Oxygen Plasma Exfoliated Vertically-Aligned Carbon Nanotubes as Electrodes for Ultrasensitive Stripping Detection of Pb^{2+}

E. Saito,[a,z] E. F. Antunes,[a] H. Zanin,[a] F. R. Marciano,[b] A. O. Lobo,[b] V. J. Trava-Airoldi,[a] and E. J. Corat[a]

[a]*Associate Laboratory of Sensors and Materials of the National Institute for Space Research, São José dos Campos, São Paulo 12227-010, Brazil*
[b]*Laboratory of Biomedical Nanotechnology/Institute of Research and Development at the University of Vale do Paraíba, São José dos Campos, São Paulo 12244-000, Brazil*

In the present paper we report the production of vertically aligned carbon nanotubes exfoliated (at the tips) by oxygen plasma for electrochemical applications. The fast and dry process produces graphene oxide tips and oxygen functionalization. The electrodes are evaluated by cyclic voltametry by ferri/ferrocyanide redox couple and applied for electrochemical detection of lead (II) by differential pulsed anodic stripping voltammetry. The electrode presents high sensitivity (35.47 uA.uM^{-1}) and low detection limit (48.3 pM). As far as we know, this is the lowest LoD in comparison with other works using CNT or graphene electrodes. The high electrochemical response is attributable to high density of functionalized edges on carbon nanotubes tips.
© 2014 The Electrochemical Society. [DOI: 10.1149/2.039405jes] All rights reserved.

Restriction of Hazardous Substance directive (RoHS) limits the maximum Lead concentration and other elements or substances[1] to European products. Lead is present in several products (e.g. batteries, solder, organo-lead compounds, lubricants, etc). The cumulative exposure to lead may affect the kidney, reproductive, immune, cardiovascular and developmental systems.[2] Lead is risky for several kinds of cancer.[3] This public health impact and consequent law restriction evoke a sensitive, reliable and quick detection. Atomic Absorption Spectroscopy[4] and Inductively Coupled Plasma Mass Spectrometry (ICP/MS)[5] are precise but lack readiness because of longer time for sample digestion and analysis. Electroanalytical Methods present low detection limit, short time analysis and small sample size,[6] with reliable measurements performed in small scale for detection of important analytes[7] or in portable equipments.[8]

Since the success of polarographic methods with mercury electrodes,[9] several kinds of electrodes have been tested and evaluated for heavy metals detection.[10–21] Recently, several new materials and methodologies as functionalized membranes present a promising perspective for several analytes.[22–32] As an example, the potentiometric determination of lead can be achieved in a wide range of concentrations (10^{-4}–10^{-8} M) and low limit of detection (4 nM).[33,34]

For carbonaceous electroactive materials, carbon fibers microelectrodes,[35] doped diamond,[36] carbon paste,[37,38] carbon nanotubes,[39] and, recently, graphene[40] are good examples. There was an enthusiastic wave of works about the carbon nanotubes electrodes and prospects about its electrocatalytic effects.[41–43] Some groups addressed local parts contribution in graphite, carbon nanotubes and graphene.[44] Compton's group enlightens that edges of sp^2 carbonaceous materials present an improved electrochemical activity compared to graphite and CNT basal planes.[45] They detected lower background currents and electrocatalytic activity compared to boron doped diamond, CNT basal planes and glassy carbon. They also claimed the advantage of edges over CNT chemical modification for electrochemical detection.[46,47] Several groups studied routes and electrochemical outcomes of inserting oxygen functionalities to carbon nanotubes.[48–50] Oxygen functionalization also presents positive effects on electrode performance as quantified by heterogeneous electron transfer (HET) rate.[51] However, HET rate is lower for graphite[52] and Graphene[53] after oxygen functionalization. the readiness of some functionalities to cathodic reduction in graphene samples[54] may explain this response. This may limit applications in cathodic region. Few works produced as grown CNT with longitudinal exfoliated graphene structures.[55,56]

In the present paper, we report on producing and characterizing oxygen plasma treated vertically aligned carbon nanotubes (VACNT) electrodes. The oxygen plasma treatment exfoliated VACNT tips to provide, simultaneously, oxygen fuctionalized and graphene tips. Such electrodes present good electrochemical response and high sensitivity on lead detection.

