indicating restoration of sp^2 domains. Fructose reduction at pH 10 (Fig. 1d) only makes the maximum absorption of graphene oxide redshift to 236 nm. Nevertheless, a stronger absorption at larger wavelengths in comparison to ascorbic acid is present. A similar effect can be seen for the reduction reaction with glucose at pH 10 (Fig. 1c), while the oxidized and the partially reduced graphenes show their maximum in the UV region. The NH$_4$OH treatment (Fig. 1b) also shows some reduction effect.

It can be seen from the UV–Vis spectra that the light absorption increases with the reduction time for fructose (Fig. 1c), indicating the re-established graphitic structure. The optical band gap calculated from Tauc plots considering an indirect band gap is 2.7 eV for graphene oxide, as shown in Fig. 2. It is clear that the slow reduction results in a stepwise recovery of the π conjugation system as reported elsewhere [21]. The band gap decreases with reduction time to 2.5 eV for 10 min, 1.4 eV for 2 days and 1.15 eV for 6 days. However, when ascorbic acid is used (Fig. 1d), UV–Vis spectra overlap after 10 min reduction, corresponding to a final band gap of 1.55 eV. The behavior observed in Fig. 1e at the 450–800 nm zone for ascorbic acid reduced GO at 2 days and 6 days, could be related to rapid particles agglomeration, as the phenomenon was only seen in this case.

The calculated band gap showed in Table 1 indicates a continuous decrease from 2.7 eV to approximately 1.15 eV after
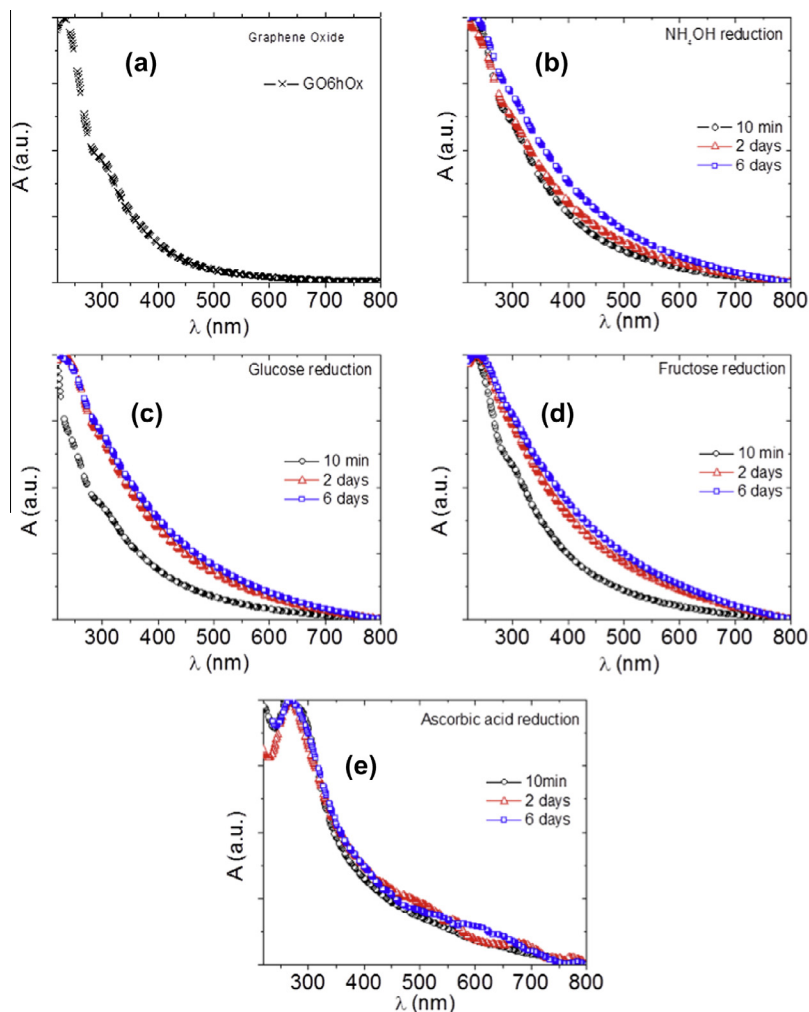

