Int. J. Electrochem. Sci., 11 **(2016)** 7430 – 7439, doi: 10.20964/2016.09.38

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Graphene Ink Fabricated Screen Printed Electrode for Cd^{2+} and Pd^{2+} Determination in Xiangjiang River

Hong Shuai[*], *Yanjin Lei*

College of Resources and Environment Sciences, Hunan Normal Univerty, No. 36 Lushan Rd, Changsha, P.R. China
[*]E-mail: shuaih823@163.com

Received: 16 June 2016 / *Accepted:* 11 July 2016 / *Published:* 7 August 2016

A disposable and sensitive screen-printed electrode constructed with an ink containing graphene was successfully prepared. Owing to the combination of the disposable characteristic of electrode and specific advantages of graphene, the as-prepared electrode demonstrated low background current, fast electron transfer kinetics and wide potential window. Screen-printed graphene electrode (SPG) exhibited excellent electrocatalytic activity in the simultaneous determination of Cd^{2+} and Pb^{2+}. Moreover, the proposed SPG was also successfully employed for the determination of concentrations of Pb^{2+} and Cd^{2+} in Xiangjiang river in China.

Keywords: Graphene ink; Screen-printed electrode; Cd^{2+}; Pd^{2+}; Electrochemical sensor; Xiangjiang river

1. INTRODUCTION

Heavy metals (*e.g.* Pb^{2+}, Cd^{2+}), widely used in various industrial applications such as batteries and electroplating, have recently attracted worldwide attention due to its environmental pollution. What’s worse, owing to the non-biodegradability, the accumulation of toxic lead (Pb^{2+}) and cadmium (Cd^{2+}) in the human body will cause damages to central nervous system and internal organs including kidney and liver [1]. Accompanied with the dramatic economic growth in China over the last several decades, serious environmental problems have occurred. As the source of life, water is of great importance to living things. However, the water resources are extremely scarce in China since the water supply per person is only 1/4 of the global average [2, 3]. Even more disastrous was the deterioration of water shortage caused by pollutant discharges, especially heavy metals. Nowadays, a water quality survey all over China was carried out and the results have demonstrated that only 64.2%

of the rivers, 58.8% of the lakes and 23.2% of the ground water wells have reached international standard for drinking water. Heavy metals involved in water not only possess long-term risks to human health but also limit the sustainable development of economy and society [4-7]. As demonstrated by Liu's study [8], industrial wastewater discharged from many factories should be responsible to the high cancer incidences in surrounding villages. Till now, almost 459 cancer villages have formed across China. As a result, effective control of the concentration of heavy metals in water is critical important. Recently, several techniques including inductively couple plasma optical mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) and X-ray fluorescence spectroscopy (XRF) have been employed for the determination of the concentrations of Pb^{2+} and Cd^{2+} in water resources. Nevertheless, all the above-mentioned determination methods have certain disadvantages such as long analysis time and the requirement of specialized operator and expensive instrumentation [9]. Electrochemical techniques, by contrast, has various advantages including low cost and fast analysis with high sensitivity [10, 11].

Nowadays, screen-printed electrodes (SPEs) have obtained the widespread application in the field of electrochemical sensing owing to its superior property. The greatest advantage is that the preparation method of SPEs is simple, fast, cheap and easy to enlarge [12, 13]. Till now the study of the application of SPEs in the determination of heavy metal ions has not received a wide range of attention. Certain researchers have found that the modified SPEs with Bi nanoparticles [14], Au nanoparticles [15], Bi_2O_3 or Sb_2O_3 [16] and bismuth precursor compounds [17] could be successfully employed for detection of heavy metal ions. Nevertheless, the studied electrodes still have many shortcomings such as low sensitivity, poor reproducibility and complex preparation process. Since the screen-printing ink dictated the performance of SPEs, developing a suitable ink is the most important challenge automatically. As demonstrated in reported literatures, the composite of cellulose acetate and graphite has been found to be promising material that can be used in ink system of SPEs [18, 19]. The ink composed of the composite could also be doped with catalysts simply and the modified ink could be used for the determination of various analytes. In addition, through incorporating ionic liquid for binding, the conductivity and stability of the ink can be remarkably enhanced [20].