Experimental

The growth of Vertically Aligned Carbon Nanotubes (VACNT) (on sanded titanium substrates) was accomplished by microwave plasma reactor (produced at our laboratory) with 2.45 GHz (MWCVD). Before growth, we deposited a thin catalyst layer (Fe, 12 nm) by an electron beam evaporator on each substrate. A pretreatment reduces the iron layer and creates nanoparticles for nanotubes growth.[56] Pretreatment consists on N$_2$/H$_2$ (10/90 sccm) plasma for 5 min at a 1053 K substrate temperature. After this step, CH$_4$ (14 sccm) addition to gas mixture promote VACNT growth during 2 min at 1095 K substrate temperature. After growth, samples are removed from microwave reactor and placed into pulsed-DC plasma reactor. The standard oxygen plasma treatment took 2 minutes in oxygen pulsed – DC plasma with 1 sccm oxygen flow rate at 1.1×10^{-1} Torr[57] and a peak pulse of 700 V at 20 kHz and 45% duty-cycle. The functionalized film will be named VACNT-GO. Scanning Electron Microscopy (SEM) with a JEOL JSM-5310, and high resolution SEM with a FEI Inspect F50 allowed morphological characterization. Raman spectroscopy with a Renishaw system 2000 excited by a 514.5 nm argon laser enabled VACNT structural comparison before and after functionalization.

The electrochemical measurements of VACNT-GO films were carried out in a three-electrode cell with Ag/AgCl (3 M-Autolab) as a reference electrode and a pure platinum wire as a counter electrode. Pontentiostat (Autolab 302 N) performed all measurements at room temperature and atmosphere.

First, typical cyclic voltammetry technique allowed the potential window measurement of VACNT-GO electrodes. The sweep potential procedure also enabled the electrochemical characterization of VACNT-GO thin films with well know potassium ferrocyanide(II) (Synth-F1008) in 0.5 M H$_2$SO$_{4(aq.)}$ (Synth-A1060) solution.

The analytical procedure was DPAS (differential pulsed anodic stripping) for Pb^{2+} detection in acetate buffer. The deposition potential of −1.2 V applied for 300s under magnetic bar stirring (900 rpm) forced initial Pb adsorption to working electrode. We recorded the DPAS responses between −1.2 to −0.2 V with modulation amplitude of 0.4 V, modulation time of 0.1 V and time interval of 2s. A +0.7 V desorption potential applied for 360s under stirring removed the residual analyte.

The reagents were of analytical grade used as received without any purification. We prepared all solutions from water treated with mili-Q (milipore system) purifier. All flasks used in measurements were maintained in a concentrated nitric acid (2 M) (Synth) to avoid

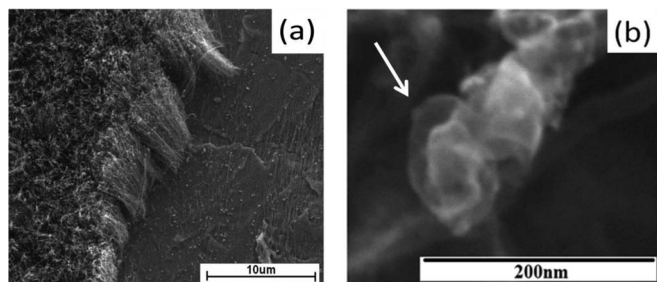[z]E-mail: esaito135@gmail.com

Figure 1. (a) Scanning Electron Microscopy (SEM) images from VACNT as grown electrode. (b) Exfoliated carbon nanotubes by oxygen plasma treatment (VACNT-GO). The arrow indicates the exfoliation at the tip of CNT shown in focalized region of high resolution image.

Figure 2. Raman spectra of VACNT thin films before and after plasma treatment.

contamination. We freshly prepared 0.2 M buffer solutions with different contents of sodium acetateand acetic acid (both from Sigma-Aldrich supplier). An independent pH meter (703 pH meter, Autolab) checked solution's pH during experiments. We prepared the Pb^{2+} solutions daily by proper dilution of 1000 mg.L^{-1} stock standard solution ICPMS calibrated (Specsol Quimlab-QLBICPPB1000-125).

Results and Discussion

Figure 1 presents the SEM images of as grown VACNT electrodes over TiAl6V4 substrates. The samples are covered by uniform aligned nanotubes with average 20 nm diameter and 35 um height. Oxygen plasma treatment does not change main morphological characteristics as alignment tube diameter and height. However, the closer observation at high magnification (Fig. 1b) shows partial exfoliation of CNT tips. The exfoliated nanotube tips show graphene sheets around the nanotubes. Owing to plasma oxidation these are most likely graphene oxide (GO).

