

A comparative study of electrochemical performances of carbon nanomaterial-modified electrodes for DNA detection. Nanotubes or graphene?

Daniela F. Bález¹ · Soledad Bollo¹

Received: 17 May 2015 / Revised: 13 July 2015 / Accepted: 27 July 2015 / Published online: 8 August 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract A comparative study about the electrochemical response of glassy carbon electrode modified with four different carbon nanomaterial (CNM) against dsDNA is reported. The CNM used were oxidized and nonoxidized multiwalled carbon nanotubes (MWNT-OX and MWNT, respectively), graphene oxide (GO) and chemically reduced graphene oxide (RGO) and dispersed in 3:1 chitosan/water mixture. The electrodes were characterized by cyclic voltammetry, scanning electrochemical microscopy, and contact angle measurements. The results showed that the type and degree of oxidation have a strong effect on the electroactivity of the modified electrode. GCE/RGO clearly exhibited the most electroactive surface among the CNMs, demonstrating that the graphitic structure is highly important. A more sensitive electrochemical response against dsDNA was obtained when GCE/RGO electrode was used. Therefore, RGO is the CNM recommended for further consideration in the development of DNA biosensors.

Keywords Carbon nanotube · Graphene · Electrochemical · Chitosan · DNA

Introduction

Since the introduction of carbon nanomaterials (CNM), a large number of CNM-based electrochemical (bio)sensors have been developed, demonstrating the great value provided by the incorporation of these materials on the transducer surface [1, 2]. The first reports were focused on carbon nanotube (CNT)-based materials [3, 4]; more recently, there have been many reports on the advantages of using graphene derivatives (Gr) [5–7].

Each material, CNT or Gr, has its own advantages that allow for obtaining better electrical conductance, a large area and a wide variety of possible structural modifications. Thus, currently CNT and Gr are considered to be some of the more versatile materials used in biosensor development [6].

However, a review of the scientific literature reveals a dearth of reports comparing the use of these materials for the detection of a specific analyte. The majority of the published works describe new systems using a unique nanomaterial that are compared with other similar systems from the literature. Although these comparisons show that a specific system is more sensitive and selective than another, they are complicated by the highly variable origins of the CNM.

The first comparative analyses of these nanomaterials appeared over the last 5 years. A wide-ranging survey of both nanomaterials was performed by Yang et al. [8] who described the latest advances in electrochemical, electrical, and optical biosensors that use carbon nanotubes and graphene and critically compared their performance. They concluded that while there are still many challenges in their fabrication and handling, CNM have a bright future in terms of biosensor development.

Additionally, several reports comparing graphene and nanotubes as materials for electrochemical sensors have appeared in recent years. Cheng et al. [9] investigated the

✉ Soledad Bollo
sbollo@ciq.uchile.cl

¹ Centro de Investigación de Procesos Redox (CiPRex) and Advanced Center for Chronic Diseases (ACCDiS), Departamento de Química Farmacológica y Toxicológica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile

interactions between lectins and carbohydrates using field-effect transistor (FET) devices containing either graphene or single-walled carbon nanotubes (SWNTs). Their main results showed that SWNT-FET exhibits a larger response and better selectivity than Gr-FET. They proposed that this difference is due to the structural differences between the materials (1D versus 2D) as well as due to the more favorable lectin binding to sugar moieties attached to the SWNT surface.

In 2013, Zheng et al. [10] compared the use of graphene and multiwalled carbon nanotubes (MWCNTs) as nanomaterials for fabrication of electrochemical glucose biosensors using glucose oxidase (GOx). They reported that both sensors showed the same linear range for blood glucose in humans. However, direct electron transfer between the GOx and the modified surface was only observed for the MWCNT-based biosensor; this sensor also provided higher current signals (by a factor of four) than the graphene-modified electrode.

Nevertheless, until now, no comparative studies have been conducted on the performance of nanotubes and graphene in DNA biosensors, in spite of abundant reports of individual use of different CNM.