Graphene, a two-dimensional material with only one-atom-thick layer of carbon, has numerous applications including catalyst, electrochemical devices, polymer filler, supercapacitor and solar cells [21-24]. Owing to the large surface area, very fast electron conductivity and good biocompatibility, graphene has demonstrated to be a promising material in the application of electrochemical devices [25, 26].

In our work, a screen-printing ink composed of graphene and ionic liquid was employed in the fabrication of SPG. Then the electrochemical performances of the as-synthesized SPG toward Cd^{2+} and Pd^{2+} were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). According to the obtained results of electrochemical activity above, a method was established for simultaneous determining the analysts sensitively and selectively, and the method was further used for the analysis of real water sample in Xiangjiang river in southern China.

2. EXPERIMENTS

2.1. Materials

Graphite powder (SP-1 graphite) was supplied by Bay Carbon Corporation. Cellulose acetate and hydrazine were purchased from Analytical Chemical Reagent Co., Ltd. Ionic liquid *n*-butylpyridinium hexafluorophosphate (BPFP) was supplied by Tianjing Chemical Co., Ltd. The standard solutions of $Cd^{2+}$and Pb^{2+} (1000 mg/L) were obtained from VWR International Ltd. (Poole, England) and diluted before use. All chemicals were used as purchased without further purification. Double distilled water was employed throughout the experiments. SSLtd. (USA).

2.2. Preparation graphene oxide and reduced graphene oxide

According to the reported Hummers method [27], graphene oxide (GO) was successfully prepared by harsh oxidation of graphite powder. Then the obtained GO powder could be thermally reduced to reduced graphene oxide (RGO). The specific experimental procedures were as follows: the GO powder was firstly transferred into a porcelain boat that was placed in the Quartz tube of furnace, then the powder was heated to 800 °C with the heating rate of 10 °C min^{-1} and kept at 800 °C for 2 h. The entire high temperature calcination process was under anoxic conditions realized by flowing mixture gas Ar-H_2 (85:15 vol%) with the flow rate of 150 cc/min [28]. Finally, the fluffy and highly exfoliated RGO was successfully synthesized and the yield was higher than 84 %. Before use, the RGO should be heated at 100 °C for 12 h in order to remove the adsorbed water.

2.3. Electrode fabrication

The screen-printing ink was synthesized using the following method. Firstly, cellulose acetate (0.02 g), acetone (1 mL) and cyclohexanone (1 mL) were mixed together and sonicated for 10 min to make sure that cellulose acetate achieved a complete dissolution. Then, BPFP (0.20 g) and RGO powder (0.78 g) were added into the obtained solution and sonicated for 30 min until the formation of homogeneous solution with viscosity. The formed solution was used as ink. For comparison, inks modified with graphite powder or GO powder were also synthesized using the exactly same method, respectively. In this work, bare SPE, graphene oxide modified SPE and graphene ink modified SPE were denoted as SPE, SPO and SPG, respectively. In order to evaluate the performance of the prepared inks, the printed process was carried out manually through a screen printer. Before use, the poly(vinyl chloride) (PVC) substrate was washed with double distilled water, ethanol and then dried at room temperature. Then a squeegee was employed to print the ink onto the PVC substrate through a screen mesh with the size of 200 μm. In order to remove the solvents, the as-synthesized electrode was heated at 70 °C for 30 min in an oven. Finally, the surface of carbon film was further modified with an insulating layer and then solidified through irradiating by the 254 nm ultraviolet. For comparison, commercially available graphite ink was also used for the preparation of electrode. The working area of the prepared SPEs was 0.08 cm^2 (4 mm × 2 mm) and the size of connecting strip was 8 mm × 4 mm.

2.4. Characterizations

A CHI 440 electrochemical workstation (CH Instruments, USA) was employed for the entire electrochemical measurements. Three-electrode system including working electrode (as-prepared SPE), auxiliary electrode (platinum wire) and reference electrodes (Ag/AgCl) was used. The detection of Cd^{2+} and Pb^{2+} was performed in a 10.0 mL aliquot with the pH of 3.5 at room temperature by the SWASV method. Before each measurement, the potential was set at 0.9 V for 30 s. A potential of -1.1 V was set for 190 s in the pre-concentration step. While the potential swept from -1.25 to -0.22 V, SWASV were recorded. Electrochemical impedance spectroscopy (EIS) with 5 mM $[Fe(CN)_6]^{3-/4-}$ as probe and 0.1 M KCl as electrolyte was studied for characterizing the electrode resistance performance. The specific parameters are set as follows: the frequency range from 10^1 to 10^5 Hz and the amplitude 5 mV. Field emission scanning electron microscope (SEM, Hitachi-S4800) was applied for measuring the morphology feature of SPG.

