

Simultaneous Electrochemical Determination of Lead and Copper Based on Graphenated Multi-walled Carbon Nanotubes

Enyu Guo

Operation Management Department, Zhengzhou People's Hospital, Zhengzhou, P. R. China, 450003
E-mail: enyuguo@yahoo.com

Received: 2 June 2015 / Accepted: 19 June 2015 / Published: 28 July 2015

This work presents a fast and sensitive method for simultaneous electrochemical determination of lead and copper based on a graphenated multi-walled carbon nanotubes (G-MWCNT) modified indium tin oxide electrode (ITO). The G-MWCNT was prepared by electrochemical reduction of graphene oxide wrapped multi-walled carbon nanotubes. The modified ITO was characterized by SEM and 3D optical surface profiler. Significantly enhanced electrochemical activity was observed in square wave anodic stripping voltammetry compared to that of bare ITO. The G-MWCNT modified ITO showed a wide detection range of lead from 0.05 to 2.5 μM with a limit of detection of 6 nM and copper from 0.05 to 2.5 μM with a limit of detection of 12 nM. Moreover, the proposed sensor exhibited excellent anti-interference property and reproducibility.

Keywords: Graphene; Multi-walled carbon nanotube; Electroanalysis; Sensor; Lead; Copper

1. INTRODUCTION

Heavy metal contamination has received lots attention due to its non-biodegradable property, severe hazards to human health and environment. Many researchers were dedicated on the development of specific sensors for the quick determination of toxic metal ions [1-3]. Among the heavy metals, lead and copper are two heavy metals have been extensively exploited and discharged in various manufacturing, mining and casting industry [4, 5]. More specifically, lead has found numerous applications in human history, and giving rise to the occurrence of toxic Pb^{2+} contamination [6, 7]. Excessive intake of lead has been implicated in neurological, neurobehavioural, haematological and renal diseases, inhibition of fetal development and malfunctioning of many organs including brain [8-11]. Common analytical techniques for lead detection are polarography method and furnace atomic absorption spectroscopy. Although these methods are very sensitive for lead detection, but they are

very expensive and time consuming in practice [12]. On the other hand, intake of excess of copper will cause various intoxications. For instance, high concentration of copper cations in body could lead imbalance in cellular processes resulting in pathogenesis such as Wilson's disease [13-21]. Several methods have been developed for determining copper ions such as ion chromatography, inductively coupled plasma-mass spectrometry, colorimetric analysis and atomic adsorption [22-27]. However, most of these techniques are expensive, complicated operation procedures and time consuming.

Therefore, development of electrochemical sensor for lead and copper ions detection is an alternative approach because of its outstanding merits in terms of instrumentation costs, operation convenience and on-site rapid application [28, 29]. In order to enhance the electrochemical property of the electrode, many materials have been used as electrode modifier. Many studies showed that the electrochemical performance of the electrode could be enhanced by modification of carbon materials. Graphene, a two-dimensional sp^2 -hybridized carbon material, with a large surface area, has attracted attention of various research groups as it exhibited excellent electron transfer rate, large surface area, high electrocatalytic property and relatively low cost [30-32]. On the other hand, multi-walled carbon nanotubes have a unique structure and excellent chemical stability, make it very attractive in electrochemical applications [33]. Since carbon nanomaterials could highly enhance the electrochemical activity of the electrode, combining between various carbon nanomaterials is exciting and expected to generate a suitable electrode material for lead and copper detection [34].

In this work, we fabricated an electrochemical sensor for simultaneous determination of lead and copper based on the electrochemically reduced graphenated multi-walled carbon nanotubes modified ITO. Square wave anodic stripping voltammetry (SWASV) was applied for evaluating the performance of the modified electrode. The anti-interference property and reproducibility of the proposed sensor also were discussed.

2. EXPERIMENTS

Synthetic graphite was purchased from Sigma-Aldrich. MWCNT was purchased from Shenzhen Nanotech Port Co. Ltd. (China). All other chemicals used were analytical grade reagents without further purification. Milli-Q water was used throughout the experiments.

