Performance and stability of counter electrodes based on reduced few-layer graphene oxide sheets and reduced graphene oxide quantum dots for dye-sensitized solar cells

D. Torres^a, D. Sebastián^{a,b}, M.J. Lázaro^a, J.L. Pinilla^a, I. Suelves^a, A.S. Aricò^b, V. Baglio^b*

^a Instituto de Carboquímica (CSIC), Miguel Luesma Castán 4, 50018 Zaragoza, Spain

^b Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (CNR), Via Salita Santa Lucia sopra Contesse 5, 98126 Messina, Italy

* e-mail: dsebastian@icb.csic.es

Abstract

Graphene-based materials represent an attractive alternative to platinum in dye-sensitized solar cells (DSSC) counter electrodes to contribute to an efficient conversion of solar energy into electricity. Despite the slower kinetics of carbon for the reduction of triiodide compared to platinum, they are characterized by low cost and promising stability. In this work, two different materials are investigated: reduced few-layer graphene oxide (rFLGO) and reduced graphene oxide quantum dots (rGOQD). The electrochemical performance of DSSC assembled with either rFLGO or rGOQD at the counter electrode is correlated to their most important physico-chemical features. The domain size of graphene sheets had an important effect on the performance at the counter electrode, with quantum dots performing 13% higher efficiency than rFLGO, correlated with a higher density of active sites. Both graphene nanostructures exhibited a better stability behavior upon electrochemical cycling and seasoning of the cells as compared to Pt counter electrode.

Keywords: *dye-sensitized solar cells, counter electrode, reduced few-layer graphene oxide, reduced graphene oxide quantum dots, stability*

1. INTRODUCTION

Since the initial work of O'Regan and Grätzel [1], the research in dye-sensitized solar cells (DSSCs) has experienced an exponential increase as they are a low-cost and efficient alternative in photovoltaic devices if compared to conventional silicon solar cells [2]. DSSC components include a photoanode composed of a dye-sensitized wide-bandgap semiconductor, a redox electrolyte (e.g. iodide/triiodide), and a counter electrode (CE) for reducing oxidized species in the electrolyte, generally based on a noble metal thin film. The CE collects the electrons from the external circuit to reduce the redox species used as a mediator in regenerating the sensitizer after electron injection into the photoanode. Platinum is well known as benchmark CE due to its high catalytic activity [J. Mater. Chem. A, 2014, 2, 4474]. Efforts are nowadays directed to decrease the fabrication cost and increase the stability through alternative CE formulations, as reported in recent and extensive review papers [J. Mater. Chem. A, 2014, 2, 4474; Adv. Mater., 2014, 26, 6210-37; Chem. Soc. Rev., 2017, 46, 5975], including metal alloys [3] or carbon materials [4]. In this context, graphene (or reduced graphene oxide) has been postulated as a very promising alternative to platinum [5, 6].

Graphene is the basic structural unit found in all sort of conductive carbon materials among which those based on graphite (where graphene is stacked) have been extensively used as component in electrochemical devices [7]. While any nanostructured carbon material has high electrical and thermal conductivities, oxidation stability, low production cost and low mass density [8], graphene beats all records with its unique electronic properties [9, 10]: very high electron mobility ($10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), ballistic conduction or very high electrical conductivity (10^8 S m^{-1}). These properties are due to the cloud of delocalized electrons inherent to its structure. In the case of graphite, it exhibits electrical conductivity in a very wide range due to its anisotropy (from 10^2 to 10^6 S m^{-1}) [11, 12], since π -electrons move mainly along the 2D sp^2 -carbon network. However, in a graphene or graphite-based carbon material, the electrical conductivity will depend on the connection between stacks. Likewise, the size of the graphene

sheets is also a factor to consider in terms of enhancing its development in the optoelectronic field. In this way, quantum confinement and edge effects make graphene nanoribbons with a width less than 10 nm be semiconductors [13]. Following the same mechanism, narrower graphene fragments like the well-known graphene quantum dots (diameters less than 100 nm) present strong edge effects and quantum confinement [14], generating photoluminescence properties [15] for many potential application including not only the aforementioned solar cells but also LEDs, biosensors or photocatalysis [16, 17].

Motivated by its exceptional properties, graphene has been incorporated in different parts of DSSC: in the photoanode as transparent electrode, semiconducting layer or sensitizer, in the electrolyte or in the counter electrode [18]. Since 2008, when a small amount of graphene (1 wt%) in PEDOT-PSS composite films was demonstrated to enhance CE activity [19], it has been validated as a remarkable material in its use as a DSSC counter electrode in a number of works [5, 6, 18, 20-26].

This work presents the use of reduced graphene oxide materials in the preparation of counter electrodes for DSSC where the edge effects and quantum confinement associated with their small sizes and their functionalization degree could have an important role in terms of catalytic activity for the electro-reduction of triiodide together with a proper stability. Few-layer graphene oxides (FLGO) and graphene oxide quantum dots (GOQD) were obtained from multi-wall carbon nanotubes through a scalable and high yield method and tested in the cell separately where they are partially thermoreduced (complete deoxygenation is not achieved) at 450 °C during the electrode preparation. Graphene domains, defects and oxygen and sulfur functional groups generated during the acidic oxidation process provided them with a good electron conduction and an increased number of active sites (most of which prevail and/or are generated during the reduction stage), respectively, for I_3^-/I^- electrocatalysis. As far as we know, this is the first time rGOQD are tested as counter electrodes in a DSSC, offering values that improve

those exhibited by few-layer graphene material. Stability tests were carried out to assess the resistance to degradation processes related to electrochemical cycling and seasoning effects.