2.5. Collection and preparation of water samples from Xiangjiang river

The real water samples were collected from Xiangjiang River using plastic tube (50 mL). Prior to analysis, the water samples were required to be filtrated using filter paper with the pore size of 200 nm. After that, 3% nitric acid was used for the acidification of the water samples and the acid-treated samples were brought to boil by heating on a hot plate. Then two aliquots of milli Q water were added. During the interval of adding milli Q water, the sample solution could be heated in order to evaporate the remaining nitric acid. Finally, HCl was used for adjusting the pH of the solution. For the sake of evaluating the accuracy of the results, standard addition procedure was employed.

3. RESULTS AND DISCUSSION

The morphology feature of SPG was characterized by SEM. As can be seen form Fig. 1, the electrode fabricated with the ink composed of graphene and ionic liquid showed a uniform surface with no voids, suggesting good interaction between RGO sheets and ionic liquid.

The effects of electrolytes on the background currents of the developed SPG were investigated by using different electrolytes such as HCl (1.0 M), NaOH (0.5 M), KCl (0.1 M), PBS with pH of 7.0 (0.1 M) and ABS with pH of 4.5 (0.1 M). As demonstrated in Fig. 2A, broad potential window extended to ~2.4 V was observed for all of the tested electrolytes. The background currents of SPG recorded in all electrolytes were highly stable under the non-stop scan cycles, suggesting the promising potential of developed SPG constructed using graphene-based ink for application in electro-analysis.

Impedance measurements were carried out for evaluating the performance of SPG and SPE for electron transfer kinetics and the results were shown in Fig. 2B. Here $Fe(CN)_6^{3-/4-}$ was used as the redox probe. The diameter of semicircle in the high- frequency region of Nyquist plots is exactly the charge transfer resistance (R_{ct}) value. As calculated form Fig. 2B, the R_{ct} value (430 Ω) obtained on SPG is much smaller than that obtained on SPE (1218 Ω), suggesting the remarkable enhancement of electron conductivity by graphene, which was also found in other graphene modified electrodes [29, 30]. These results were compared with the recent report. After the surface functionalization of RGO at the SPE, the R_{ct} value could greatly decreasing [31].

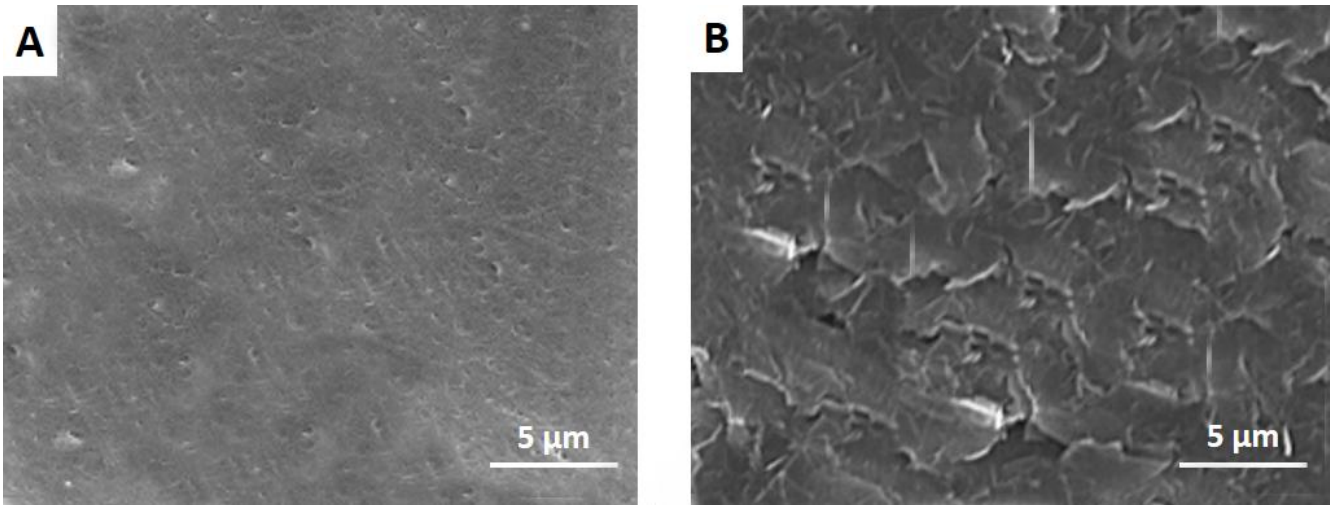

Figure 1. SEM images of SPG at (A) low magnification and (B) High magnification.