In the present work, a comparative study of four different CNM on the double-stranded DNA (dsDNA) electrochemical response using modified glassy carbon electrode (GCE) is reported. We have evaluated oxidized and nonoxidized multiwalled carbon nanotubes (MWNT-OX and MWNT, respectively) and two graphene derivatives: graphene oxide (GO) and chemically reduced graphene oxide (RGO). To avoid the introduction of new variables and enable a simpler comparison, the dispersions were prepared according to the methodology described in our previous works on DNA biosensors [11–14]. The electrodes were characterized by cyclic voltammetry; scanning electrochemical microscopy (SECM) and differential pulse voltammetry were the electroanalytical techniques to evaluate the figure of merit against dsDNA.

Experimental

Materials and reagents

Glutaraldehyde (25 % v/v in water) was received from Aldrich and used at 3 % (v/v). Double-stranded calf thymus DNA (dsDNA) (activated and lyophilized, cat. no. 4522), ferrocenemethanol (FcOH) and medium-molecular-weight chitosan (CHIT) (cat. no. 44887-7) were purchased from Sigma. Buffer solutions with 0.20 M formate and a pH of 5.00 and with 0.1 M phosphate and a pH of 7.00 were used for DNA adsorption and electrode characterization, respectively. Graphene oxide (GO) and reduced oxide graphene (RGO) were purchased from GRAPHENEA (Spain), and multiwalled

carbon nanotubes (MWNT) 1–5 μm in length were obtained from NanoLab (USA).

Oxidized carbon nanotubes (MWNT-OX) was prepared as described previously, briefly 200 mg of MWNTs immersed in 130 mL of a mixture of 3 M $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1) solution, refluxing for 3 h. MWNT-OXs were filtered and washed with Milli-Q water until neutral pH was reached and were then dried for 12 h at 50 °C [13].

Apparatus

Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and scanning electrochemical microscopy (SECM) measurements were performed on a CHI 440 or CHI 900 setup (CH Instruments Inc., USA). A platinum wire and 3 M Ag/AgCl were used as the counter and reference electrodes, respectively. A magnetic stirrer provided the connective transport when necessary.

For SECM experiments, we used 0.1 M phosphate buffer solution with a pH of 7 and 0.05 mM FcOH as a redox mediator. A ~10- μm diameter homemade carbon fiber electrode served as the SECM tip, while GCE with a diameter of 3 mm (Model CH Instruments) was used as the SECM substrate.

Contact angle measurements were performed with a Ramé-Hart, 21 AC (USA) using the DROP image software.

Preparation of the working electrode

The dispersions were obtained by mixing 1.0 mg of carbon nanomaterial (MWNT, MWNT-OX, GO, or RGO) with 1.0 mL of chitosan-water (3:1) solution followed by sonication for 15 min at room temperature. Chitosan 1.0 % w/v was prepared in 1.0 % v/v acetic acid solution.

Prior to the modification, a glassy carbon electrode with a diameter of 3 mm was polished with 0.3 and 0.05 μm alumina slurries for 1 min, rinsed with Milli-Q water and then dried at room temperature. Carbon nanomaterials were dispersed by sonication for 15 min. The clean surface was then modified with 10 μL of each nanomaterial dispersion (1 mg/mL) and dried at 50 °C for 15 min.

Procedures

SECM experimental procedure The experiments were carried out in a 0.10 M phosphate buffer solution with a pH of 7.40, using FcOH as the redox mediator. While the tip potential was held at 0.500 V to oxidize the FcOH, the substrate potential was held at 0.000 V to permit the feedback between the electrodes; this enabled the reduction of the FcOHox generated at the tip, regenerating the parent FcOH.

A series of $100\ \mu\text{m} \times 100\ \mu\text{m}$, constant-height SECM images were recorded at a tip scan rate of $1\ \mu\text{m/s}$. The results are presented in the dimensionless form (I_T), by normalizing the experimental feedback current (i_T) by the steady-state current obtained when the tip was far from the substrate ($i_{T,\infty}$), i.e., $I_T = i_T/i_{T,\infty}$.

Capacitances Capacitances were calculated from the CV curves using the linear relationship between the current and the potential scan rate ($c = i/v$), where the slope of this plot corresponds to the capacitance in μF . Voltammograms were measured in the -0.4 – 0.5 V potential window to avoid the region where oxidized multiwalled nanotubes and graphene oxide are electroactive and using scan rates from 0.025 to 0.50 V/s in 0.1 M phosphate buffer solution with a pH of 7.