2. EXPERIMENTAL SECTION

2.1 Synthesis of few layer sheets and quantum dots of graphene oxide by carbon nanotubes unzipping

Multiwall carbon nanotubes (MWCNT), whose synthesis procedure is found in [27, 28], were obtained by catalytic methane decomposition in a rotary bed reactor. MWCNT were purified with concentrated HNO_3 during 30 min at boiling temperature to eliminate the catalyst and generate oxygenated surface groups that facilitate the subsequent unzipping [29]. FLGO sheets and GOQD were obtained jointly from the purified MWCNT using the modified Hummers method for their opening and oxidation, ultrasounds for the exfoliation and suspension of the oxidized graphene layers in the liquid medium, and differential centrifugation for final separation in GO-based components [28, 30]. In order to obtain the GO suspension, 1.5 g of MWCNT, 1.5 g of NaNO_3 (purity $\geq 99.0\%$) and 69 ml of H_2SO_4 (96.0 %) were stirred together in an ice bath. 13.8 g of KMnO_4 was slowly added to the mixture under vigorous stirring to obtain an oxidation ratio ($\text{OR} = \text{KMnO}_4/\text{MWCNT}$; wt./wt.) of 10 [28]. After addition of KMnO_4 , temperature was kept below $20\text{ }^\circ\text{C}$ during mixing and then the solution was stirred at $30 \pm 5\text{ }^\circ\text{C}$ for 2 h and at room temperature overnight. After oxidation, a brownish thick paste was formed. Then, 120 ml of deionized water was slowly added while maintaining the temperature below $70\text{ }^\circ\text{C}$. Subsequently, the solution was stirred for 60 min and then diluted with 300 ml of deionized water. A volume of 14 ml of H_2O_2 (33.0 %) was added dropwise turning the solution colour to yellowish brown. Material exfoliation was carried out by sonication for 4 hours. The product (containing both FLGO and GOQD with unreacted MWCNT) was washed by centrifugation at 9500 rpm with HCl (10.0 %) (5 cycles of 5 min with redispersion of the precipitate in new solvent in each cycle), and then with deionized water (2 cycles of 2 h). The

precipitate was redispersed in deionized water by 5 min in a bath of ultrasounds and then centrifuged at 9500 rpm (4 cycles of 1 h) to obtain the GOQD fraction as supernatant. The precipitate was again redispersed in deionized water and centrifuged at 1000 rpm (in cycles of 10 min) to obtain the GOQD fraction as supernatant, and unreacted MWCNT and coarse particles as precipitate. Finally, GOQD and FLGO that accounted for 31 and 62 % of the products obtained, respectively, were dried at 65 °C overnight.

2.2 Physicochemical characterization of FLGO and GOQD

Characterization of FLGO and GOQD was carried out by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), Raman spectroscopy, atomic force microscopy (AFM) and UV/Vis and fluorescence spectroscopies. rFLGO and rGOQD were also characterized by XRD, XPS and Raman. Diffractograms of dried samples were acquired in a diffractometer (Bruker D8 Advance Series 2). The angle range 5°-80° was scanned using 0.02° and 4 s as counting step and time per step. Data were fitted using a structure analysis software (TOPAS, Bruker AXS) including peak deconvolution by fitting to a split pseudo-Voigt functions. Interlayer spacings (d) were calculated from the position of the peaks of the graphite planes: (002)* and (002) applying Bragg's Law [31]. (002)* correspond to the displaced (002) plane [28]. Mean crystallite size (L_c , perpendicular to the graphene layer) was calculated using the Scherrer formula with a value of $K = 0.89$ [31]. The average number of (002) and (002)* graphene layers (n) was estimated as $n = (L_c/d) + 1$ [28].

Raman spectrum of samples was acquired in a confocal Raman microscope (Horiba Jobin-Yvon: LabRAM HR800 UV) equipped with a CCD detector. Scans (21 per sample) were measured from 600 to 3000 cm^{-1} , with exposure times of 5 s, using an Ar laser at 532 nm (2.33 eV), power of 20 mW and a 50X objective. Peak assignment was made according to previous work [28]. I_D/I_G ratios of oxidized and reduced GO samples were calculated from the peak intensities corresponding to disordered (D) and graphitic (G) carbon.

XPS analyses were carried out with a spectrometer (ESCAPlus OMICROM) equipped with a hemispherical electron energy analyser. It was operated at 15 kV and 10 mA using a MgK α X-ray source 1253.6 eV in the non-monochromatic mode and under vacuum ($< 5 \times 10^{-9}$ Torr). Survey scans (1 sweep/200 ms dwell) were acquired between 1200 eV and 0 eV. Pass energy of 50 eV and 20 eV were used for the scans of survey and C1s region, respectively. C1s binding energy (BE) was referenced at 284.5 eV for calibration. The CASA XPS data processing software allowed peak fitting and quantification.

TGA profiles were obtained in a thermobalance (NETZSCH TG 209 F1 Libra, Selb, Germany) from a sample amount of 8 ± 1 mg and using a heat rate of $5 \text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $1000 \text{ }^{\circ}\text{C}$ and N_2 (50 ml min^{-1}).