The electrochemical performance of SPG and SPO for 1.0 mM $Fe(CN)_6^{3-/4-}$ was compared by testing cyclic voltammograms (CVs) and the results were shown in Fig. 2C. For SPO, only a pair of poor redox peaks was observed, indicating that the electron transfer was very slow at the interface, possibly owing to the poor conductivity of GO and the resistance caused by the oxygen-containing moieties on the surface [32]. As to SPG, a pair of well-defined peaks was observed, suggesting the fast electron transfer at the interface promoted by graphene. The peak current obtained on SPG was much higher than that obtained on other electrodes. Owing to a great deal of graphitic edges on the surface of electrode and high electron conductivity of graphene, the electron transfer kinetics on SPG was remarkably enhanced.

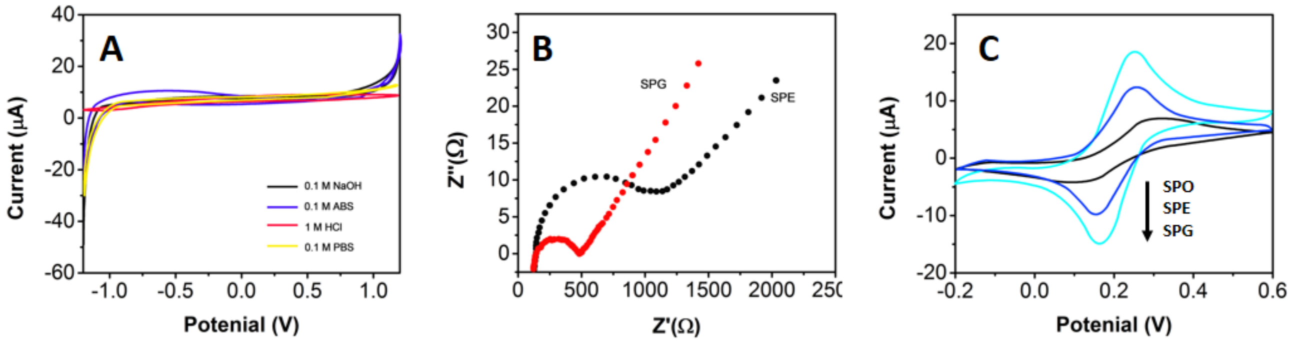

Figure 2. (A) background response of the SPG in various buffer electrolyte, scan rate 10 mV/s. (B) Impedance plots of the SPG and SPE in 0.1 M KCl solution containing 5.0 mM $Fe(CN)_6^{3-/4-}$. (C) CVs for 1.0 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M KCl solution recorded at SPG , SPE and SPO, scan rate 50 mV/s.

SWASV for Cd^{2+} and Pb^{2+} on SPE, SPO and SPG was carried out. By comparing the obtained peak currents on three electrodes, the electron transfer was found to greatly increase by the RGO sheets and the signal was also enhanced by the addition of graphene. The metal ion peak current depends on various parameters of the deposition and stripping steps, as well as on the characteristics of the metal ion to be detected and the electrode geometry.