Figure 2 presents the first and second order Raman spectra of electrodes before and after plasma treatment. The physical origin of G, D, D′ and G′ bands have been well explained previously.[58,59] The effects of the plasma treatment on our samples were already thoughtfully analyzed elsewhere.[60,61] Deconvolutions of first order fitted D and G as Lorentzian bands and D′, the shoulder around 1250 cm^{-1} and a band around 1510 cm^{-1} as Gaussian functions. The oxygen plasma treatment decreased the I_D/I_G ratio and increased the bands at 1250 and 1510 cm^{-1}. VACNT normally has a I_D/I_G ratio larger than 1 because it probes the defective structure of the domed tips. The decrease of I_D/I_G ratio suggests tip opening as characterized in Fig. 1b. Some authors assign the 1250 cm^{-1} band[58] to the isolated or convoluted iTA, LA or LO modes near K point. Its increase on oxidized samples may stand for exfoliation. The Gaussian function at ~1520 cm^{-1} is credited to polar oxygen groups on CNT surface.[57] In second order there is a pronounced G′ band increase after plasma treatment. This suggests a higher nanoscale order that may evidence exfoliation into graphene sheets.
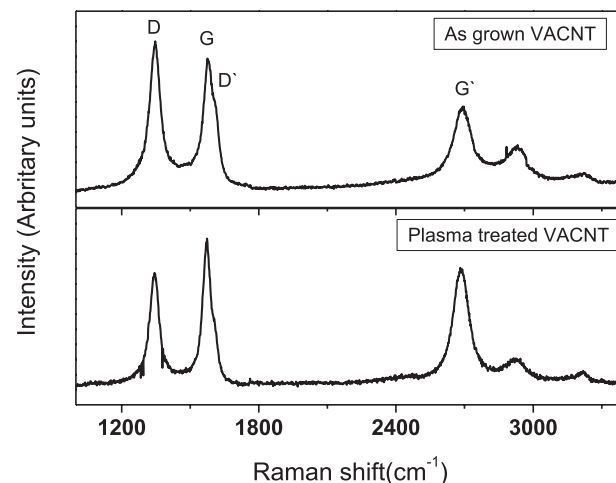
Cyclic voltammetry (CV) (not shown) in 0.5 M $H_2SO_{4(aq.)}$ electrolyte reveal a 1.7 V potential window for the VACNT-GO electrode. Figure 3 presents the voltammogram measured for 5 mM potassium ferrocyanide(II) couple and 0.5 M $H_2SO_{4(aq)}$ as supporting electrolyte. The oxidation and reduction peaks at 0.53 and 0.39 V (Vs.Ag/AgCl (3 M)), respectively, using 50 mV.s^{-1} is associated with quinine, lactone and other groups oxireduction.[62] The (CV) measurements at variable scan rates give a linear relation ($R^2 = 0.988$) between peak current (I_p) and square root of scan rate ($v^{0.5}$), as shown in the inset of Fig. 3.

Prior any measurements for Pb(II) detection at VACNT-GO electrodes, 50 cycles from −1.0 to 0.2 V cleaned and activated the electrode surface (not shown). This procedure also tested the effects of reductive readiness of surface functionalities in GO tips of VACNT-GO, as appointed earlier.[54] Figure 4 presents the DPAS of Pb(II) at concentrations from 0.1 mM to 0.4 mM in acetate buffer (pH 3.4), which shows the background behavior. For calibration curve we used standard addition method for peak current quantification with background correction of analytical responses.[63,64] Figure 5 presents the stripping measurements with spline curve fitting for background correction, in the range from 1 nM to 1.7 μM. Figures 5a shows the analytical curves got from DPAS measurement of Pb(II) in 0.2 M acetate buffer (pH 4.2). Figure 5b presents linear response of the peak current vs. lead concentration. It can be seen the linear peak current dependence with metal ions addition. The sensitivity and limit of detection (LOD) were 35.47 μA.μM^{-1} and 48.3 pM (3σ method), respectively The Lod was calculated in accordance with acknowledge procedure (on 10 times the standard deviation of 10 measurements of the blank solution).[65,66]

The LoD of the VACNT-GO electrode is the lowest when compared with CNT based electrodes in same supporting electrolyte,[67–69] EPPG (Edge Plane Pyrolytic Graphite),[70] and graphene electrodes.[67] It is even comparable to the already recognized mercury electrodes[71] and
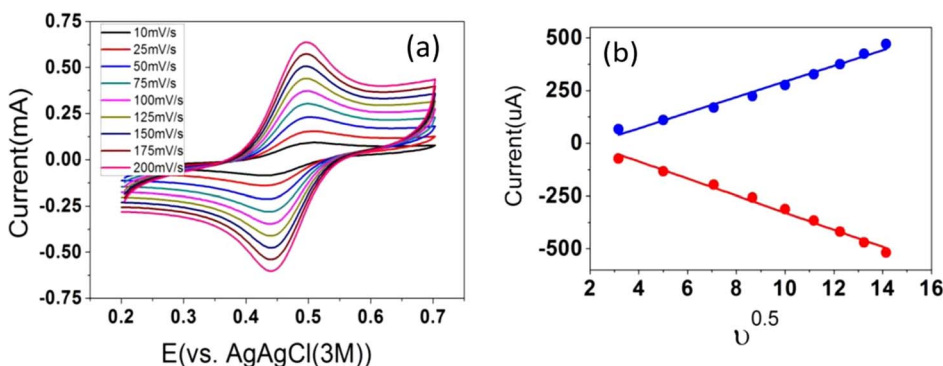