Contact angle measurements Static water contact angles were measured with water drops under ambient conditions. A glassy carbon disk (12.7 mm) was modified using $40\ \mu\text{L}$ of each carbon nanomaterial dispersions in 3:1 CHIT-W and then dried at $50\ ^\circ\text{C}$ for 15 min. It was then transferred to the Contact Angle equipment, where a $4\ \mu\text{L}$ drop of water was used.

DNA detection

DNA adsorption was obtained by first immersing the modified electrode in a glutaraldehyde solution for 2 s and then washing with 0.2 M formate buffer solutions with a pH of 5.0; the electrode was then immersed in a stirred supporting electrolyte solution containing the DNA, and the accumulation was performed at open circuit potential for a given time. Prior to transduction experiments, the electrode containing the adsorbed DNA layer was washed for 10 s with the buffer solution.

Voltammetric transduction was performed by DPV under the following conditions: potential increment of 0.04 V, pulse amplitude of 0.05 V, pulse width of 0.017 s, and pulse period of 0.2 s. The anodic current at approximately 1.0 V, corresponding to the oxidation of guanine, was used as the analyte signal.

Results and discussion

Electrochemical characterization

Figure 1 shows the cyclic voltammetric profiles of electrodes modified with $1\ \text{mg/mL}$ of dispersion for the -0.4 – 0.6 V (vs Ag/AgCl) range obtained using 0.1 M phosphate buffer solution with a pH of 7.0 as the supporting electrolyte. The response obtained for bare glassy carbon electrode is also

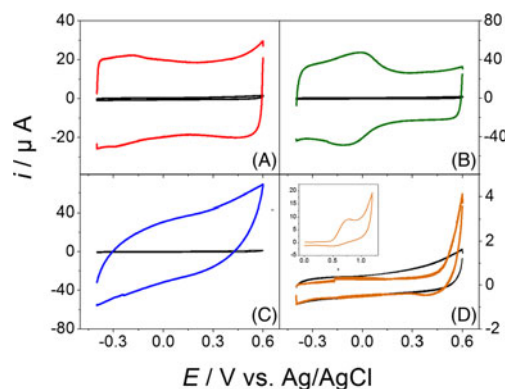


Fig. 1 Cyclic voltammograms obtained at 0.100 V/s of GCE (black lines) and GCE modified with $1\ \text{mg/mL}$ of CHIT-W dispersed carbon nanomaterials. **a** GCE/MWNT, **b** GCE/MWNT-OX, **c** GCE/RGO, and **d** GCE/GO. 0.1 M phosphate buffer solution with a pH of 7.0 was used as the supporting electrolyte

included for comparison (black line). Completely different profiles were observed for each CNM. While GCE/MWNT (Fig. 1a) exhibits a double-layer behavior with a typical rectangular curve, GCE/RGO (Fig. 1c) shows a slightly distorted quasi-rectangular shape that is a signature of resistive electrode behavior. In contrast, a redox couple was observed for GCE/MWNT-OX; according to previous reports, this corresponds to a redox process of carboxylic acid groups and other oxygenated functions introduced as defects on the MWNT structure [13, 15]. Finally, the GCE/OG voltammetric profile (Fig. 1d) was similar to those obtained for bare glassy carbon electrode, with a capacitive current that was ten times lower than those observed for the other CNM.

No redox signals appear for voltammetry performed using a wider potential range except for the case of GCE/GO (inset Fig. 1d), where a signal was present at 0.75 V.