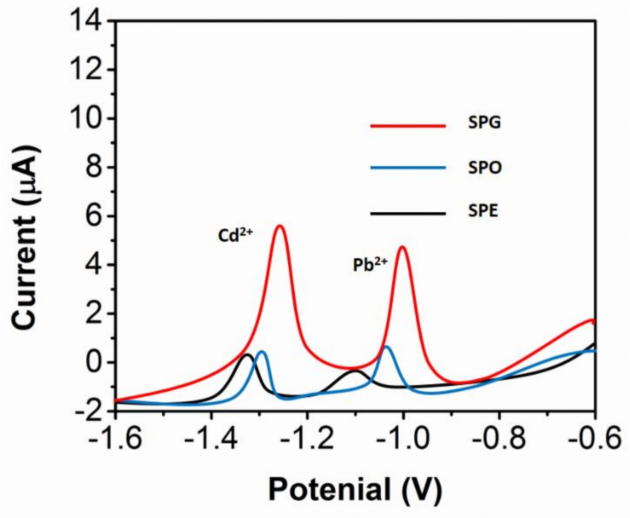

Figure 3. Square-wave voltammogram of 200 μg/L of Cd^{2+} and Pb^{2+} in 1.0 M ABS pH 4.5 measured on SPE, SPO and SPG.

Owing to the linearity and high sensitivity, SWASV can be used for the determination of of Zn(II), Cd(II) and Pb(II) with extremely low levels. The measured potentials of anodic peak for Cd^{2+} and Pb^{2+} were -1.27 and -0.99 V, respectively. Fig.4 showed the anodic peak currents obtained on SPG for the detection of Zn(II), Cd(II) and Pb(II). As can be seen from the calibration plots (Fig. 4B), for all metals, the linear plots were obtained with the concentration ranging from 1.0 to 300 μg/L and the correlation coefficients were all higher than 0.98. Based on S/N=3 (signal to noise ratio), the limits of detection (LOD) for SPG system was 0.1 μg/L for both Cd^{2+} and Pb^{2+}. All tested performances are listed in Table 1. In general, SPG can determine Cd^{2+} and Pb^{2+} sensitively and selectively. Electrochemical performance of the SPG was compared with similar systems in the literature for measuring Cd^{2+} and Pb^{2+}. For the determination of Cd^{2+} and Pb^{2+}, the SPG system demonstrated a wider linear range compared with other reports despite of the fact that the comparable LOD obtained. Moreover, we also used the atomic absorption spectroscopy as a reference method for evaluating the performance of our proposed electrochemical heavy metal ions sensor. The results recorded from SPG could precisely match to the result recorded from atomic absorption spectroscopy (within 5 % RSD). The reproducibility of the developed electrode was evaluated by repetitive measurement of 30 μg/L Pb(II) and Cd(II). For one electrode, the relative standard deviation (RSD) was 4.3% for Cd(II) and 2.7% for Pb(II) in five times measurements. For five different electrodes prepared in a same batch, the RSD was 5.6% for Cd(II) and 2.1% for Pb(II), respectively.

Table 1. Electrode performance for measuring Cd^{2+} and Pb^{2+}.

Electrode	Detection limit of Cd^{2+} (μg/L)	Detection limit of Pb^{2+} (μg/L)	Linear range of Cd^{2+} (μg/L)	Linear range of Pb^{2+} (μg/L)	Reference
CNT arrays	1.8	1.5	1.5-4.5	1-4	[33]
Bismuth/poly(p-aminobenzene sulfonic acid)	0.63	0.8	1-110	1-110	[34]
Nitrogen-doped microporous carbon/Nafion/bismuth-film electrode	1.5	0.05	2-10	0.5-10	[35]
Bi/Au–GN–Cys/GCE	0.1	0.05	0.5-40	0.5-40	[36]
Bi/Nafion/PANI-MES/GCE	0.04	0.05	0.1-20	0.1-30	[37]
Clioquinol/HMDE	0.06	0.1	0-15	0-15	[38]
Carbon paste bulk-modified with antimony powder	0.9	1.4	2-20	5-50	[39]
Cu/Nafion/Bi	0.7	0.9	2-12	2-12	[40]
Gold microwire electrode	—	0.2	—	—	[41]
SPG	0.1	0.1	1-300	1-300	This work