Figure 3. CV for the VACNT-GO thin film in 5 mM $K_3Fe(CN)_6$ / 0.5M $H_2SO_{4(aq.)}$.
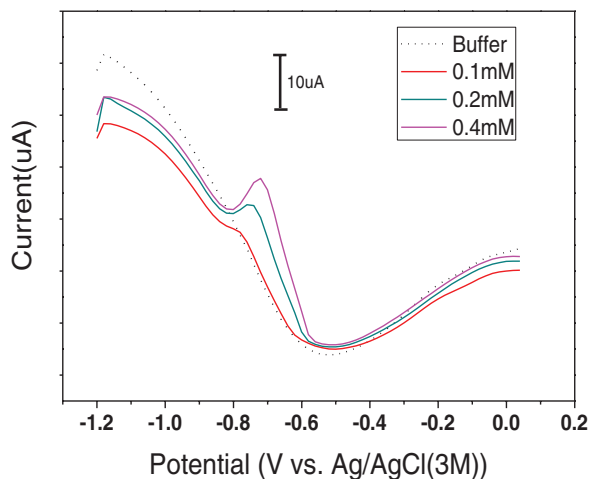
Figure 4. DPAS responses of VACNT-GO electrodes.

to the promising bismuth plated ones.[72] Table I presents some results for Pb detection collected in literature for comparison with the results of this work.

CNT Paste electrodes,[67] can be applied with Potentiometric stripping analysis for electrochemical detection of heavy metals with good reliability. However the dispersion of CNT is not the configuration to expose high density of CNT tubes as in VACNT design.

Graphene electrode for Pb detection also gives a good response (at nM level)[68] when compared with boron doped diamond. However as appointed by Dale et. al,[69] there is a severe restriction associated with graphene on cathodic potentials because of film disruption.

Multiwall carbon nanotubes dispersion in ion exchange resin, as Nafion, may produce an electrode composite.[70] Those electrodes use low MWCNT content and show nanomolar LoD. However, electrode manufacturing demands a controlled elaboration in several steps as sonication and polishing before its final application.

The unmodified EPPG electrodes[71] corroborate the superior electrochemical activity of edges on adsorptive process (e.g. for silver and manganese anodic stripping) when compared with Boron doped diamond. Additionally in this work, the authors suggests a superior electroanalytical performance of edges with lower cost and fast synthesis when compared with doped diamond.

Considering CNT modified electrodes[72] the detection proceeds through metal ions complexation by ionophore molecules linked to nanotube surface. Despite the good sensitivity and selectivity achieved, this functionalization demands also multi step procedure and sometimes expensive reagents (ionophores).

The mercury electrode (in a hanging drop, thin film or other arrangement) presents several properties which favors the high electrochemical performance. The wide cathodic potential limit and the easily refreshment of the surface allied with amalgamation results in good electroanalytical responses[73] with impressive pM LoD level. However mercury electrode high toxicity in any arrangement imposes a severe restriction as electrochemical sensor.

Bismuth emerges as a "environmentally friendly" (mercury-free) alternative electrode for electroanalytical applications.[74] The metal
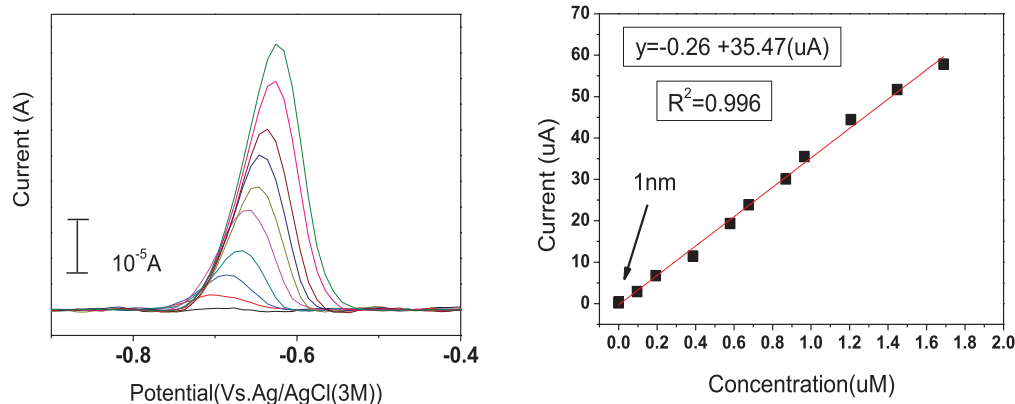