Graphene oxide (GO) was firstly prepared with the modified Hummers method with little modifications [35, 36]. The GO wrapped MWCNT dispersion was prepared by adding GO (80 mg) into 160 mL water through 1 h ultrasound under ambient condition, then 20 mg MWCNT was introduced to the dispersion for further 3 h ultrasound until a homogeneous black suspension was achieved. After that, 1 mL GO-MWCNT dispersion was dropped onto the ITO substrate and dried at room temperature.

The electro-reduction of GO-MWCNT to graphenated multi-walled carbon nanotubes (G-MWCNT) was conducted using a conventional three-electrode system. A GO-MWCNT/ITO was used as working electrode, one platinum wire was used as the auxiliary electrode and an Ag/AgCl (3M KCl) as the reference electrode. The electrochemical reduction process was applied to obtain G-

MWCNT/ITO by immersing GO-MWCNT/ITO into 0.1 M pH 7.0 PBS solution with cyclic sweeping in the potential range from 0.0 to -1.5 V at a scan rate of 10 mV/s for 20 cycles.

The morphology of the MWCNT-RGO thin film was characterized using a scanning electron microscope (SEM, S-4700, Hitachi). The thickness of the thin film was measured using optical 3D profiler (Contour GT-I, Bruker).

3. RESULTS AND DISCUSSION

The morphology of the G-MWCNT was observed using SEM. Figure 1A shows the typical top-view SEM image of the G-MWCNT/ITO. A clear film was observed on the ITO surface, which consists with a very dense structure of graphenated MWCNT. The thickness of the G-MWCNT film was measured by an optical 3D profiler. Figure 1B shows the scanning profile of the cross-section of the G-MWCNT film. As shown in the figure, the thickness of the G-MWCNT can be measured as 0.7 μm . In addition, the both SEM and optical 3D profiler characterizations reveal that the G-MWCNT prepared by our proposed method could display a uniform surface morphology.

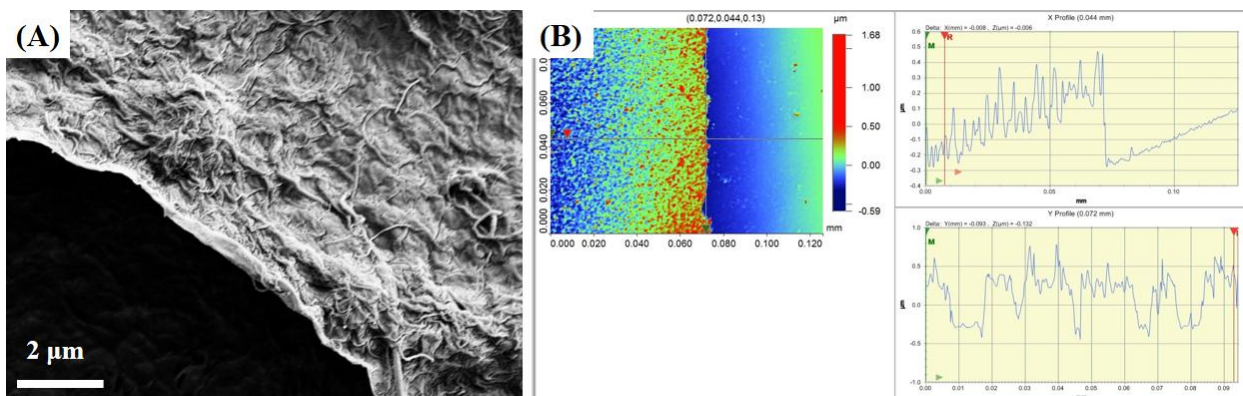


Figure 1. (A) SEM image and (B) optical 3D profiler image of G-MWCNT/ITO.