Capacitances were determined from VC experiments performed at different scan rates and calculated at the 0.3 V. The capacitance values for GCE/MWNT, GCE/MWNT-OX, GCE/RGO, and GCE/GO are 37.10 ± 0.06 , 46.30 ± 0.35 , 30.50 ± 1.28 , and 0.53 ± 0.10 F/g, respectively. The values for MWNT and RGO are ten times higher than that reported by Pumera who disperse MWNT and RGO with DMF [16] but are in concordance with our previous results for MWNT and MWNT-OX using the same experimental conditions [13]. The values of capacitances are similar for the CNMs excepting that obtained for GO. The capacitance gives insight of the electrochemical area of the electrode, but its determination also can be affected by faradaic reactions of surface-bonded oxides or “pseudocapacitance.” Thus, we decided to obtain the surface areas using Brauner, Emmet and Teller (BET) method to determine if there is a relationship between capacitance values and geometric areas. The values for MWNT, MWNT-OX, RGO, and GO are 333.1 ± 1.1 , 261.8 ± 0.4 , 462.9 ± 0.8 , and 289.1 ± 0.1 m^2/g , respectively. Thus, we can conclude that

the very low capacitance determined for GCE/GO is not due to a surface area factor, and then probably the explanation would be related to greater compaction or densely packed GO electrodes which result in a electrochemical response similar to a solid planar macroelectrode decreasing the active coverage [17, 18].

SECM experiments allowed us to evaluate the topography and electroactivity of the modified surfaces. Figure 2 displays SECM images obtained at GCE modified with 1.0 mg/mL of GCE/MWNT (A), GCE/MWNT-OX (B), GCE/RGO (C), and GCE/GO (D) carbon nanomaterial dispersions. The observed surfaces of graphene-based nanomaterials (Fig. 2c, d) are clearly more homogenous than those obtained when MWNTs were used for GCE modification. The latter show areas with different electroactivities, revealing the existence of variation in the MWNT amount on the surfaces. This result is in agreement with our previously reported work where chitosan was used as the MWNT dispersing agent [11, 19].

Although graphene derivative (GO and RGO)-modified surfaces are homogeneous, they show a large difference between their normalized current intensities. The normalized current for GCE/GO was 2.5 times lower than $i_{T,\infty}$, i.e., the surface exhibits an almost nonconductive behavior. In the case of GCE/RGO, the normalized current is almost five times higher than $i_{T,\infty}$, clearly showing that the presence of RGO significantly improves the electroactivity of the resulting electrode. The SECM results are concordant with capacitance values described earlier.

Contact angle

Static water contact angles (WCAs) were measured with water drops under ambient conditions, thus characterizing the

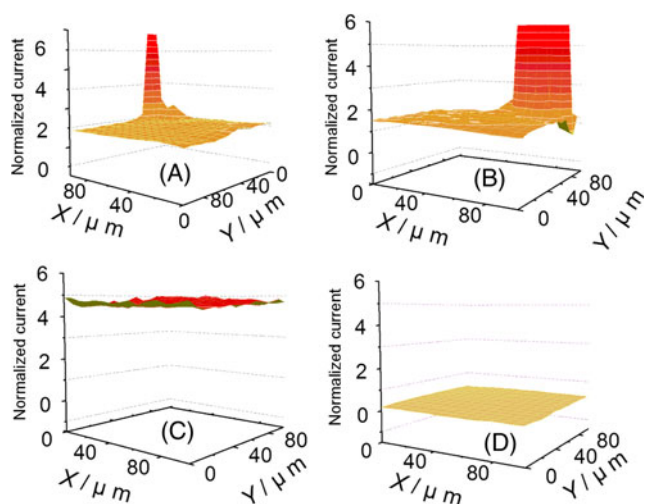


Fig. 2 SECM surface plot images of **a** GCE/MWNT, **b** GCE/MWNT-OX, **c** GCE/RGO, and **d** GCE/GO. Experimental conditions 5.0×10^{-4} M FcOH, supporting electrolyte 0.050 M phosphate buffer solution with a pH of 7.00, ET=0.050 V, ES=0.000 V, UME scan rate 10 $\mu\text{m/s}$