Morphology of GOQD and FLGO was analyzed using a TEM microscope (Tecnai F30; FEI) equipped with a cannon of 300 KeV and a maximum resolution of $1.5 \text{ \AA}$. Topography of GOQD was visualized using a Multimode 8 scanning probing microscopy (Veeco-Bruker) in tapping mode. Image processing and particles analysis were performed with Gwyddion software.

Optical properties of the GOQD suspension at ambient conditions was characterized in 10 mm pathlength quartz cuvettes using a UV-VIS spectrophotometer (Shimadzu UV-2401PC) and a spectrofluorometer (FluoroMax-P, HORIBA Jobin Yvon). Sample was excited at 355 nm for GOQD).

2.3 Dye-sensitized solar cell electrochemical tests

Working and counter electrodes were prepared on F-doped SnO_2 glass (sheet resistance: $15 \text{ } \Omega/\square$) substrates (FTO). The photo-anode was prepared by first spraying a thin film of TiO_2 aqueous solution, obtained from TiCl_4 (40 mM), and subsequent spray coating deposition of TiO_2 paste from commercial powder (Degussa P90) dispersed in water and iso-propyl alcohol (50% v/v) and Triton surfactant, onto the substrate [32]. Afterwards, electrodes were sintered at $450 \text{ }^{\circ}\text{C}$ for 30 minutes; the sintering process allows the titanium dioxide nanocrystals to melt partially together in order to ensure electrical contact and mechanical adhesion on the FTO.

Dye sensitization was carried out by immersing the sintered electrodes in 0.5 mM ruthenium dye (N719, Solaronix, *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium)) solution in ethanol for about 18 hours.

The electrolyte consisted of 0.4 M LiI, 0.04 M I₂, 0.3 M 4-tertbutylpyridine (TBP) and 0.4 M tetrabutylammonium iodide (TBAI) in acetonitrile.

Carbon materials (FLGO and GOQD) were mixed with a 15% w/w of TiO₂ (Degussa P90) as binder. The powders were dispersed in ethanol. Counter electrodes were prepared by spraying the slurry of graphene based materials onto FTO/glass substrates, and then electrodes were sintered in inert atmosphere at 450 °C for 10 minutes. Under this treatment, FLGO and GOQD are partially reduced so they are labeled as rFLGO and rGOQD, respectively.

A spacer thick 60 µm (Surlyn[®] SX1170-60, Solaronix SA) was used to allocate the electrolyte between the photo-anode and the counter electrode. Generally, the spacing between these electrodes is about 30 µm in the state-of-art DSSCs to avoid ohmic constraints. Nonetheless, being the aim of this work to compare different materials in the same conditions, we have preferred to use a suitable amount of liquid electrolyte in between the two electrodes in order to avoid short circuit effects and improve reproducibility of the cells.

Current-voltage curves of the devices were recorded under simulated AM 1.5 solar illumination (Osram, 300 W) at 25 °C. The incident light intensity was adjusted to 100 mW cm⁻² by using a photometer (3M Photodine Inc.). The cells operating under simulated solar illumination were connected to an Autolab Potentiostat/Galvanostat (Metrohm) equipped with a frequency response analyzer (FRA). The active area of the cells was 0.28 cm² (circle of 6 mm diameter). EIS measurements were carried out at room temperature in the frequency range 100 mHz - 100 kHz at open circuit voltage (OCV); the amplitude of potential pulse was 0.01 V.

3. RESULTS AND DISCUSSION

3.1 Materials synthesis and characterization

A solution containing GO-based materials was obtained as a result of the oxidation/exfoliation process of MWCNT (see TEM pictures of MWCNT in Fig. S1 in the Supplementary Information). These materials -unreacted MWCNT, FLGO and GOQD- were separated by degressive differential centrifugation according to a methodology previously developed for the effective fractionation of the resulting GO materials of the exfoliation of fishbone carbon nanofibers [33]. Centrifugation by degressive rates minimized the entrainment of small particles and maximized its weight yield. Due to a different arrangement of the graphite crystals in nanofibers and nanotubes, the size distribution of GO materials obtained after the oxidation/exfoliation process is different in each case. While fishbone CNF consist of an arrangement of small graphene cones, MWCNT present large concentric graphene sheets forming a tubular structure. The layered morphology of FLGO and GOQD obtained from MWCNT can be seen in Fig. 1, where the profiles of height and size of the latter are included for some representative dots observed by AFM. FLGO sheets (Fig. 1a-b) showed transparent and flake-like shape individuals with a low number of layers as reported before [28]. Likewise, no formation of straight graphene nanoribbons was detected due to the entanglement thereof, what was already claimed by Kosynkin *et al.* [34], and the low selectivity of this method to the longitudinal nanotube unzipping [35]. In the case of GOQD (Fig. 1c and inset), small graphene sp^2 nanodomains can be visualized by AFM. As happened with graphene dots obtained from nanofibers [33], they overlap forming a continuous membrane due to the drying process. GOQD presented diameters and heights below 100 nm and 10 nm, respectively, according to their height profiles (Fig. 1d).

Figure 1. a-b) TEM images of FLGO; c) AFM images and d) height profiles of GOQD (of those numbered in the inset in c)).