Then, the proposed G-MWCNT/ITO was used for determination of Pb(II) and Cu(II) in water. Figure 2 presents the SWASV analytical characteristic of bare ITO, RGO/ITO, MWCNT/ITO and G-MWCNT/ITO in 0.1 M acetate buffer (pH 5.0) containing 0.5 μM Pb(II) and Cu(II). It can be observed that the bare ITO shows two very weak peaks in the potential range of -0.5 to 0.5 V. The characteristic stripping potentials of Pb(II) and Cu(II) are recorded at -0.21 and 0.12 V, respectively. The higher peak currents were observed at RGO/ITO and MWCNT/ITO, indicating the surface modification of carbon materials could efficiently enhance the electrochemical performance of the electrode. Moreover, the even sharper and higher peak currents were observed at G-MWCNT/ITO, which indicated that G-MWCNT had much better electrocatalysis toward Pb(II) and Cu(II) than other cases. This enhancement could attribute to the high specific surface area and defective sites of the G-MWCNT, which may produce many active sites for electron transfer route for copper ions [37, 38].

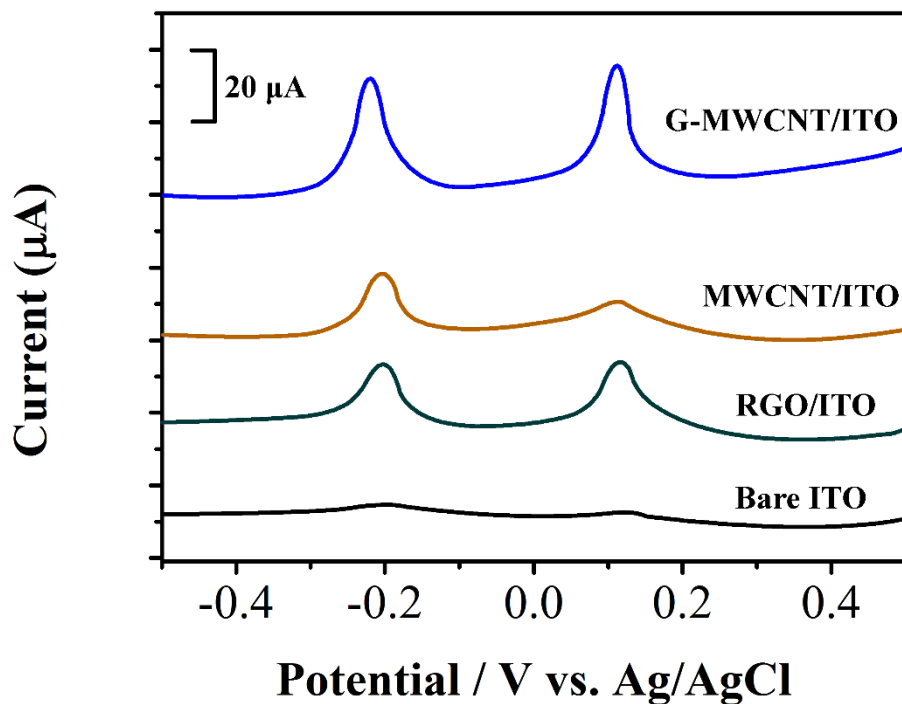


Figure 2. SWASVs for 0.5 μM of Pb(II) and Cu(II) on bare ITO, RGO/ITO, MWCNT/ITO and G-MWCNT/ITO in 0.1 M acetate buffer (pH 5.0).