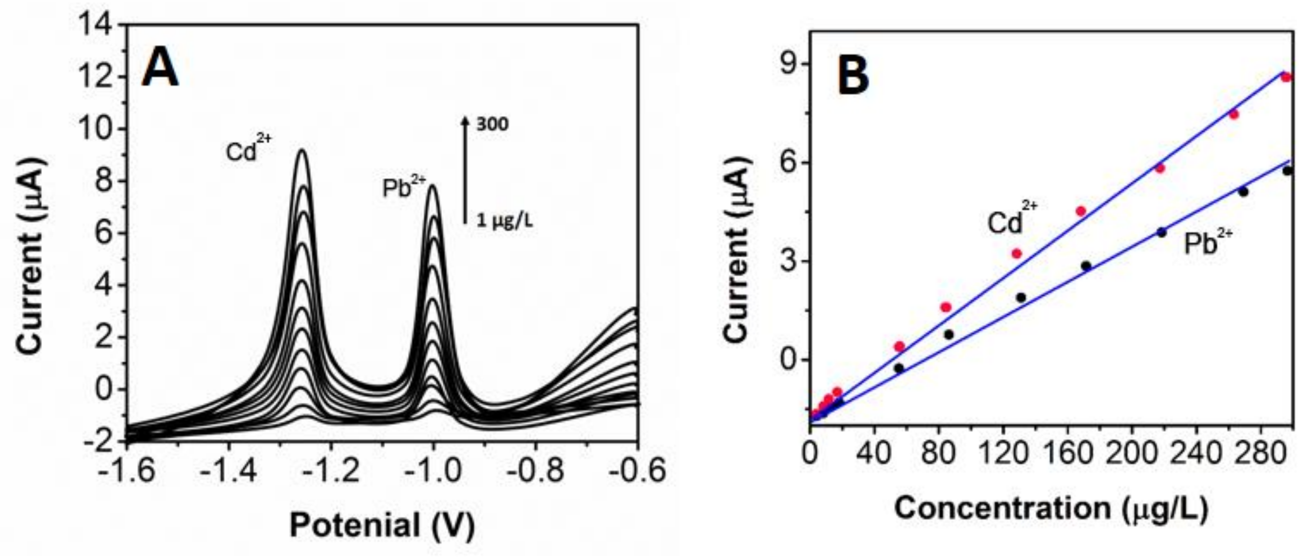

Figure 4. (A) Square-wave voltammogram of Cd^{2+} and Pb^{2+} from 1.0 to 300 μg/L. (B) Representative calibration graph for Cd^{2+} and Pb^{2+}.

The established SPG system was also employed for the determination of real water sample. During the first four month in 2016, water samples from Xiangjiang river were collected from four different locations each month. The average determination results of Cd^{2+} and Pb^{2+} over the four months were shown in Fig. 5. Small amount of heavy metal ions was clearly observed each month. The content of Pb^{2+} was relatively higher than that of the Pb^{2+}. The average concentrations of Cd^{2+} and Pb^{2+} in Xiangjiang river were 12.45 and 14.22 μg/L. Fortunately, both the contents of Cd^{2+} and Pb^{2+}were still acceptable according to the Chinese environmental water quality handbook.