The oxidative process resulted in the bond cleavage of the sp^2 graphene network in the nanotube outer wall and the intercalation of oxygenated groups between layers, enabling their subsequent separation or exfoliation. As a result of this intercalation, graphene oxide stacks, whose characteristic (002)* plane is located at $2\theta = 10.9^\circ$ - 11.9° , were clearly observed in the XRD patterns of FLGO and GOQD shown in Fig. 2. Structural data calculated for this one and for (002) plane, also observed by XRD, are listed in Table 1 (peak position and FWHM can be found in Table S1 in the Supplementary Information). The d spacings were 0.745 and 0.810 nm in FLGO and GOQD, respectively, which double that measured in the starting MWCNT (0.337 nm). The presence of graphene/graphite (002) or graphene oxide (002)* stacks evidences that sheets might continue separating into isolated layers which, obviously, do not present this

reflection. In addition, (100) and (101) planes about Bragg angles of 42.9° and 44.5°, respectively, are also found in the spectra. (100) plane corresponds to graphene in-plane reflections and it is more intense the larger the sp^2 domains are [29]. In case of (101) plane, this crosses the graphene stacking obliquely and it increases as the number of layers does [36]. Regarding their transversal sizes, graphene oxide stacks present similar values of L_c (3.3-3.5 nm) and around 5 graphene layers in FLGO and GOQD. Small non-oxidized graphene stacks (1.1 nm and 4 graphene layers in average) were deconvoluted in GOQD diffractogram (in FLGO they were even smaller making their deconvolution impossible). In any case, both materials did not show the presence of stacks of graphene (oxidized or not) with a number of layers above 5. The thermal reduction that both materials suffer during the electrode preparation (rFLGO and rGOQD) recovered the (002) peak at the expense of (002)* due to the approach of the graphene layers after the removal of intercalated oxygenated groups. A small restacking of the exfoliated graphene layers occurred as indicated by the increment in the calculated number of layers (around 7) as well as in the slight increase of the (101) peaks in rFLGO and rGOQD. However, no large structural differences were detected by Raman spectroscopy (spectra in Fig. 3) after reduction, according to their I_D/I_G ratios listed in Table 1 (in the range 0.89-1.00). A reduction temperature of 450 °C was not found to be enough in order to achieve significant structural changes by Raman [37]. However, in case of deconvolution of the first-order Raman spectra, as previously reported in [28], the I_D/I_G ratio for GOQD would be obviously lower. In this regard, rGOQD presents a slightly lower number of defects although it could be due to the stacking suffered by the sample as observed in the 2D growth (I_{2D}/I_G is proportional to the number of graphene layers). D+D' is only observed in samples with significant amounts of defects [38] (observed in all samples but more accentuated in rGOQD). These defects are derived from its limited size (< 100 nm) and, as a consequence, a higher ratio of edge-to-basal carbon atoms.

Figure 2. XRD patterns of FLGO, GOQD, rFLGO and rGOQD.

Figure 3. Raman spectra for FLGO, rFLGO, GOQD and rGOQD (peak fitting according to [28]).

Table 1. Structural parameters of FLGO, GOQD, rFLGO and rGOQD determined by XRD and Raman.

Sample	XRD				Raman
	Plane	d (nm)	L_c (nm)	n	I_D/I_G
FLGO	(002)*	0.745	3.3	5.4	0.94
rFLGO	(002)	0.352	2.1	6.9	1.00
GOQD	(002)*	0.810	3.5	5.4	0.92
	(002)	0.350	1.1	4.1	
rGOQD	(002)	0.349	2.3	7.6	0.89

Atomic compositions measured by XPS for FLGO and GOQD are shown in Table 2. O- and S-based functionalities, which are more numerous in GOQD, are due to the oxidation process and disrupt the electronic conduction on the sp^2 carbon network in graphene. The oxidation/exfoliation process generates graphene oxide sheets with contents of O and S varying from 24.1-29.4 and 3.5-9.6 at. %, respectively. From C1s region deconvolution (Fig. 4a), three components were determined: an asymmetric peak [39] of sp^2 graphitic carbon (C=C) and sp^3 hybridized carbon (C-C) at 284.5 eV, C-O bonds in hydroxyls or epoxides and C-S in sulfonic acid and organosulfates at 286.4-286.7 eV, and C=O bonds in carbonyls or carboxyl groups at 288.4-288.7 eV. Although GOQD had a higher amount of oxygen, this is also bonded to S in sulfur groups. Not in vain, GOQD presents a much larger amount of organosulfates than FLGO. The oxygen content in GOQD is expected to be lower due to a lower relative contribution of in-plane oxygenated groups (hydroxyls and epoxides) as expense of out-plane groups (carbonyls and carboxyls) in thinner graphene domains [33]. In addition, the contribution of the $\pi-\pi^*$ transitions was only found in the case of GOQD at 290.8 eV. The latter is associated with aromatic and unsaturated bonds, which consider a similar value of sp^2 carbon (C=C/C-C) than that measured in FLGO, indicates a possible better electronic conductivity in GOQD. Quantum dots exhibited also photoluminescence due to quantum confinement effects attributed to its smaller size (below 100 nm). As for the S functionalization, the doublets ($p_{3/2}$ and $p_{1/2}$) of two components were identified in the XPS S2p region (Fig. 4c): sulfonic acid ($-SO_3^-$) at 168.1 eV ($p_{3/2}$) and organosulfates ($-SO_4$) at 169.1 eV ($p_{3/2}$) bonded to the graphene carbon structure [40]. Although there is a noticeable difference in the sulfur content of both GO fractions, this is due to a higher content of organosulfates in GOQD. Regarding the reduction effect, FLGO and GOQD which presented C/O ratios of 3.0 and 2.0, respectively, were reduced by the 52 and 40 % removal of oxygen-containing functional groups (both in-plane and out-plane groups) resulting in C/O ratios in rFLGO and rGOQD of 7.6 and 4.4, respectively. The highest oxygen

content in the case of rGOQD also comes from its participation in the remaining organosulfates groups. Indeed, an abrupt desulfurization also occurred after the thermal treatment: rFLGO did not presented S in its composition while rGOQD remained a 1.9 at. % in form of organosulfates. In any case, the reduction of GO materials was accompanied by sp^2 -carbon recovery and the appearance of the π - π^* transition in rFLGO.