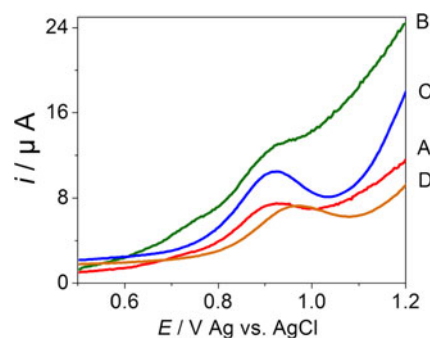


Fig. 3 Differential pulse voltammograms obtained at **a** GCE/MWNT, **b** GCE/MWNT-OX, **c** GCE/RGO, and **d** GCE/GO. (1.0 mg/mL) after 5 min accumulation in 45.0 ppm dsDNA at open circuit potential with transference to 0.20 M sodium formate solution with pH of 5.00. Treatment with GTA: 3.0 % v/v GTA for 2 s

wettability and hydrophilicity of the modified electrodes. We first evaluated the WCA for the GCE modified with the dispersing agent, i.e., the CHIT-W 3:1 solution, obtaining a value of $82.0 \pm 0.8^\circ$ (GCE/CHIT-W) that is considerably lower than the WCA of the bare GCE ($96.4 \pm 2.1^\circ$). The result is in agreement with the hydrophilic characteristics of the surface provided by the presence of chitosan. Even lower values were found for GCE/GO ($74.6 \pm 0.9^\circ$) and GCE/MWNT-OX ($80.0 \pm 0.1^\circ$), leading to the conclusion that the abundance of oxygenated functional groups introduced during the oxidation process increases the surface hydrophilicity in spite of the presence of chitosan.

On the contrary, for GCE/RGO and GCE/MWNT, decreased WCA values were not observed; for GCE/RGO, a small increase in the value from $82.0 \pm 0.8^\circ$ (GCE/CHIT-W) to $84.9 \pm 0.7^\circ$ was obtained, indicating that the RGO is more hydrophobic than the other CNM. However, no modified surface exhibited high hydrophobicity (angle greater than 90°) because of the presence of the CHIT-W functional groups.

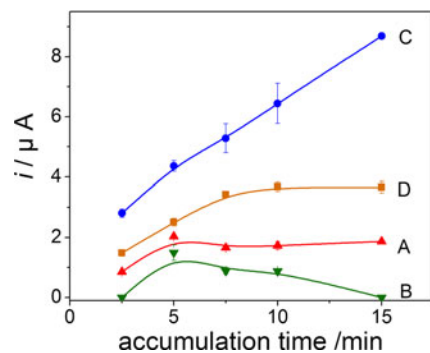


Fig. 4 Dependence of guanine oxidation current with the accumulation time from a 45 ppm dsDNA solution at open circuit potential on **a** GCE/MWNT, **b** GCE/MWNT-OX, **c** GCE/RGO, and **d** GCE/GO; other experimental conditions the same as those in Fig. 3

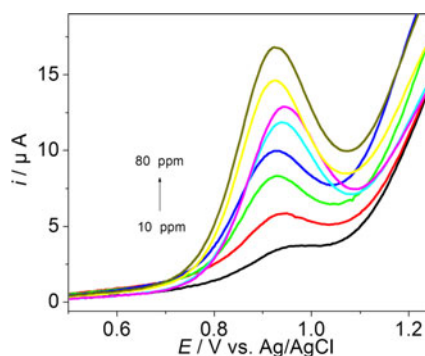


Fig. 5 Differential pulse voltammograms obtained at GCE/RGO (1.0 mg/mL) after 7.5 min accumulation at different dsDNA concentration at open circuit potential with transference to 0.20 M sodium formate solution with a pH of 5.00. Treatment with GTA: 3.0 % v/v GTA for 2 s

Electrochemical behavior of DNA on modified electrodes

The electrochemical behavior of dsDNA was evaluated through the direct oxidation of guanine base. Figure 3 shows DP Voltammograms obtained for 45 ppm dsDNA after 5 min of accumulation at the GCE/MWNT (A), GCE/MWNT-OX (B), GCE/RGO (C), and GCE/GO (D) carbon nanostructures. It can be observed that electrodes modified with graphene-based nanomaterials produce well-resolved and more intense peaks than those observed when MWNT-modified electrodes were used. The currents at graphene-based nanomaterials were 4.4 and 2.5 μA for GCE/RGO and GCE/GO, while 2.0 and 1.5 μA were obtained for GCE/MWNT and GCE/MWNT-OX, respectively. This indicates that graphene-based nanomaterials facilitate the electron transfer process of guanine oxidation, most likely due to the large graphitic surface exposed for the dsDNA adsorption. Another interesting result is that the DNA oxidation currents obtained for the electrodes modified using oxygenated carbon nanomaterials (MWNT-OX and GO) are lower than those obtained for the electrodes modified with the reduced CNM (MWNT and RGO). Such reduction of the electrochemical response to DNA has been reported by us in a previous study using carbon nanotubes with different degrees of oxidation [14]; now, we report this effect for graphene derivatives. Thus, we can conclude that the oxygenated functionalities present on MWNT-OX and GO interact with the amine groups of CHI, decreasing the electrostatic contribution of CHI to dsDNA adsorption.