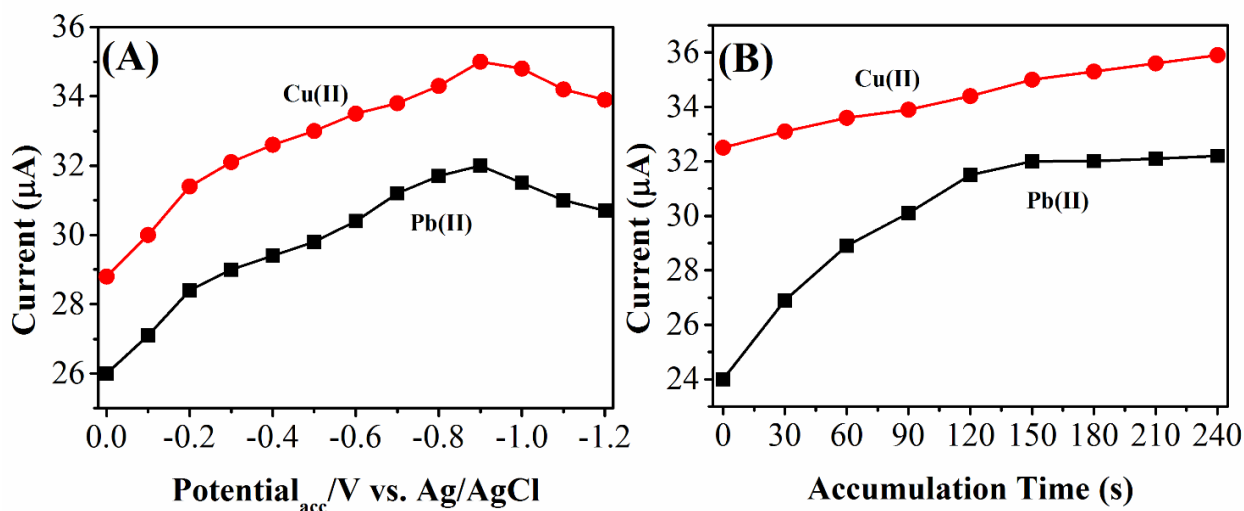


Figure 3. Effect of the (A) accumulation potential and (B) accumulation time on the current response of 0.5 μM of Pb(II) and Cu(II) at G-MWCNT/ITO.

The influence of the accumulation step has been investigated because it could highly enhance the electrochemical performance of the electrode. Figure 3 shows the effect of accumulation potential and time in the Pb(II) and Cu(II) detection. As shown in Figure 3A, the highest current responses for both Pb(II) and Cu(II) were obtained at -0.90 V. As shown in Figure 3B, the current responses were increased gradually with the increasing of accumulation time from 0 to 150 s and only had a little

change if a longer accumulation time was applied. Therefore, in this case, the accumulation conditions of -0.90 V and 150 s were chosen for determining Pb(II) and Cu(II).

The effect of pH value of electrochemical determination of Pb(II) and Cu(II) was also investigated. Figure 4 shows the effect of pH value from 3 to 7 in the Pb(II) and Cu(II) detection. It can be seen that the peak current for Pb(II) increased as the pH was increased from 3.0 to 5.0, and then decreased up to pH 7.0. On the other hand, the peak current for Cu(II) increased as the pH was increased from 3.0 to 5.0, and then remained a similar response when the pH increased to 7.0. Therefore, pH 6.0 was chosen for determining Pb(II) and Cu(II).

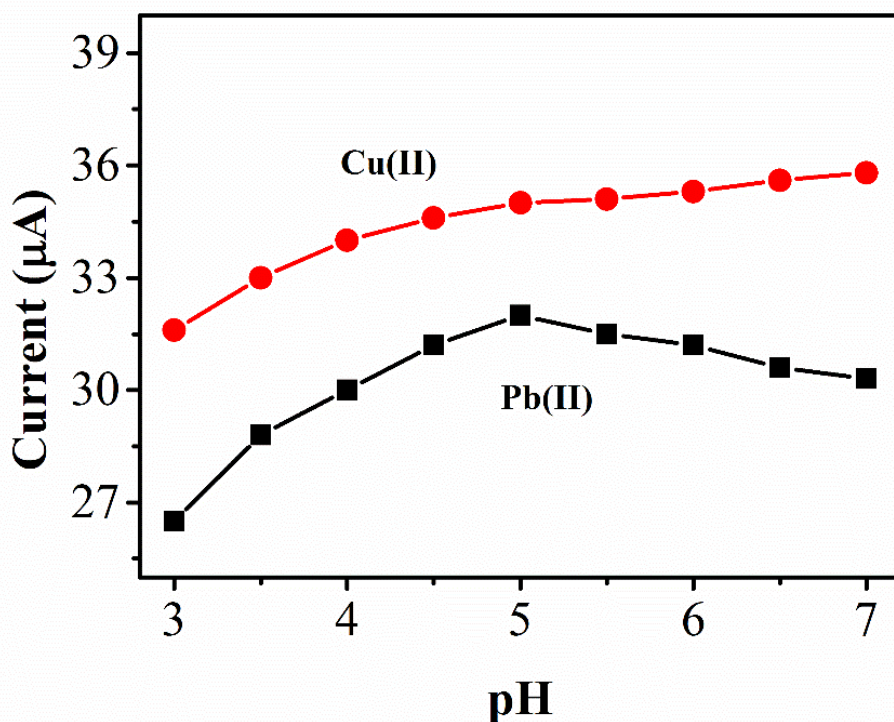


Figure 4. Effect of the pH values on the current response of $0.5 \mu\text{M}$ of Pb(II) and Cu(II) at G-MWCNT/ITO.