Figure 4. Deconvoluted XPS regions: a) C1s of FLGO and GOQD; b) C1s of rFLGO and rGOQD; c) S2p of FLGO and GOQD; d) S2p of rFLGO and rGOQD.

Table 2. Surface atomic composition (XPS).

	Survey (at. %)				C1s (%)				S2p (%)	
	C	O	S	C/O	C=C/C-C	C-O/C-S	C=O	π - π^*	C-SO ₃ ⁻	C-OSO ₃ ⁻
FLGO	71.3	24.1	3.5	3.0	63.9	27.2	8.9	0.0	80.9	19.1

rFLGO	88.4	11.6	0.0	7.6	74.5	14.1	5.8	5.6	0.0	0.0
GOQD	59.6	29.4	9.6	2.0	60.8	24.6	11.4	3.2	18.4	81.6
rGOQD	76.5	17.5	1.9	4.4	73.5	19.3	3.5	3.7	0.0	100.0

According to the TGA and DTG profiles shown in Fig. 5a and 5b, respectively, two main weight losses were appreciated. A 5 and 15 % of weight loss were registered before 150 °C for FLGO and GOQD, respectively, which are attributed to the release of water molecules trapped between graphene oxide layers during their synthesis. Subsequently, a broad band due to the liberation of labile groups of O and S is appreciated from 150 °C to 300 °C [41]. However, a widening of this band towards higher temperature is seen for GOQD, and can be attributed to the loss of organosulfate groups (still present after reduction according to the XPS data). After 350 °C, the removal of more stable O-functionalities takes place.

Figure 5. TGA and DTG of FLGO and GOQD under N₂ with a ramp rate of 5 °C min⁻¹.

3.2 DSSC electrochemical characterization

Fig. 6 shows the photocurrent-voltage (j-V) characteristics obtained for DSSCs assembled with rFLGO and rGOQD as counter electrodes, and Table 3 summarizes the most important photovoltaic parameters. Two different CE thicknesses were assessed, 15 and 25 μm . In conventional Pt counter electrodes, the film thickness has shown to have no significant effect on the j-V curve according to Fang and coworkers [42]. In this work, the thickness of rFLGO has shown a slight influence on the short-circuit current while the amount of rGOQD affects the j-V in the region closer to open circuit potential (OCP). In the first case, a larger amount of rFLGO (thicker electrode of 25 μm) results in a larger density of carbon active sites where the triiodide can be effectively reduced to iodide, thus enhancing the performance of the DSSC. In the case of rGOQD, it is the fill factor that is more sensitive to the variation of thickness, increasing from 0.48 to 0.52 when the thicker electrode is used. This can be attributed to differences in electrical conduction of the rGOQD thin film, that influence the series resistance of the cells, rather than an increase of catalytic active sites as in the case of rFLGO.

Figure 6. DSSC polarization curves with (a) rFLGO or (b) rGOQD at the counter electrode.

Effect of film thickness on initial performance

By comparing the different j - V curves, it appears that rGOQD based counter electrodes perform 13% better than rFLGO. Despite the larger oxygen and sulfur content of rGOQD, the morphology of quantum dots appears to favor the electro-reduction of triiodide to iodide at the counter electrode. The lower C/O ratio for rGOQD (4.4) compared to rFLGO (7.6) indicates a greater oxygen content and a higher density of edge to basal atoms in the former, available to reduce the triiodide species at the surface of the counter electrode. In the annealing step of the electrodes, the sulfonic acid groups and most labile oxygen groups are removed at 450 °C. The rGOQD possess more functional groups, including the remnant of organosulfates, in addition to a lower carbon sp^2 content due to its smaller size, which translates into a greater number of electrocatalytic sites for the electro-reduction of triiodide to iodide, including both network defects and edges.

A Pt counter electrode was prepared and assembled in the same way that the rest of the cells for the sake of comparison, and the results are included in Table 3. Notice that the performances here reported are in line with our previous works concerning other carbon materials [43]. In the present work, we have preferred to use a simple photoanode configuration to avoid side effects, and a thick spacer to contain the electrolyte in order to improve reproducibility and stability, focusing our attention on the behavior related only to the counter electrode. Possibly, using a more efficient but complex photoanode and a thinner spacer to contain the electrolyte should lead to higher efficiency values, much closer to the state of the art.

The reaction kinetics of Pt are much faster than those observed for the carbon materials, as evidenced by the better efficiency (η) and short-circuit current (j_{sc}), which is related to a much lower charge transfer resistance (R_{ct}). Whereas, the OCP is between 20 and 34 mV higher for the DSSCs assembled with carbon materials in the CE compared to Pt CE.

Table 3. Performance characteristics of DSSC with different counter electrodes.