Fig. 1 – Normalized UV–Vis absorption spectra for: (a) GO6hOx and GO reductions at pH 10 with: (b) NH$_4$OH (N), (c) glucose (G), (d) fructose (F) and (e) ascorbic acid (A) for 10 min, 2 days and 6 days. (A color version of this figure can be viewed online.)
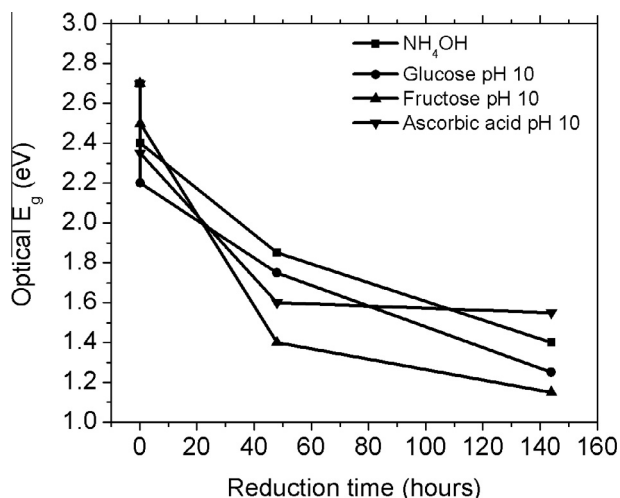
Fig. 2 – Comparison of the optical band gap decrease with different reduction agents and reduction times.

6 days of treatment, suggesting that the tested reducing agents are able to tune the band gap in a controlled way. The band gaps decrease gradually with reduction time, leading to an almost constant value.

3.2. XPS analysis

Fig. 3 presents the normalized C 1s XPS signals after the reduction treatment. The intensity of C–O functional groups located at about 286.6 eV decrease gradually with reduction time in the case of NH_4OH, glucose and fructose (Fig. 3a–c), while the process is faster for ascorbic acid (Fig. 3d) as the spectra remains the same after 10 min of reduction.

Peak fitting of XPS C1s spectra was carried out in order to understand at which extent reduction is occurring. Fig. 4 shows the fitting for GO6hOx. Area percentage of each component was obtained by curve fitting considering.

For NH_4OH a reduction recovery up to 35% in sp^2 domains can be observed. It is possible that epoxide functionalities are unstable and transformed to hydroxyl groups; hence an increase in hydroxyl groups is expected. Carbonyl and carboxyl functionalities are still present after the reduction, indicating that NH_4OH alone is not able to decrease the most oxidized states of carbon. Glucose has a similar effect on reduction as NH_4OH. Up to 37% recovery of sp^2 domains is observed. Meanwhile, the amount of hydroxyl groups is reduced slightly while that of C–O–C is increased. Fructose exhibits improved recovery of sp^2 domains and the amount of this component increases to 41.3% after 6 days. More importantly, gradual restoration of graphitic structure (sp^2) with time offers the possibility to tune the band gap in a controlled way. Among all reagents investigated, ascorbic acid provides the best recovery capability of sp^2 domains (~53% after 6 days) and elimination capability of epoxide and hydroxyl groups. Likely, the observed carbonyl and carboxyl functionalities in this case are partly from the reductants adsorbed on the surfaces of graphite oxide.

In a word, ascorbic acid is the most efficient reducing agent in the current investigation.