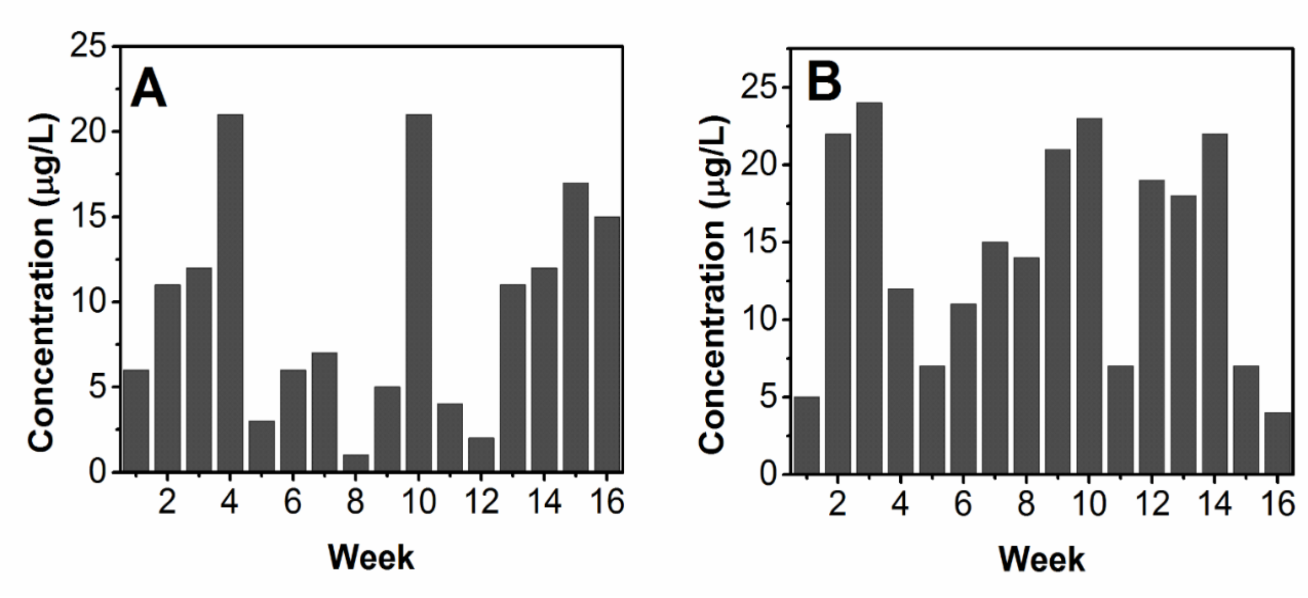

Figure 5. (A) Cd^{2+} and (B) Pb^{2+} value detected from Xiangjiang river water samples from Jan. 2016 to Apr. 2016.

4. CONCLUSIONS

In this study, the SPG system with graphene-based screen-printing ink was successfully fabricated. The developed SPG was then employed for simultaneous determination of Cd^{2+} and Pb^{2+}. As to SPG system, the kinetics of electron transfer for electroactive compound was significantly increased and the over-potential for the oxidation reaction of Cd^{2+} and Pb^{2+} was greatly decreased. Linear correlation within the concentration ranging from 1.0 to 300 μg/L was obtained with limits of detection being 0.1 μg/L for both Cd^{2+} and Pb^{2}. Moreover, the SPG system was also successfully employed for the determination of heavy metal ions in real water samples collected from Xiangjiang river. The contamination profile of heavy metal ions was recorded for Xiangjiang river over 4 months detection.

ACKNOWLEDGEMENTS
The authors would like to thank the Constrct Program of the Key Discipine in Hunan Province (2011001); Outstanding Yong of Scientific Research Fund of Hunan Province Education Department (13B07); Outstanding Yong of Scientific Research Fund of Hunan Normal University for their financial support.

References

1. N. Promphet, P. Rattanarat, R. Rangkupan, O. Chailapakul and N. Rodthongkum, *Sensors and Actuators B: Chemical*, 207 (2015) 526
2. L.-J. Bao, K.A. Maruya, S.A. Snyder and E.Y. Zeng, *Environ. Pollut.*, 163 (2012) 100
3. Y. Zheng, Z. Wang, F. Peng, A. Wang, X. Cai and L. Fu, *Fullerenes, Nanotubes and Carbon*