Figure 5 shows the SWASV curves for various concentrations of Pb(II) and Cu(II) at G-MWCNT/ITO recorded under optimum experimental conditions. Well-defined peaks, proportional to the concentration of Pb(II) and Cu(II), were observed in the range of 0.05 to $2.5 \mu\text{M}$. The linear regression equation of Pb(II) can be expressed as $I_{pa} (\mu\text{A}) = 39.3282 c (\mu\text{M}) + 5.8837$, with a correlation coefficient of 0.994. The linear regression equation of Cu(II) can be expressed as $I_{pa} (\mu\text{A}) = 42.5585 c (\mu\text{M}) + 8.6879$, with a correlation coefficient of 0.990. The limit of detections (LOD) of Pb(II) and Cu(II) were estimated to be 12 nM and 6 nM , respectively, based on signal-to-noise ratio of 3. The comparison of our proposed sensor with other literatures was summarized in Table 1. The results indicate the G-MWCNT/ITO has a higher determination performance, which could lead to practical application.

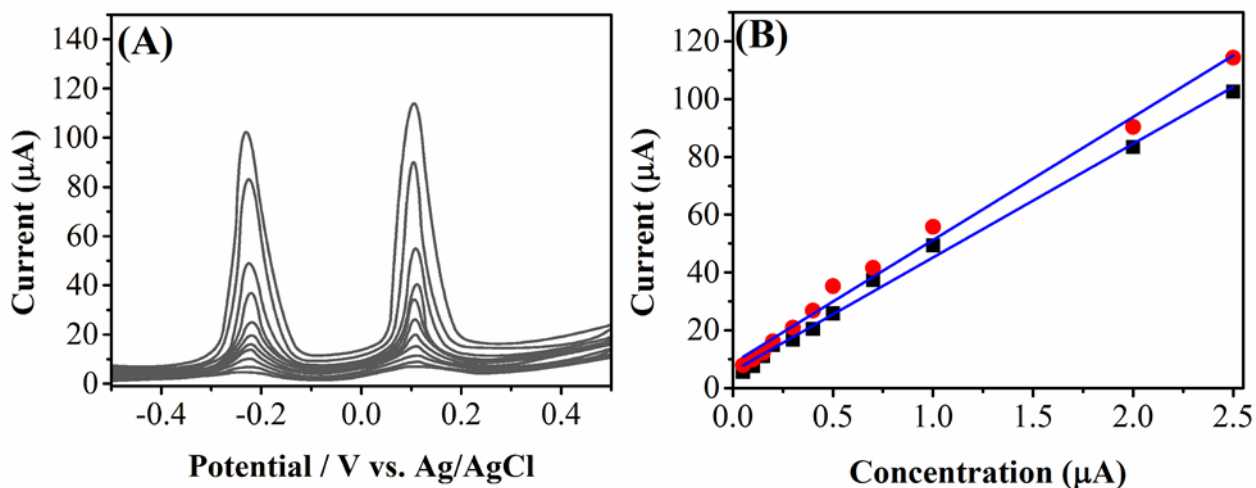


Figure 5. (A): SWASV response of the G-MWCNT/ITO for the simultaneous analysis of Pb(II) and Cu(II) over a concentration range of 0.05 to 2.5 μM.(B) Plots of the value of anodic peak currents as a function of the concentration of Pb(II) and Cu(II).

Table 1. Comparison of the analytical performance of G-MWCNT/ITO with previously reported electrochemical ion sensors.