Table 1 – Area percentage of functional groups after reduction.

| Constituents after NH_4OH reduction (%)					
Time	C–C sp^2	C–C sp^3	C–O–C and C–OH	C=O	COOH
0	18.73	21.30	52.03	3.54	4.40
10 min	30.66	30.07	28.56	6.95	3.77
2 days	34.88	21.85	32.21	5.80	5.26
6 days	35.30	27.50	22.04	7.47	7.69
Constituents after glucose reduction (%)					
Time	C–C sp^2	C–C sp^3	C–O–C and C–OH	C=O	COOH
0	18.73	21.30	52.03	3.54	4.40
10 min	31.79	25.40	34.25	5.67	2.89
2 days	30.64	19.14	39.54	5.92	4.76
6 days	37.06	20.71	30.52	5.92	5.80
Constituents after fructose reduction (%)					
Time	C–C sp^2	C–C sp^3	C–O–C and C–OH	C=O	COOH
0	18.73	21.30	52.03	3.54	4.40
10 min	32.67	21.57	36.56	5.13	4.07
2 days	34.37	23.69	33.51	2.19	6.25
6 days	41.31	19.99	20.71	1.62	16.38
Constituents after ascorbic acid reduction (%)					
Time	C–C sp^2	C–C sp^3	C–O–C and C–OH	C=O	COOH
0	18.73	21.30	52.03	3.54	4.40
10 min	30.38	21.02	35.02	7.59	5.99
2 days	51.03	17.86	9.85	6.46	14.81
6 days	53.03	16.11	12.14	7.03	11.69
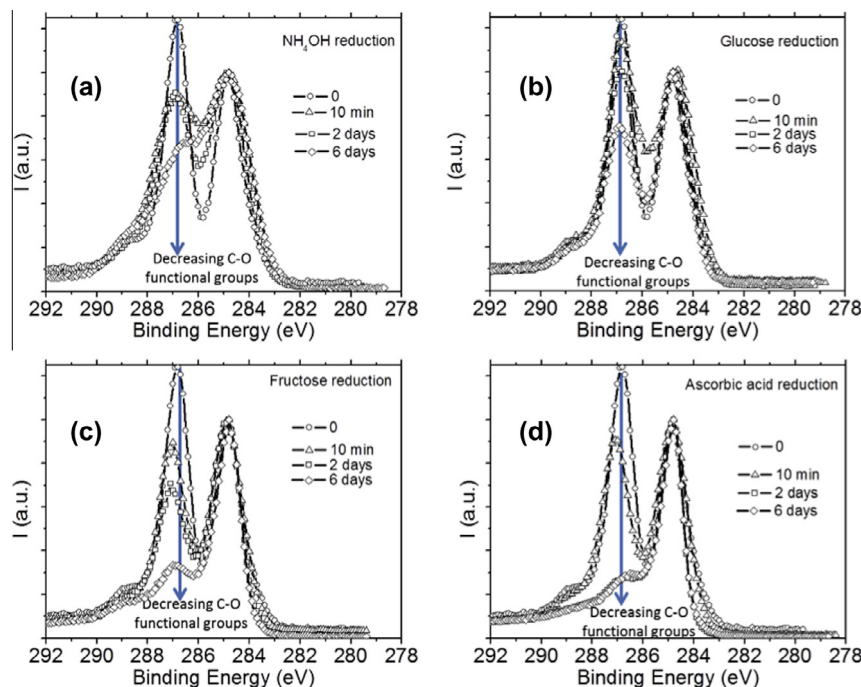
Fig. 3 – XPS C1s spectra for reduction with: (a) NH₄OH; (b) glucose at pH 10; (c) fructose at pH 10; and (d) ascorbic acid at pH 10 after 10 min, 2 days and 6 days. (A color version of this figure can be viewed online.)
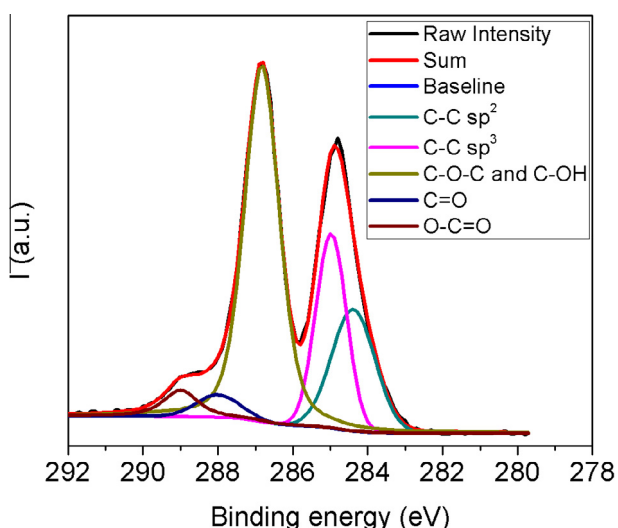