Figure 5. (a)-DPAS response of Pb^{2+} detection in acetate buffer after background correction. Figure (b) shows the linear response of the electrodes. The lowest value measured of 1 nM is indicated by the arrow.

Table I. Comparative results for electrochemical detection of Pb in acetate buffer.

Electrode	Method	Limit of Detection nM (μg.L-1)*	Lowest Value measured nM	Reference
CNT paste	PSA	31.9 (**6.6**)	282	67
Graphene	SWASV	-	**7.00****	68
CNT Nafion	DPAS	**5.09** (0.2)	80	69
EPPG	LSASV	1.01 (**0.21**)	9.7	70
CNT modified	SWASV	-	**1.00****	71
Mercury Film electrode (TMFE)	SWASV	**0.05** (0.01)	0.97	72
Bismuth	SWASV	0.97 (**0.2**)	4.84	73
Nafion - RGO/Bi	DPSAV	0.097 (**0.02**)	2,42	74
Plasma Treated CNT	SWASV	**0.057** (0.012)	500	75
VACNT-GO	DPAS	**0.048** (0.01)	1.00	This work

PSA- potentiometric stripping analysis, DPAS Differential pulse anodic Striping Voltammetry, LSASV - Linear sweep anodic stripping voltammetry and SWASV - Square wave anodic stripping voltammetry (SWASV). TMFE – Thin mercury film electrode.
*Some of the literature works present results in μg.L^{-1} and others in nM. For this comparison we present LOD values in both units writing in boldface the values found in each work.
**References 68 and 72 presented the lowest value measured as the LoD.

plated *in* or ex situ on several kinds of substrates (carbon fiber, glassy carbon, CNT, etc) presents good responsiveness and reproducibility. The multicomponent alloy formation during deposition and sequential stripping produces well defined and reproducible peaks for heavy metals detection. Recently,[75] Bi plating on graphene sheets dispersed in Nafion reached LoD in the order of 10^{-11} M for Pb(II) detection. The authors mention a synergic contribution between graphene and Bismuth in electrode electrochemical response. Besides this good result, the simultaneous response of graphene edges and Bi itself brings some difficulties in ranking the electrode material.

In a similar plasma treatment of the present work, Wei et al.[76] dispersed carbon nanotubes exposed to mild oxygen plasma in methanol and dipped on glassy carbon. They got LoD results close to this work. Both works performed the Pb(II) detection in similar experimental arrangement (acetate buffer electrolyte, stirring condition and forced deposition potential, etc.).

These similarities can suggest the same result of plasma treatment on CNT leading to similar LoD. However it is important to compare the sensitivity measured under similar experimental conditions. The VACNT-GO electrode presents one order higher sensitivity (35.47 μA.μM^{-1}) compared to Wei et al.[76] plasma treated CNT (3.55 μA.μM^{-1}). We assign this outstanding electrochemical response to the nanocomposite structure of the VACNT-GO electrode. The oxygen plasma treatment produces plentiful graphenated tips on VACNT film. The high sensitivity of those tips improve the current to concentration ratio. The LoD of VACNT-GO electrode achieved the sub nanomolar values of acknowledged works[77–81] with Hg or Bi electrodes.

As showed, the oxygen plasma treatment promotes surface changes with insertion of oxygenated groups at VACNT. Based on reported previously,[51] this insertion (solely) can improve the electrochemical responsiveness of CNT electrodes. Further, there is a structural modification on multiwall VACNT films with tips opening full of graphene edges, which have a known fast charge transfer and high sensitivity.[82] In addition, recently the high active area and fast transfer is corroborated by fundamental electrochemical characterization.[83] Thus, the electroactive contribution of the VACNT-GO electrode originates from its graphenated "brush like" tips with large amount of functionalized graphene edges. The carbon nanotubes acts fundamentally as a current collector since charge transfer at graphenated and oxygenated tips overwhelm the basal plane contribution.