Counter electrode	η [%]	OCP [V] ^(a)	j_{sc} [mA cm ⁻²] ^(b)	FF [-] ^(c)	R_{ct} [Ω cm ²] ^(d)
rFLGO15	2.1	0.776	5.1	0.53	52.1
rFLGO25	2.2	0.770	5.3	0.54	35.7
rGOQD15	2.3	0.772	6.2	0.48	107
rGOQD25	2.5	0.784	6.1	0.52	64.8
Pt	3.6	0.749	8.0	0.60	10.5

^{a)} Open circuit potential; ^{b)} Short circuit current; ^{c)} Fill factor; ^{d)} Charge transfer resistance

The stability of DSSC has often been overlooked and it has become an unknown characteristic in the research and development of new component formulations, even though it is a very relevant aspect for commercialization [44]. There are not standardized procedures to assess the stability and degradation processes. In this work, we have analyzed two different aspects in DSSC stability: the electrochemical stability and the seasoning effect, both relying on the behavior of the counter electrode, among others.

The electrochemical stability of CEs based on rFLGO and rGOQD was assessed by continuously cycling the DSSCs up to a total of 100 cycles at a scan rate of 100 mV s⁻¹ between open circuit and short circuit potentials and under illumination. The j-V curves before and after cycling are represented in Fig. 7. A slight decrease of short-circuit current is exhibited after cycling for the carbon materials, being more evident in the case of the rGOQD based DSSC. In the literature, few works report the electrochemical stability of CEs upon potential cycling, generally employing a three electrode cell configuration to establish the electrochemical behavior of Pt.

Figure 7. Effect of potential cycling between short circuit and open circuit potentials under illumination on the polarization curve. (a) rFLGO, (b) rGOQD, (c) Pt

The efficiency of DSSCs assembled with rFLGO or rGOQD counter electrodes barely changes after potential cycling (decrease < 5%), whereas the one based on Pt CE exhibits a 20% loss. Syrokostas and coworkers ascribed the degradation of Pt to its slow dissolution in the electrolyte with time [45]. This source of performance loss seems negligible in the case of carbon based electrode due to their chemical and electrochemical stability under the working

conditions of the cell. Unlike Pt, carbon materials exhibit a larger electrochemical stability towards I₂ in the potential window of operation of a DSSC [22].

Table 4. Performance characteristics of DSSC with different counter electrodes after 100 cycles between open circuit and short circuit potentials.

Counter electrode	η [%]	OCP [V] ^(a)	j_{sc} [mA cm ⁻²] ^(b)	FF [-] ^(c)	R_{ct} [Ω cm ²] ^(d)
rFLGO15	2.3	0.765	5.3	0.57	37.4
rFLGO25	2.2	0.760	5.2	0.56	28.5
rGOQD15	2.3	0.770	6.1	0.49	89
rGOQD25	2.4	0.786	5.8	0.53	57.1
Pt	2.9	0.749	7.8	0.50	19.5

^{a)} Open circuit potential; ^{b)} Short circuit current; ^{c)} Fill factor; ^{d)} Charge transfer resistance

Other technique to assess the stability of DSSCs is by monitoring the performance of a cell during a seasoning period, which has been more often used in the published literature. Typically, cells are stored in the dark at room temperature and open circuit potential. Different phenomena contribute to the loss in performance under such conditions, like dye degradation, or reaction of components with the electrolyte, like the counter electrode or the sealing materials. Fig. 8(a-c) shows *j*-*V* curves of different DSSCs assembled with rFLGO, rGOQD and Pt at the CE and the variation with time. Between one curve and the subsequent one, the cells were stored under the same conditions of temperature, darkness, relative humidity and pressure. The only differing aspect among them was the counter electrode, since the cells were

assembled using reproducible photoanodes, the same electrolyte and sealing materials and closing clamp force.

Figure 8. Effect of passive seasoning (keeping the cell in the dark at OCP) on the polarization curves for (a) rFLGO, (b) rGOQD and (c) Pt at the counter electrode. (d) Peak power density evolution upon seasoning, relative to initial power.

All cells present a decrease of performance upon seasoning, mainly accounting from the loss of short-circuit current density since the open circuit potential slightly increases with time. This can be better analyzed by the comparison of the evolution of maximum power density of each

cell with time, referred to the initial value, as depicted in Fig. 8(d). After prolonged seasoning of more than 100 hours, the DSSC based on Pt CE shows a larger decrease of power, with a loss accounting for more than 50%. Koo and coworkers attributed the loss of efficiency in ageing of Pt to the increase of charge transfer resistance related to CE-electrolyte interface [46]. Both rGO-based CE exhibited in our case a better stability, with a decay in the order of 40% after more than 200 h. The decay is mainly attributable to the loss of short-circuit current, which could be ascribed in part to a loss of active sites in the CE. However, as several degradation processes occur simultaneously, the power loss could also be caused by electrolyte or photoanode degradation phenomena. In any case, it is clear that the DSSC assembled with rGO-based CE exhibit superior stability than Pt, regardless the source of degradation.

4. CONCLUSIONS

In this work, the successful preparation of few-layer graphene oxide and graphene oxide quantum dots from multiwall carbon nanotubes is reported and applied as counter electrodes of dye-sensitized solar cells. The cells assembled with rGOQD exhibited a 13% superior performance than rFLGO despite the larger content of oxygen, which may cause a poorer electron conduction. This indicates that the small size of the dots, as evidenced by atomic force microscopy and Raman spectroscopy, had an important role in the catalytic activity of carbon sites for the electro-reduction of triiodide to iodide. Moreover, the electrochemical stability was assessed by potential cycling and the chemical resistance was evaluated by seasoning of the cells. A comparison was carried out with a Pt-based counter electrode. The enhanced behavior in terms of resistance to degradation processes compared to Pt point out to a promising application of graphene-based counter electrodes for the efficient conversion of solar energy to electricity in DSSC.