Fig. 4 – XPS C1s fitting for GO6hOx. (A color version of this figure can be viewed online.)

3.3. SEM characterization

Typical SEM micrograph of graphite nanoplatelets as starting material is shown in Fig. 5a. Layered and exfoliated structure with length in microns is present in the nanoplatelets. Fig. 5b shows graphene oxide prepared using the Hummers method and it can be seen that restacking occurs after drying with some exfoliated sheets. Micrographs for the most reduced products are shown in Fig. 5c (using only NH₄OH), 5d (glucose at pH 10), 5e (fructose at pH 10) and 5f (ascorbic acid at pH 10).

The obtained materials at maximum reduction time are rippled and exfoliated. Neither the starting graphite material nor the 6 h oxidized graphite present this wrinkles. This phenomenon is related to the reduction process, indicating that reduced GO flakes are overlapped and not segregated.

4. Conclusions

A method for controlling band gap in graphene oxide was developed. Graphene oxide was synthesized via a modified Hummers method. It has been found that NH₄OH, glucose, fructose and ascorbic acid at pH 10 can be used to tune the band gap. The XPS C1s and UV–Vis spectra show the gradual elimination of epoxide C–O groups and restoration of graphitic structure, corresponding to a decreased value of indirect band gap. Ascorbic acid at pH 10 is more efficient for C–O moieties elimination, resulting in an optical band gap of 1.55 eV. The reduction by fructose and glucose at pH 10 is slower and leads to a stepwise recovery of the π domains, which is preferred in order to control the band gap. The lowest optical band gap 1.15 eV is achieved with fructose at pH 10. The present results are important in the control of a band gap in GO, because most of the reported works use hydrazine or hydrazine monohydrate, which are hazardous and toxic, to