Table 1 Analytical parameters of DNA detection

Nanomaterial	Linear range (ppm)	Sensitivity ($\mu\text{A}/\text{ppm}$)	LOQ (ppm)	LOD (ppm)	R
MWNT	4.5–50	0.050 \pm 0.002	4.5	0.75	0.998
MWNT-OX	13–75	0.060 \pm 0.005	13	2.6	0.989
GO	2.3–70	0.120 \pm 0.003	2.3	0.91	0.998
RGO	1.7–80	0.140 \pm 0.003	1.7	0.78	0.998

Finally, while no changes were observed for guanine oxidation peak potential when MWNT, MWNT-OX and RGO were used, the use of GO as the carbon nanomaterial a shift in the potential from 0.920 V (vs. Ag/AgCl) to 0.964 V was observed and probably is due to a more weak interaction between DNA and CHI described above.

Analytical applications

The time of accumulation was studied in order to identify the optimum analysis conditions. Figure 4 shows the relationship between the peak currents of guanine oxidation and the accumulation time for a 45 ppm dsDNA solution obtained using the four modified electrodes. It can be seen that for MWNTs, the maximum accumulation peak time was achieved at 5 min, while for GO, the maximum was at 10 min. For RGO, no plateau was observed even after 15 min of accumulation time.

To compare the performance of the different electrodes, an accumulation time of 7.5 min was chosen to perform the calibration plots. Figure 5 shows the DP voltammograms obtained at different dsDNA using the GCE/RGO. The linear concentration range, sensitivity, and detection limit based on a signal to noise ratio of 3 are shown in Table 1. GCE/RGO electrode showed a wide linear range among the electrodes and the limit of detection was lower than others.

The reproducibility in the preparation of RGO-CHIT-W dispersions was analyzed from the dsDNA signal obtained using GCE modified with three fresh dispersions after adsorption for 7.5 min at open circuit potential. The I_p reproducibility for the electrodes prepared with the different dispersions was close to 7 %, which is adequate for the employed methodology.

Conclusions

Comparison of the electrochemical behavior of GCE modified with four CNM (MWNT, MWNT-OX, RGO, and GO) dispersed in identical 3:1 chitosan-water media reveals that CNM type and degree of oxidation have a strong effect on the electroactivity of the modified electrode. GCE/RGO clearly exhibited the most electroactive surface among the CNMs, demonstrating that the graphitic structure is highly important. This modified GCE electrode (GCE/RGO) also obtains the

highest analytical signals for dsDNA detection. Therefore, RGO is the CNM recommended for further consideration in the development of DNA biosensors.

Acknowledgments Financial support from the National Fund for Scientific and Technological Development-CHILE FONDECYT No. 1120246 (80 %) and FONDAF No. 15130011 (20 %) is gratefully acknowledged. D.F.B. acknowledges Chile's National Commission for Scientific and Technological Research (CONICYT) scholarships for her PhD studies in Chile.