Acknowledgements

ICB-CSIC authors acknowledge the Raw Materials Network of Infrastructure “ITO substitution in opto-electronic devices” (European Union), and the funding of the FEDER and the Spanish Science and Universities Ministry (MICINN) (ENE2011-28318-C03-01 and ENE2014-52189-C02-01-R). JLP and DS thank MICINN for their Ramón y Cajal research contracts (RyC-2013-12494 and RyC-2016-20944).

References

- [1] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, *Nature*, 353 (1991) 737.
- [2] J. Gong, K. Sumathy, Q. Qiao, Z. Zhou, Review on dye-sensitized solar cells (DSSCs): Advanced techniques and research trends, *Renew. Sust. Energ. Rev.*, 68 (2017) 234-246.
- [3] Q. Tang, J. Duan, Y. Duan, B. He, L. Yu, Recent advances in alloy counter electrodes for dye-sensitized solar cells. A critical review, *Electrochim. Acta*, 178 (2015) 886-899.
- [4] M. Chen, L.-L. Shao, Review on the recent progress of carbon counter electrodes for dye-sensitized solar cells, *Chem. Eng. J. (Lausanne)*, 304 (2016) 629-645.
- [5] H. Wang, Y.H. Hu, Graphene as a counter electrode material for dye-sensitized solar cells, *Energy & Environmental Science*, 5 (2012) 8182-8188.
- [6] D. Tasis, Recent Progress on the Synthesis of Graphene-Based Nanostructures as Counter Electrodes in DSSCs Based on Iodine/Iodide Electrolytes, *Catalysts*, 7 (2017) 234.
- [7] C. Hou, M. Zhang, A. Halder, Q. Chi, Graphene directed architecture of fine engineered nanostructures with electrochemical applications, *Electrochim. Acta*, 242 (2017) 202-218.
- [8] W. Zhang, A.A. Dehghani-Sanij, R.S. Blackburn, Carbon based conductive polymer composites, *J Mater Sci* 42 (2007) 3408-3418.
- [9] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nature Materials*, 6 (2007) 183.
- [10] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric Field Effect in Atomically Thin Carbon Films, *Science*, 306 (2004) 666-669.
- [11] J.C. Charlier, J.P. Issi, Electrical conductivity of novel forms of carbon, *Journal of Physics and Chemistry of Solids*, 57 (1996) 957-965.
- [12] K. Kinoshita, *Carbon: electrochemical and physicochemical properties*, 1988.
- [13] X. Li, X. Wang, L. Zhang, S. Lee, H. Dai, Chemically Derived, Ultrasoft Graphene Nanoribbon Semiconductors, *Science*, 319 (2008) 1229-1232.
- [14] L.A. Ponomarenko, F. Schedin, M.I. Katsnelson, R. Yang, E.W. Hill, K.S. Novoselov, A.K. Geim, Chaotic Dirac Billiard in Graphene Quantum Dots, *Science*, 320 (2008) 356-358.
- [15] D. Pan, J. Zhang, Z. Li, M. Wu, Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots, *Adv. Mater.*, 22 (2010) 734-738.
- [16] L. Li, G. Wu, G. Yang, J. Peng, J. Zhao, J.-J. Zhu, Focusing on luminescent graphene quantum dots: current status and future perspectives, *Nanoscale*, 5 (2013) 4015-4039.
- [17] Z. Zhang, J. Zhang, N. Chen, L. Qu, Graphene quantum dots: an emerging material for energy-related applications and beyond, *Energy Environ. Sci.*, 5 (2012) 8869-8890.
- [18] J.D. Roy-Mayhew, I.A. Aksay, Graphene Materials and Their Use in Dye-Sensitized Solar Cells, *Chem. Rev. (Washington, DC, U. S.)*, 114 (2014) 6323-6348.
- [19] W. Hong, Y. Xu, G. Lu, C. Li, G. Shi, Transparent graphene/PEDOT-PSS composite films as counter electrodes of dye-sensitized solar cells, *Electrochem. Commun.*, 10 (2008) 1555-1558.