achieve the reduction of GO. While the method presented in this work uses glucose, fructose and ascorbic acid and takes longer time for reduction to take place in comparison to hydrazine method, it shows that control of band gap can be achieved to some extent without minimizing the negative impact to the environment. From the point of view of solar cells, it is important because the PCE in organic solar cells depends strongly on the effective dissociation of the exciton; which
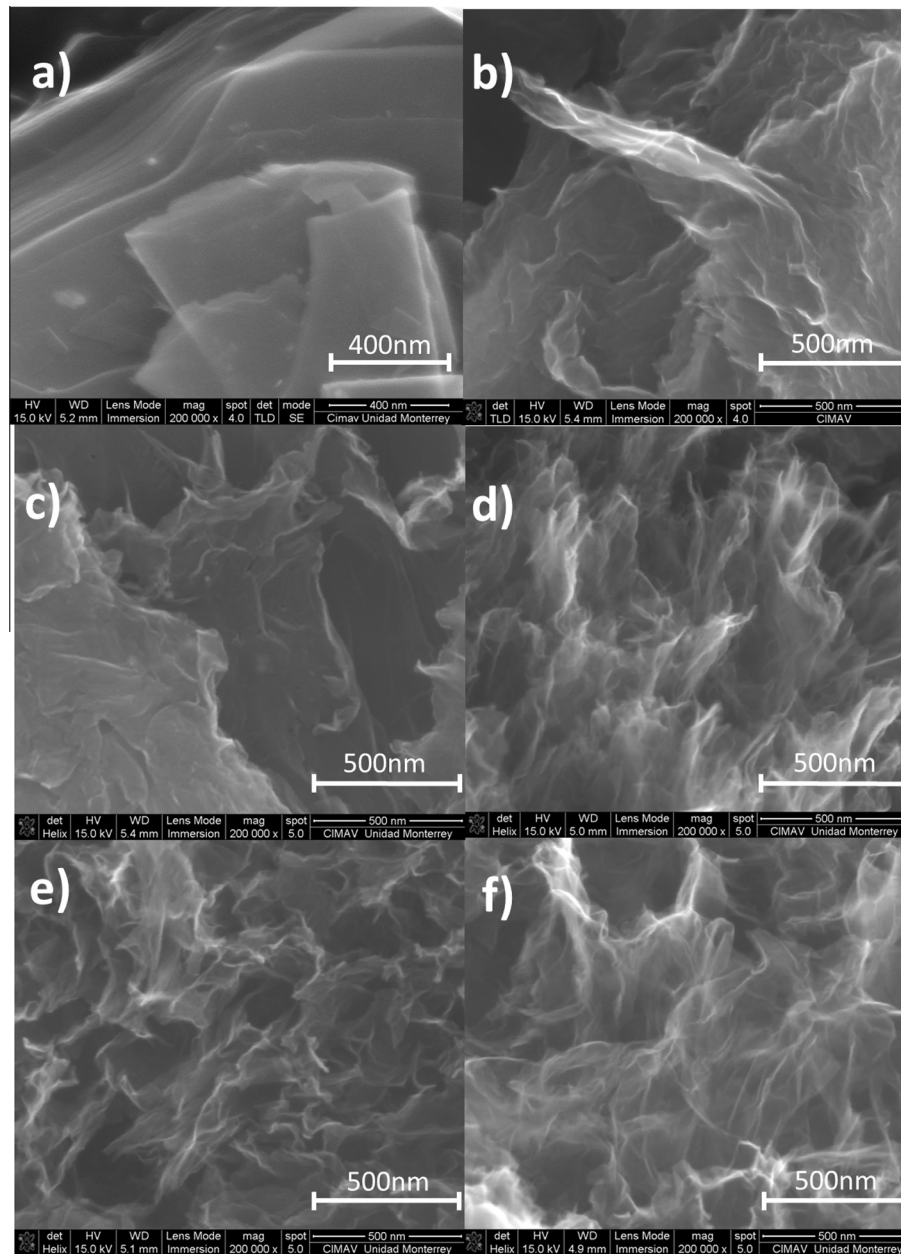
Fig. 5 – SEM micrographs of: (a) starting graphite platelets with 200 kX; (b) graphite oxidized for 6 h by modified Hummer's method, zoom at 200 kX; (c) graphene oxide reduction for 6 days with NH₄OH, (d) graphene oxide reduction for 6 days with glucose at pH 10, (e) graphene oxide reduction for 6 days with fructose at pH 10, (f) graphene oxide reduction for 6 days with ascorbic acid at pH 10.

in terms of energy is favorable only if the exciton binding energy in the acceptor layer is lower than the difference between the ionization potentials of the acceptor and donor materials, as well as the exciton binding energy in the donor layer must be lower than the difference between the electron affinities of the acceptor and donor materials. In order to attain such condition necessarily is required a tuning of the optical bandgap which would result in a tuning of the transport bandgap.

Acknowledgements

REFERENCES

[1] Sun J, Cole MT, Lindvall N, Teo KBK, Yurgens A. Noncatalytic chemical vapor deposition of graphene on high-temperature substrates for transparent electrodes. Appl Phys Lett 2012;100(2).

[2] Hill CM, Zhu Y, Pan S. Fluorescence and electroluminescence quenching evidence of interfacial charge transfer in poly (3-hexylthiophene): graphene oxide bulk heterojunction photovoltaic devices. ACS Nano 2011;5(2):942–51.