The reversibility of the CNT film, evaluated by a known redox couple, confirms the good electrochemical performance of the electrode. The possible oxygenated species (at surface) reduction at negative potentials could restrict the electrode application. Considering the possible readiness of oxygenated terminations, Zhou et al.[54] discussed the electro reduction of oxidized graphene by a proton contribution to Fray-Farthing-Chen Cambridge process.[84] However, in the present paper, we did not find electrode performance restriction for lead detection at cathodic region. The possible electroreduction of these oxygenated terminations did not have any noticeable prejudice to the VACNT-GO electrode. Seemingly the high oxygen amount at VACNT-GO attenuates the electroreduction or the high number of active edges counterbalances the quantity of electroreduced edges. As far as we know, VACNT-GO electrode (studied in this paper) presents the lowest LoD for Pb(II) detection in similar supporting electrolyte.

Conclusions

We report vertically aligned carbon nanotubes preparation and oxygen plasma treatment to exfoliate their tips and simultaneously produce high oxygen functionalization. The VACNT-GO electrode presented good reversibility when evaluated by known redox couple (K$_3$Fe(CN)$_6$). For Pb(II) electrochemical detection by Differential Pulse Anodic Stripping gives high sensitivity (35.47 uA.uM^{-1}) and low detection limit (48.3 pM). As far as we know, this is the lowest LoD in comparison with other works using CNT or graphene electrodes. The low LoD is even comparable to the sensitive bismuth based electrodes and the most sensitive thin film mercury electrode reported.

Allied with low LoD, the VACNT-GO electrode presents an impressive sensitivity. We assign the good electrode performance to plentiful graphene edges at CNT tips and its oxygen functionalization. This is a new promising electrode material for application in electroanalysis.