References

- Primo E, Gutierrez F, Luque G, Dalmaso P, Gasnier A, Jalit Y, Moreno M, Bracamonte M, Eguilaz-Rubio M, Pedano M, Rodríguez M, Ferreyra N, Rubianes M, Bollo S, Rivas G (2013) Comparative study of the electrochemical behavior and analytical applications of (bio)sensing platforms based on the use of multi-walled carbon nanotubes dispersed in different polymers. *Anal Chim Acta* 805:19–35
- Ambrosi A, Chua CK, Bonanni A, Pumera M (2014) *Electrochemistry of Graphene and Related Materials*. *Chem Rev* 14:7150–7188
- Musameh M, Wang J, Merkoci A, Lin Y (2002) Low-potential stable NADH detection at carbon-nanotube-modified glassy carbon electrodes. *Electrochem Commun* 4:743–746
- Sotiropoulou S, Gavalas V, Vamvakaki V, Chaniotakis NA (2003) Novel carbon materials in biosensor systems. *Biosens Bioelectron* 18:211–215
- Lin CW, Wei CC, Liao SS, Huang CY, Sun CL, Wu PJ, Lu YJ, Yang HW, Ma CCM (2015) A reusable magnetic graphene oxide-modified biosensor for vascular endothelial growth factor detection in cancer diagnosis. *Biosens Bioelectron* 67:431–437
- Kumar S, Ahlawat W, Kumar R, Dilbaghi N (2015) Graphene, carbon nanotubes, zinc oxide and gold as elite nanomaterials for fabrication of biosensors for healthcare. *Biosens Bioelectron* 70:498–503
- Kuila T, Bose, Mishra AK, Khanra P, Kim NH, Lee JH (2012) Chemical functionalization of graphene and its applications. *Prog Mater Sci* 57:1061–1105
- Yang W, Ratinac KR, Ringer SP, Thordarson P, Gooding JJ, Braet F (2010) Carbon nanomaterials in biosensors: should you use nanotubes or graphene? *Angew Chem Int Ed* 49:2114–2138
- Chen Y, Vedala H, Kotchey GP, Audfray A, Cecioni S, Imberty A, Vidal S, Star A (2012) Electronic detection of lectins using carbohydrate-functionalized nanostructures: graphene versus carbon nanotubes. *ACS Nano* 6:760–770
- Zheng D, Vashist SK, Dykas MM, Saha S, Al-Rubeaan K, Lam E, Luong JHT, Sheu FS (2013) Graphene versus multi-walled carbon nanotubes for electrochemical glucose biosensing. *Materials* 6: 1011–1027
- Bollo S, Ferreyra NF, Rivas GA (2007) Electrooxidation of DNA at glassy carbon electrodes modified with multi-wall carbon nanotubes dispersed in chitosan. *Electroanalytical* 19:833–840
- Arias P, Ferreyra NF, Rivas GA, Bollo S (2009) Glassy carbon electrodes modified with CNT dispersed in chitosan: analytical applications for sensing DNA- methylene blue interaction. *J Electroanal Chem* 634:123–126
- Cañete-Rosales P, Ortega V, Álvarez-Lueje A, Bollo S, Gonzalez M, Ansón A, Martínez MT (2012) Influence of size and oxidative treatments of multi-walled carbon nanotubes on their electrocatalytic properties. *Electrochim Acta* 62:163–171
- Cañete-Rosales P, Álvarez-Lueje A, Bollo S (2014) Electrooxidation of DNA at glassy carbon electrodes modified with multi-walled carbon nanotubes with different oxidation degree. *J Chil Chem Soc* 49:2494–2497
- Cañete-Rosales P, Álvarez-Lueje A, Bollo S (2014) Ethylenediamine-functionalized multi-walled carbon nanotubes prevent cationic dispersant use in the electrochemical detection of DNA. *Sensor Actuators B Chem* 191:688–694
- Buglione L, Pumera M (2012) Graphene/carbon nanotube composites not exhibiting synergic effect for supercapacitors: The resulting capacitance being average of capacitance of individual components. *Electrochem Commun* 14:5–8
- Li J, Cassell A, Delzeit L, Han J, Meyyappan M (2002) Novel three-dimensional electrodes: electrochemical properties of carbon nanotube ensembles. *J Phys Chem B* 106:9299–9305
- Li H, Luo JY, Zhou XF, Yu CZ, Xia YY (2007) An ordered mesoporous carbon with short pore length and its electrochemical performances in supercapacitor applications. *J Electrochem Soc* 154: A731–A736
- González-Segura K, Cañete-Rosales P, del Rio R, Yáñez C, Ferreyra NF, Rivas GA, Bollo S (2012) Effect of the dispersing agent on the electrochemical response of glassy carbon electrodes modified with dispersions of carbon nanotubes. *Electroanalytical* 24:2317–2323