[3] Liu Q, Liu Z, Zhang X, Yang L, Zhang N, Pan G, et al. Polymer photovoltaic cells based on solution-processable graphene and P3HT. Adv Funct Mater 2009;19(6):894–904.

[4] Yuan Z, Yu J, Wang N, Jiang Y. Well-aligned ZnO nanorod arrays from diameter-controlled growth and their application in inverted polymer solar cell. J Mater Sci: Mater Electron 2011;22(11):1730–5.

[5] Holt JM, Ferguson AJ, Kopidakis N, Larsen BA, Bult J, Rumbles G, et al. Prolonging charge separation in P3HT−SWNT composites using highly enriched semiconducting nanotubes. Nano Lett 2010;10(11):4627–33.

[6] Kanai Y, Grossman JC. Role of semiconducting and metallic tubes in P3HT/carbon-nanotube photovoltaic heterojunctions: density functional theory calculations. Nano Lett 2008;8(3):908–12.

[7] Xiang H, Wei S-H, Gong X. Identifying optimal inorganic nanomaterials for hybrid solar cells. J Phys Chem C 2009;113(43):18968–72.

[8] Gao H, Wang L, Zhao J, Ding F, Lu J. Band gap tuning of hydrogenated graphene: H coverage and configuration dependence. J Phys Chem C 2011;115(8):3236–42.

[9] Yang D, Velamakanni A, Bozoklu G, Park S, Stoller M, Piner RD, et al. Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy. Carbon 2009;47(1):145–52.

[10] Pei S, Zhao J, Du J, Ren W, Cheng H-M. Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids. Carbon 2010;48(15):4466–74.

[11] Shin H-J, Kim KK, Benayad A, Yoon S-M, Park HK, Jung I-S, et al. Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance. Adv Funct Mater 2009;19(12):1987–92.

[12] Williams G, Seger B, Kamat PV. TiO_2–graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. ACS Nano 2008;2(7):1487–91.

[13] Zhang B, Li L, Wang Z, Xie S, Zhang Y, Shen Y, et al. Radiation induced reduction: an effective and clean route to synthesize functionalized graphene. J Mater Chem 2012;22(16):7775–81.

[14] Shen Y, Yang S, Zhou P, Sun Q, Wang P, Wan L, et al. Evolution of the band-gap and optical properties of graphene oxide with controllable reduction level. Carbon 2013;62:157–64.

[15] Hunt A, Kurmaev EZ, Moewes A. Band gap engineering of graphene oxide by chemical modification. Carbon 2014;75:366–71.

[16] Wang Y, Han C, Liu B, Zhao D, Zhao D, Sun L. A mild and efficient approach for the reduction of graphene oxide. Adv Mater Res 2013;652–654:206–9.

[17] Zhu C, Guo S, Fang Y, Dong S. Reducing sugar: new functional molecules for the green synthesis of graphene nanosheets. ACS Nano 2010;4(4):2429–37.

[18] Fernández-Merino MJ, Guardia L, Paredes JI, Villar-Rodil S, Solís-Fernández P, Martínez-Alonso A, et al. Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions. J Phys Chem C 2010;114(14):6426–32.

[19] Xu Z, Qin L, Xiaohua Z, Chunlan L, Maotian X, Yong L. Reduction of graphene oxide via ascorbic acid and its application for simultaneous detection of dopamine and ascorbic acid. Int J Electrochem Sci 2012;7:5172–84.

[20] Loryuenyong V, Totepvimarn K, Eimburanapravat P, Boonchompoo W, Buasri A. Preparation and characterization of reduced graphene oxide sheets via water-based exfoliation and reduction methods. Adv Mater Sci Eng 2013;2013:5.

[21] Mathkar A, Tozier D, Cox P, Ong P, Galande C, Balakrishnan K, et al. Controlled, stepwise reduction and band gap manipulation of graphene oxide. J Phys Chem Lett 2012;3(8):986–91.

[22] Thakur S, Karak N. Green reduction of graphene oxide by aqueous phytoextracts. Carbon 2012;50(14):5331–9.