Electrode	Method	LOD (μM) for Pb(II)	Linear range (μM) for Pb(II)	LOD (μM) for Cu(II)	Linear range (μM) for Cu(II)	Reference
Boron-doped diamond film electrodes	SWASV	0.5	2.5-100	0.5	2.5-100	39
3MT/3TA/Au/Al	CV	N/A	N/A	0.06	0.1–10	40
Carnosine–Silica	SLV	N/A	N/A	0.04	0.05-1	41
MWCNT based GCE	DPASV	0.09	0.5-2	0.23	1-5	42
Carbon NPs SPE	SWASV	0.048	0.5-10	0.079	0.5-10	43
MWCNT tower based GCE	SWASV	0.12	2-10	0.67	2-10	44
G-MWCNT /ITO	SWASV	0.012	0.05-2.5	0.06	0.05-2.5	This work

The selectivity of the G-MWCNT/ITO was investigated in the presence of common metal ion interferences, such as Ni²⁺, Zn²⁺ and Co²⁺. The results showed that the 50-folds of Ni²⁺, Zn²⁺ and Co²⁺ did not interfere with the analysis of Pb(II) and Cu(II) (less than ±5%). Therefore, detection of Pb(II) and Cu(II) in our proposed sensor is not influenced by the common interferences. The stability of the G-MWCNT/ITO was studied by SWASV eight repetitive stripping voltammograms for 0.5 μM Pb(II) and Cu(II) detection. Relative standard deviations of 2.77% and 1.78% were obtained for Pb(II) and

Cu(II), respectively. The reproducibility of the G-MWCNT/ITO, six freshly prepared electrodes were tested for determination of 0.5 μM Pb(II) and Cu(II). The relative standard deviation for the peak currents was determined to be 2.22 %, suggesting a satisfactory reproducibility of the sensor preparation procedure.

4. CONCLUSION

In this work, we demonstrated a simple, inexpensive and highly sensitive electrochemical sensor for the simultaneous detection of Pb(II) and Cu(II) based on a G-MWCNT modified ITO. The preparation method is simple and inexpensive. The proposed electrochemical sensor can detect as low as 12 nM and 6 nM for Pb(II) and Cu(II), respectively, with a linear detection range between 0.05 to 2.5 μM . Moreover, the proposed sensor also exhibited an excellent anti-interference property and reproducibility.

Reference

1. A. Miyawaki, J. Llopis, R. Heim, J.M. McCaffery, J.A. Adams, M. Ikura and R.Y. Tsien, *Nature*, 388 (1997) 882
2. A.P.F. Turner, *Science*, 290 (2000) 1315
3. L. Fu and Z. Fu, *Ceram Int*, 41 (2015) 2492
4. R. Kumar Sharma, M. Agrawal and F. Marshall, *Ecotoxicology and environmental safety*, 66 (2007) 258
5. L. Fu, T. Xia, Y. Zheng, J. Yang, A. Wang and Z. Wang, *Ceram Int*, 41 (2015) 5903
6. J.O. Nriagu and J.M. Pacyna, *Nature*, 333 (1988) 134
7. L. Fu, Y.-H. Zheng and Z.-X. Fu, Ascorbic acid amperometric sensor using a graphene-wrapped hierarchical TiO_2 nanocomposite, *Chemical Papers*, 2015, pp. 655.
8. L. Patrick, *Alternative Medicine Review*, 11 (2006) 2
9. M.F. Aleo, F. Bettoni, J. Boniotti, F. Morandini, R. Giuliani, N. Steimberg, P. Apostoli and G. Mazzoleni, *Toxicology in Vitro*, 20 (2006) 874
10. L. Fu, Y. Zheng, Z. Wang, A. Wang, B. Deng and F. Peng, *Digest Journal of Nanomaterials and Biostructures*, 10 (2015) 117
11. Y. Zheng, L. Fu, A. Wang and W. Cai, *Int. J. Electrochem. Sci*, 10 (2015) 3530
12. Z. Wang, Y. Qin, C. Wang, L. Sun, X. Lu and X. Lu, *Appl Surf Sci*, 258 (2012) 2017
13. T. Hirayama, G.C. Van de Bittner, L.W. Gray, S. Lutsenko and C.J. Chang, *Proceedings of the National Academy of Sciences*, 109 (2012) 2228
14. E. Madsen and J.D. Gitlin, Copper and iron disorders of the brain, *Annual Review of Neuroscience*, 2007, pp. 317.
15. J.S. Valentine and P.J. Hart, *Proceedings of the National Academy of Sciences*, 100 (2003) 3617
16. C. Vulpe, B. Levinson, S. Whitney, S. Packman and J. Gitschier, *Nature Genetics*, 3 (1993) 7
17. S.G. Kaler, *Nature Reviews Neurology*, 7 (2011) 15
18. Y.H. Hung, A.I. Bush and R.A. Cherny, *Journal of Biological Inorganic Chemistry*, 15 (2010) 61
19. J.C. Lee, H.B. Gray and J.R. Winkler, *Journal of the American Chemical Society*, 130 (2008) 6898
20. L. Fu, W. Cai, A. Wang and Y. Zheng, *Materials Letters*, 142 (2015) 201
21. L. Fu, W. Cai, A.W. Wang, Y.H. Zheng, L. He and Z.X. Fu, *Mater. Technol.*, 30 (2015) 264