- [20] J.D. Roy-Mayhew, G. Boschloo, A. Hagfeldt, I.A. Aksay, Functionalized Graphene Sheets as a Versatile Replacement for Platinum in Dye-Sensitized Solar Cells, *ACS Appl. Mater. Interfaces*, 4 (2012) 2794-2800.
- [21] J.D. Roy-Mayhew, D.J. Bozym, C. Punckt, I.A. Aksay, Functionalized Graphene as a Catalytic Counter Electrode in Dye-Sensitized Solar Cells, *ACS Nano*, 4 (2010) 6203-6211.
- [22] D.W. Zhang, X.D. Li, H.B. Li, S. Chen, Z. Sun, X.J. Yin, S.M. Huang, Graphene-based counter electrode for dye-sensitized solar cells, *Carbon*, 49 (2011) 5382-5388.
- [23] S.S. Nemala, K.S. Aneja, P. Bhargava, H.L.M. Bohm, S. Mallick, S. Bohm, Novel high-pressure airless spray exfoliation method for graphene nanoplatelets as a stable counter electrode in DSSC, *Electrochim. Acta*, 285 (2018) 86-93.
- [24] A. Kaniyoor, S. Ramaprabhu, Thermally exfoliated graphene based counter electrode for low cost dye sensitized solar cells, *J. Appl. Phys.*, 109 (2011) 124308.
- [25] R. Cruz, J.P. Araújo, L. Andrade, A. Mendes, Transparent graphene-based counter-electrodes for iodide/triiodide mediated dye-sensitized solar cells, *Journal of Materials Chemistry A*, 2 (2014) 2028-2032.
- [26] H. Choi, H. Kim, S. Hwang, W. Choi, M. Jeon, Dye-sensitized solar cells using graphene-based carbon nano composite as counter electrode, *Sol. Energy Mater. Sol. Cells*, 95 (2011) 323-325.
- [27] D. Torres, J.L. Pinilla, M.J. Lázaro, R. Moliner, I. Suelves, Hydrogen and multiwall carbon nanotubes production by catalytic decomposition of methane: thermogravimetric analysis and scaling-up of Fe–Mo catalysts, *Int. J. Hydrogen Energy*, 39 (2014) 3698-3709.
- [28] D. Torres, J.L. Pinilla, R. Moliner, I. Suelves, On the oxidation degree of few-layer graphene oxide sheets obtained from chemically oxidized multiwall carbon nanotubes, *Carbon*, 81 (2015) 405-417.
- [29] D. Torres, J.L. Pinilla, I. Suelves, Unzipping of multi-wall carbon nanotubes with different diameter distributions: Effect on few-layer graphene oxide obtention, *Appl. Surf. Sci.*, 424 (2017) 101-110.
- [30] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.*, 80 (1958) 1339-1339.
- [31] J. Biscoe, An x-ray study of carbon black, *J. Appl. Phys.*, 13 (1942) 364-371.
- [32] V. Baglio, M. Girolamo, V. Antonucci, A.S. Aricò, Influence of TiO₂ film thickness on the electrochemical behaviour of dye-sensitized solar cells, *Int. J. Electrochem. Sci.*, 6 (2011) 3375-3384.
- [33] D. Torres, J.L. Pinilla, E.M. Galvez, I. Suelves, Graphene quantum dots from fishbone carbon nanofibers, *RSC Adv.*, 6 (2016) 48504-48514.
- [34] D.V. Kosynkin, A.L. Higginbotham, A. Sinitskii, J.R. Lomeda, A. Dimiev, B.K. Price, J.M. Tour, Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons, *Nature*, 458 (2009) 872-876.
- [35] A.L. Higginbotham, D.V. Kosynkin, A. Sinitskii, Z. Sun, J.M. Tour, Lower-defect graphene oxide nanoribbons from multiwalled carbon nanotubes, *ACS Nano*, 4 (2010) 2059-2069.
- [36] D.K. Singh, P.K. Iyer, P.K. Giri, Diameter dependence of interwall separation and strain in multiwalled carbon nanotubes probed by X-ray diffraction and Raman scattering studies, *Diamond Relat. Mater.*, 19 (2010) 1281-1288.
- [37] S.H. Huh, Thermal Reduction of Graphene Oxide, in: S. Mikhailov (Ed.) *Physics and Applications of Graphene - Experiments*, InTech2011, pp. 73-90.
- [38] L.G. Cançado, A. Jorio, E.H.M. Ferreira, F. Stavale, C.A. Achete, R.B. Capaz, M.V.O. Moutinho, A. Lombardo, T.S. Kulmala, A.C. Ferrari, Quantifying Defects in Graphene via Raman Spectroscopy at Different Excitation Energies, *Nano Lett.*, 11 (2011) 3190-3196.
- [39] H. Estrade-Szwarczkopf, XPS photoemission in carbonaceous materials: A "defect" peak beside the graphitic asymmetric peak, *Carbon*, 42 (2004) 1713-1721.
- [40] B. Garg, T. Bisht, Y.C. Ling, Graphene-based nanomaterials as heterogeneous acid catalysts: A comprehensive perspective, *Molecules*, 19 (2014) 14582-14614.
- [41] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, 45 (2007) 1558-1565.

- [42] X. Fang, T. Ma, G. Guan, M. Akiyama, T. Kida, E. Abe, Effect of the thickness of the Pt film coated on a counter electrode on the performance of a dye-sensitized solar cell, *J. Electroanal. Chem.*, 570 (2004) 257-263.
- [43] D. Sebastián, V. Baglio, M. Girolamo, R. Moliner, M.J. Lázaro, A.S. Aricò, Carbon nanofiber-based counter electrodes for low cost dye-sensitized solar cells, *J. Power Sources*, 250 (2014) 242-249.
- [44] S. Yun, P.D. Lund, A. Hinsch, Stability assessment of alternative platinum free counter electrodes for dye-sensitized solar cells, *Energy & Environmental Science*, 8 (2015) 3495-3514.
- [45] G. Syrokostas, A. Siokou, G. Leftheriotis, P. Yianoulis, Degradation mechanisms of Pt counter electrodes for dye sensitized solar cells, *Sol. Energy Mater. Sol. Cells*, 103 (2012) 119-127.
- [46] B.K. Koo, D.Y. Lee, H.J. Kim, W.J. Lee, J.S. Song, H.J. Kim, Seasoning effect of dye-sensitized solar cells with different counter electrodes, *Journal of Electroceramics*, 17 (2006) 79-82.