References

1. DIRECTIVE 2002/95/EC - Official Journal of the European Union - 27/01/2003.
2. L. Fewtrell, R. Kaufmann, and A. Prüss-Üstün, (2003). Geneva, World Health Organization (Environmental Burden of Disease Series, No. 2).
3. A. Jemal, R. Siegel, E. Ward, Y. Hao, J. Xu, T. Murray, and M. J. Thun, *Ca-a Cancer Journal for Clinicians*, **58**, 71 (2008).
4. S. L. C. Ferreira, H. S. Ferreira, G. D. Matos, D. S. Anunciacao, W. N. L. dos Santos, V. P. Campos, J. B. de Andrade, B. Welz, R. G. O. Araujo, A. J. Curtius, P. C. Nascimento, L. Tormen, and C. L. Jost, *Applied Spectroscopy Reviews*, **47**, 633 (2012).
5. J. F. Wu and E. A. Boyle, *Anal. Chem.*, **69**(13), 2464 (1997).
6. B. J. Feldman, J. D. Osterloh, B. H. Hata, and A. D'Alessandro, *Anal. Chem.*, **66**(13), 1983 (1994).
7. D. S. Kim, J. E. Park, J. K. Shin, P. K. Kim, G. Lim, and S. Shoji, *Sensors and Actuators B: Chemical*, **117**(2), 488 (2006).
8. K. Ashley, *Electroanalysis*, **7**(12), 1189 (1995).
9. J. Heyrovsky, *Analyst*, **72**, 229 (1947).
10. V. K. Gupta, A. K. Jain, P. Kumar, S. Agarwal, and G. Maheshwari, *Sensors and Actuators B: Chemical*, **113**(1), 182 (2006).
11. V. K. Gupta, A. K. Singh, and B. Gupta, *Analytica chimica acta*, **583**(2), 340 (2007).
12. V. K. Gupta, S. Chandra, and R. Mangla, *Electrochimica Acta*, **47**(10), 1579 (2002).
13. V. K. Gupta, A. K. Singh, M. Al Khayat, and B. Gupta, *Analytica chimica acta*, **590**(1), 81 (2007).
14. V. K. Gupta, S. Chandra, and H. Lang, *Talanta*, **66**(3), 575 (2005).
15. V. K. Gupta, S. Jain, and U. Khurana, *Electroanalysis*, **9**(6), 478 (1997).
16. V. K. Gupta, B. Sethi, R. A. Sharma, S. Agarwal, and A. Bharti, *Journal of Molecular Liquids*, **177**, 114 (2013).
17. V. K. Gupta, R. Prasad, and A. Kumar, *Talanta*, **60**(1), 149 (2003).
18. V. K. Gupta, L. P. Singh, R. Singh, N. Upadhyay, S. P. Kaur, and B. Sethi, *Journal of Molecular Liquids*, **174**, 11 (2012).
19. V. K. Gupta, A. K. Singh, S. Mehtab, and B. Gupta, *Analytica chimica acta*, **566**(1), 5 (2006).
20. V. K. Gupta, A. K. Jain, and P. Kumar, *Sensors and Actuators B: Chemical*, **120**(1), 259 (2006).
21. A. K. Jain, V. K. Gupta, L. P. Singh, and J. R. Raisoni, *Electrochimica Acta*, **51**(12), 2547 (2006).
22. B. Mokhtari and K. Pourabdollah, *Journal of The Electrochemical Society*, **159**(3), K61 (2012).
23. B. Mokhtari and K. Pourabdollah, *Journal of The Electrochemical Society*, **160**(6), B67 (2013).
24. B. Mokhtari and K. Pourabdollah, *Electroanalysis*, **24**(2), 219 (2012).
25. B. Mokhtari and K. Pourabdollah, *Electrochimica Acta*, **76**, 363 (2012).
26. B. Mokhtari and K. Pourabdollah, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **76**(3-4), 403 (2013).
27. V. K. Gupta, R. Mangla, U. Khurana, and P. Kumar, *Electroanalysis*, **11**(8), 573 (1999).
28. R. N. Goyal, V. K. Gupta, and S. Chatterjee, *Biosensors and Bioelectronics*, **24**(12), 3562 (2009).
29. R. N. Goyal, V. K. Gupta, N. Bachheti, and R. A. Sharma, *Electroanalysis*, **20**(7), 757 (2008).
30. R. N. Goyal, V. K. Gupta, and N. Bachheti, *Analytica chimica acta*, **597**(1), 82 (2007).
31. V. K. Gupta, R. Jain, K. Radhapyari, N. Jadon, and S. Agarwal, *Analytical biochemistry*, **408**(2), 179 (2011).
32. V. K. Gupta, A. Nayak, S. Agarwal, and B. Singhal, *Combinatorial chemistry & high throughput screening*, **14**(4), 284 (2011).
33. V. K. Gupta, Rajni Mangla, and S. Agarwal, *Electroanalysis*, **14**(15-16), 1127 (2002).
34. V. K. Gupta, M. R. Ganjali, P. Norouzi, H. Khani, A. Nayak, and S. Agarwal, *Critical Reviews in Analytical Chemistry*, **41**(4), 282 (2011).
35. G. Sanna, M. I. Pilo, P. C. Piu, A. Tapparo, and R. Seeber, *Analytica Chimica Acta*, **415**, 165 (2000).
36. C. Prado, S. J. Wilkins, F. Marken, and R. G. Compton, *Electroanalysis*, **14**, 262 (2002).
37. R. N. Adams, *Analytical Chemistry*, **30**, 1576 (1958).
38. K. Kalcher, *Electroanalysis*, **2**, 419 (1990).
39. J. Morton, N. Havens, A. Mugweru, and A. K. Wanekaya, *Electroanalysis*, **21**, 1597 (2009).
40. D. A. C. Brownson and C. E. Banks, *Rsc Advances*, **2**, 5385 (2012).
41. M. Pumera, *Chem. Eur. J.*, **15**, 4970 (2009).
42. C. E. Banks and R. G. Compton, *Analyst*, **131**, 15 (2006).