22. X. Zhang, X. Jing, T. Liu, G. Han, H. Li and C. Duan, *Inorganic Chemistry*, 51 (2012) 2325
23. J. Zhang, M. Riskin, R. Tel-Vered, H. Tian and I. Willner, *Langmuir*, 27 (2011) 1380
24. Z. Guo, W. Zhu, Y. Xiong and H. Tian, *Macromolecules*, 42 (2009) 1448
25. S. Chen, Y. Yang, Y. Wu, H. Tian and W. Zhu, *Journal of Materials Chemistry*, 22 (2012) 5486
26. M.A. Chamjangali, S. Soltanpanah and N. Goudarzi, *Sensors and Actuators, B: Chemical*, 138 (2009) 251
27. N. Narayanaswamy and T. Govindaraju, *Sensors and Actuators, B: Chemical*, 161 (2012) 304
28. R.J. Reay, A.F. Flannery, C.W. Stormont, S.P. Kounaves and G.T.A. Kovacs, *Sensors and Actuators B: Chemical*, 34 (1996) 450
29. Y. Zheng, A. Wang, H. Lin, L. Fu and W. Cai, *RSC Advances*, 5 (2015) 15425
30. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov, *Science*, 306 (2004) 666
31. S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen and R.S. Ruoff, *Nature*, 442 (2006) 282
32. L. Fu, A. Wang, Y. Zheng, W. Cai and Z. Fu, *Materials Letters*, 142 (2015) 119
33. Y. Zou, C. Xiang, L.-X. Sun and F. Xu, *Biosensors and Bioelectronics*, 23 (2008) 1010
34. X. Chen, J. Zhu, Q. Xi and W. Yang, *Sensors and Actuators B: Chemical*, 161 (2012) 648
35. W.S. Hummers and R.E. Offeman, *Journal of the American Chemical Society*, 80 (1958) 1339
36. T. Gan and S. Hu, *Microchim Acta*, 175 (2011) 1
37. S. Woo, Y.-R. Kim, T.D. Chung, Y. Piao and H. Kim, *Electrochimica Acta*, 59 (2012) 509
38. A. Wang, H.P. Ng, Y. Xu, Y. Li, Y. Zheng, J. Yu, F. Han, F. Peng and L. Fu, *Journal of Nanomaterials*, 2014 (2014) 6
39. C. Prado, S.J. Wilkins, F. Marken, and R.G. Compton, *Electroanalysis*, 14 (2002) 262
40. M. Lin, M.S. Chob, W.S. Choea, Y. Sonc and Y. Lee. *Electrochimica Acta*, 54 (2009) 7012
41. S. Sayen, C. Gérardin, L. Rodehüser and A. Walcarius. *Electroanalysis*, 15 (2003) 422
42. J. Morton, N. Havens, A. Mugweru, and A.K. Wanekaya. *Electroanalysis*, 21 (2009) 1597
43. G. Aragay, J. Pons, and A. Merkoçi. *Journal of Materials Chemistry*, 21 (2011) 4326
44. X. Guo, Y. Yun, V.N. shanov, H.B. Halsall and W.R. Heineman. *Electroanalysis*, 23 (2011) 1252