Nanostructures, 24 (2016) 149
4. J. Liu and J. Diamond, *Nature*, 435 (2005) 1179
5. R. Carr, C. Zhang, N. Moles and M. Harder, *Environmental Geochemistry and Health*, 30 (2008) 45
6. F. Han, H. Li, J. Yang, X. Cai and L. Fu, *Physica. E*, 77 (2016) 122
7. L. Fu, Y. Zheng, A. Wang, W. Cai, B. Deng and Z. Zhang, *Arab J Sci Eng*, 41 (2016) 135
8. L. Liu, *Environment: Science and Policy for Sustainable Development*, 52 (2010) 8
9. G. Aragay and A. Merkoçi, *Electrochimica Acta*, 84 (2012) 49
10. M. Lv, X. Wang, J. Li, X. Yang, C.a. Zhang, J. Yang and H. Hu, *Electrochimica Acta*, 108 (2013) 412
11. L. Fu, M.M. Sokiransky, J. Wang, G. Lai and A. Yu, *Physica. E*, 83 (2016) 146
12. M. Alonso-Lomillo, O. Domínguez-Renedo and M. Arcos-Martínez, *Talanta*, 82 (2010) 1629
13. J.P. Metters, R.O. Kadara and C.E. Banks, *The Analyst*, 136 (2011) 1067
14. M.Á.G. Rico, M. Olivares-Marín and E.P. Gil, *Talanta*, 80 (2009) 631
15. S. Laschi, I. Palchetti and M. Mascini, *Sensors and Actuators B: Chemical*, 114 (2006) 460
16. R. PAULIUKAITE, R. METELKA, I. SVANCARA, A. KROLICKA, A. BOBROWSKI, E. NORKUS, K. KALCHER and K. VYTRAS, *Scientific papers of the University of Pardubice. Series A. Faculty of Chemical Technology*, 10 (2004) 47
17. N. Lezi, A. Economou, P.A. Dimovasilis, P.N. Trikalitis and M.I. Prodromidis, *Anal. Chim. Acta.*, 728 (2012) 1
18. S. Ledru, N. Ruillé and M. Boujtita, *Biosensors and Bioelectronics*, 21 (2006) 1591
19. S. Miserere, S. Ledru, N. Ruillé, S. Griveau, M. Boujtita and F. Bedioui, *Electrochemistry communications*, 8 (2006) 238
20. J. Ping, J. Wu and Y. Ying, *Electrochemistry Communications*, 12 (2010) 1738
21. Z.-Y. Li, M.S. Akhtar, J.H. Kuk, B.-S. Kong and O.-B. Yang, *Mater. Lett.*, 86 (2012) 96
22. Y. Wang, Y. Li, L. Tang, J. Lu and J. Li, *Electrochemistry Communications*, 11 (2009) 889
23. Y. Wang, Y. Shao, D.W. Matson, J. Li and Y. Lin, *ACS nano*, 4 (2010) 1790
24. M.L. Yola, T. Eren and N. Atar, *Sensors and Actuators B: Chemical*, 210 (2015) 149
25. T. Kuila, S. Bose, P. Khanra, A.K. Mishra, N.H. Kim and J.H. Lee, *Biosensors and Bioelectronics*, 26 (2011) 4637
26. N.G. Shang, P. Papakonstantinou, M. McMullan, M. Chu, A. Stamboulis, A. Potenza, S.S. Dhesi and H. Marchetto, *Adv Funct Mater*, 18 (2008) 3506
27. Z. Fan, K. Wang, T. Wei, J. Yan, L. Song and B. Shao, *Carbon*, 48 (2010) 1686
28. B.K. Gupta, P. Thanikaivelan, T.N. Narayanan, L. Song, W. Gao, T. Hayashi, A. Leela Mohana Reddy, A. Saha, V. Shanker and M. Endo, *Nano letters*, 11 (2011) 5227
29. M. Mallesha, R. Manjunatha, C. Nethravathi, G.S. Suresh, M. Rajamathi, J.S. Melo and T.V. Venkatesha, *Bioelectrochemistry*, 81 (2011) 104
30. M. Zhou, Y. Zhai and S. Dong, *Anal. Chem.*, 81 (2009) 5603
31. Z. Wang, H. Wang, Z. Zhang and G. Liu, *Sensors and Actuators B: Chemical*, 199 (2014) 7
32. D.V. Stergiou, E.K. Diamanti, D. Gournis and M.I. Prodromidis, *Electrochemistry Communications*, 12 (2010) 1307
33. D. Zhao, X. Guo, T. Wang, N. Alvarez, V.N. Shanov and W.R. Heineman, *Electroanalysis*, 26 (2014) 488
34. Y. Wu, N.B. Li and H.Q. Luo, *Sensors and Actuators B: Chemical*, 133 (2008) 677
35. L. Xiao, H. Xu, S. Zhou, T. Song, H. Wang, S. Li, W. Gan and Q. Yuan, *Electrochimica Acta*, 143 (2014) 143
36. L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan and S. Yao, *Electrochimica Acta*, 115 (2014) 471
37. L. Chen, Z. Su, X. He, Y. Liu, C. Qin, Y. Zhou, Z. Li, L. Wang, Q. Xie and S. Yao, *Electrochemistry Communications*, 15 (2012) 34
38. E. Herrero, V. Arancibia and C. Rojas–Romo, *Journal of ElectroAnalytical Chemistry*, 729

(2014) 9
39. E. Svobodova-Tesarova, L. Baldrianova, M. Stoces, I. Svancara, K. Vytras, S.B. Hocevar and B. Ogorevc, *Electrochimica Acta*, 56 (2011) 6673
40. S. Legeai and O. Vittori, *Anal. Chim. Acta.*, 560 (2006) 184
41. G.M.S. Alves, J.M.C.S. Magalhães, P. Salaün, C.M.G. van den Berg and H.M.V.M. Soares, *Anal. Chim. Acta.*, 703 (2011) 1