43. K. Scida, P. W. Stege, G. Haby, G. A. Messina, and C. D. García, *Anal. Chim. Acta.*, **691**, 6 (2011).
44. F. Wantz, C. E. Banks, and R. G. Compton, *Electroanalysis*, **17**, 655 (2005).
45. C. E. Banks, T. J. Davies, G. G. Wildgoose, and R. G. Compton, *Chemical Communications*, **7**, 829 (2005).
46. C. E. Banks and R. G. Compton, *Analytical Sciences*, **21**, 1263 (2005).
47. R. R. Moore, C. E. Banks, and R. G. Compton, *Analytical Chemistry*, **76**, 2677 (2004).
48. M. Musameh, N. S. Lawrence, and J. Wang, *Electrochemistry Communications*, **7**, 14 (2005).
49. A. I. Aria and M. Gharib, *Langmuir*, **27**, 9005 (2011).
50. A. O. Lobo, S. C. Ramos, E. F. Antunes, F. R. Marciano, V. J. Trava-Airoldi, and E. J. Corat, *Materials Letters*, **70**, 89 (2012).
51. A. Chou, T. Böcking, N. K. Singh, and J. J. Gooding, *Chemical communications*, **7**(7), 842 (2005).
52. X. Ji, C. E. Banks, A. Crossley, and R. G. Compton, *ChemPhysChem.*, **7**, 1337 (2006).
53. A. Ambrosi, A. Bonanni, Z. Sofer, J. S. Cross, and M. Pumera, *Chem. Eur. J.*, **17**, 10763 (2011).
54. M. Zhou, Y. L. Wang, Y. M. Zhai, J. F. Zhai, W. Ren, F. A. Wang, and S. J. Dong, *Chem. Eur. J.*, **15**, 6116 (2009).
55. K. Yu, G. Lu, Z. Bo, S. Mao, and J. Chen, *J. Phys. Chem. Lett.*, **2**(13), 1556 (2011).
56. E. F. Antunes, A. O. Lobo, E. J. Corat, and V. J. Trava-Airoldi, *Carbon*, **45**, 913 (2007).
57. A. O. Lobo, S. C. Ramos, E. F. Antunes, F. R. Marciano, V. J. Trava-Airoldi, and E. J. Corat, *Materials Letters*, **70**, 89 (2012).
58. R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, and M. S. Dresselhaus, *Advances in Physics*, **60**, 413 (2011).
59. V. W. Brar, G. G. Samsonidze, M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. K. Swan, M. S. Unlu, B. B. Goldberg, A. G. Souza, and A. Jorio, *Physical Review B*, **66**, 155418 (2002).
60. S. C. Ramos, A. O. Lobo, G. de Vasconcelos, E. F. Antunes, V. J. Trava-Airoldi, and E. J. Corat, *Theoretical Chemistry Accounts*, **130**, 1061 (2011).
61. S. C. Ramos, G. Vasconcelos, E. F. Antunes, A. O. Lobo, V. J. Trava-Airoldi, M. Massi, and E. J. Corat, *Diamond and Related Materials*, **20**, 931 (2011).
62. H. P. Boehm, *Carbon*, **32**, 759 (1994).
63. P. Sonthalia, E. McGaw, Y. Show, and G. M. Swain, *Analytica Chimica Acta*, **522**, 35 (2004).
64. A. M. Bond and B. S. Grabaric, *Analytical Chemistry*, **51**(3), 337 (1979).
65. A. C. Lloyd, *Pure and Applied Chemistry*, **67**, 1699 (1995).
66. G. L. Long and J. D. Winefordner, *Anal. Chem.*, **55**, A712 (1983).
67. C. R. Teixeira Tarley, V. S. Santos, B. E. Lobo Baeta, A. C. Pereira, and L. T. Kubota, *Journal of Hazardous Materials*, **169**, 256 (2009).
68. Z. Wang and E. Liu, *Talanta*, **103**, 47 (2013).
69. Dale A. C. Brownson and Craig E. Banks *RSC Advances*, **2**, 5385 (2012).
70. D. Sun and Z. Sun, *Journal of Applied Electrochemistry*, **38**, 1223 (2008).
71. M. Lu, K. E. Toghill, and R. G. Compton, *Electroanalysis*, **23**, 1089 (2011).
72. S. Anandhakumar and J. Mathiyarasu, *Microchimica Acta*, **180**(11-12), 1065 (2013).
73. T. M. Florence, *Analyst*, **111**, 551 (1986).
74. D. Li, J. Ji, and J. Wang, *Talanta*, **61**, 603/610 (2003).
75. J. Li, S. Guo, Y. Zhai, and E. Wang, *Analytica Chimica Acta*, **649**, 196 (2009).
76. Y. Wei, Z.-G. Liu, X.-Y. Yu, L. Wang, J.-H. Liu, and X.-J. Huang, *Electrochemistry Communications* **13**, 1506 (2011).
77. C. Colombo and C. M. van den Berg, *Analytica chimica acta*, **337**(1), 29 (1997).
78. V. D. Nguyen, P. Valenta, and H. W. Nürnberg, *Science of the Total Environment*, **12**(2), 151 (1979).
79. G. Hanrahan, D. G. Patil, and J. Wang, *Journal of Environmental Monitoring*, **6**(8), 657 (2004).
80. J. Dagner, *Analyst*, **107**(1275), 593 (1982).
81. P. Ostapczuk, P. Valenta, H. Rützel, and H. W. Nürnberg, *Science of the Total Environment*, **60**, 1 (1987).
82. R. Sharma, J. H. Baik, C. J. Perera, and M. S. Strano, *Nano letters*, **10**(2), 398 (2010).
83. T. A. Silva, H. Zanin, E. Saito, R. A. Medeiros, F. C. Vicentini, E. J. Corat, and O. Fatibello-Filho, *Electrochimica Acta*, **119**, 114 (2014).
84. D. Wang, X. Jin, and G. Z. Chen, *Annu. Rep. Prog. Chem., Sect. C*, **104**, 189 (2008).