



Detection of Heavy Metals Based on Boron-doped Diamond Nanograss Array, Boron-doped Diamond Film and Glassy Carbon Electrodes

MIN WEI^{1,*}, GAO YING ZENG¹, YONG LIU² and QIYU LU¹

¹College of Food Science and Technology, Henan University of Technology, Zhengzhou 450052, P.R. China

²College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P.R. China

*Corresponding author: E-mail: wei_min80@163.com

(Received: 28 October 2011;

Accepted: 22 August 2012)

AJC-11996

In this work, boron-doped diamond nanograss array, boron-doped diamond film and GC electrode were used to investigate the voltammetric response of Cd²⁺ and determination of the mixture of Cd²⁺, Pb²⁺ and Cu²⁺ with differential pulse stripping voltammetry. For the stripping of Cd, although GC electrode was slightly better than boron-doped diamond nanograss array and boron-doped diamond film electrode in terms of peak current response, the reproducibility of boron-doped diamond nanograss array electrode was superior to that of boron-doped diamond film and GC electrode. In case of determination of the mixture of Cd²⁺, Pb²⁺ and Cu²⁺, boron-doped diamond nanograss array electrode provided better analytical detection when compared to boron-doped diamond film and GC electrode. These results demonstrated that the boron-doped diamond nanograss array electrode was quite satisfactory with less surface adsorption, better reproducibility and higher resolution.

Key Words: Heavy metals, Boron-doped diamond nanograss array, Differential pulse stripping voltammetry.

INTRODUCTION

Due to their tendency to accumulate in the body, toxicity and low rate of clearance, there existed health problems associated with exposure to high levels of metal ions such as Cd²⁺, Pb²⁺, Hg²⁺. Therefore, it is essential to detect toxic trace metals in the environment and aquatic food product for human health and safety. Currently, the recommended techniques for metal ion analysis are atomic absorption spectroscopy, atomic emission, inductively couple plasma mass spectrometry and anodic stripping voltammetry. Among these techniques, anodic stripping voltammetry has attracted a great deal of attention due to its advantages including wide linear dynamic range, low detection limit, multi element analysis capability, simplicity of the instrumentation, easy operational procedures and portability^{1,2}.

The glassy carbon (GC) electrode is commonly considered to be the electrode material for anodic stripping voltammetry³ and numerous applications in trace metal analysis involve the mercury-coated GC electrode^{4,5} or polymer-covered GC electrode^{6,7}. However, these types of electrodes pose some problems such as the inherent toxicity of the material, the introduction of discouraging environmental legislation^{5,8-9}, film stability^{10,11} and preparation and deactivation of the electrode surface¹².

Because the boron-doped diamond (BDD) film electrode is free of above-mentioned problems^{13,14}, it has become an attractive working electrode in anodic stripping voltammetry

for the detection of toxic trace metal ions^{1-3,8}. Although BDD film electrodes exhibit several advantages including wide potential window, low background current, long-term stability and excellent resistance to electrode fouling, they do have some inevitable drawbacks such as chemical inertness, unfavorable electrocatalytic activity, which may limit their applications. Therefore, surface modification of BDD film electrodes is necessary to improve their detection performance.

In our previous reports^{15,16}, the BDD nanograss array was obtained and has been approved to improve reactive site, accelerate electron transfer, promote electrocatalytic activity and enhance selectivity by detecting different substances. In this work, BDD nanograss array electrode was used to investigate the voltammetric response of Cd²⁺ and determination of the mixture of Cd²⁺, Pb²⁺ and Cu²⁺ by differential pulse stripping voltammetry. It has been compared with BDD film and GC electrode in terms of sensitivity, reproducibility and resolution for the mixture.

EXPERIMENTAL

(Cd(NO₃)₂·4H₂O), Pb(NO₃)₂, Cu(NO₃)₂·3H₂O, (CH₃COOH), (CH₃COONa) were obtained from Shanghai chemical reagent factory. All reagents were used as received without any further treatment. Milli-Q water (> 18 MΩ cm) was used throughout the experiments. The supporting electrolyte was acetate buffer solution (pH 4.7) prepared with (CH₃COONa) and (CH₃COOH).

Electrochemical measurements were performed with a CHI 660 electrochemical analyzer (CH Instruments, Chenhua Co. Shanghai, China) with a three electrode electrochemical cell. An Ag/AgCl (saturated KCl) reference electrode and a Pt wire counter electrode were used. The BDD film and the BDD nanograss array electrodes were sonicated successively in 2-propanol and Milli-Q water before use. GC electrodes were polished with 0.10 and 0.05 mm alumina powder, respectively, rinsed thoroughly with Milli-Q water between each polishing step and then sonicated in acetone and Milli-Q water successively. The geometric areas of the working electrodes in the cell were estimated to be 0.07 cm².

Preparation of the BDD film and the BDD nanograss array: The preparation of the BDD film and the BDD nanograss array was reported elsewhere¹⁵.

RESULTS AND DISCUSSION

Detection of Cd²⁺ on BDD nanograss array, BDD film and GC electrode: The voltammetric response of Cd²⁺ on BDD nanograss array, BDD film and GC electrode was investigated with differential pulse stripping voltammetry (DPSV). First, using a fixed concentration of 50 μM Cd²⁺ in 0.1 M acetate buffer solution (pH 4.7), different parameters such as pulse amplitude (A_p), deposition potential (E_{dep}), deposition time (T_{dep}) were optimized to produce the best stripping signal on different electrodes and the results are shown in Table-1.

Electrode	A _p (mV)	E _{dep} /V vs. Ag/AgCl	T _{dep} (s)
BDD nanograss array	50	-1.10	60
BDD film	50	-1.15	90
GC	50	-1.40	60

Using the experimental conditions described above, comparison of DPSV curves and reproducibility for the stripping of Cd was studied with different electrodes in 0.1 M acetate buffer solution (pH 4.7) containing 50 μM Cd²⁺ and the results are shown in Fig.1 and Table-2. As seen in Fig. 1, for the stripping of Cd, well-defined stripping peaks were observed on the three electrodes. The stripping peak potential for Cd²⁺ was similar on each electrode indicating that BDD is as active as GC for metal phase formation and oxidation. Due to the more heterogeneous chemical and electrical properties across the BDD film surface, the stripping peak was broader and more asymmetric than that for BDD nanograss array and GC electrode¹. The peak current on the GC electrode was largest and then that on the BDD nanograss array electrode. In comparison with the BDD film electrode, the increase in peak current for the detection of Cd²⁺ on the BDD nanograss array electrode was ascribed to that the structure of nanograss array could increase the surface area, provide better electric linkage between electrode active sites, promote the electrocatalytic ability and accelerate the electron transfer¹⁵.

Table-2 shows comparison of eight-successive voltammetric responses of 50 μM Cd²⁺ on BDD nanograss array, BDD film and GC electrode. It can be seen that on the three

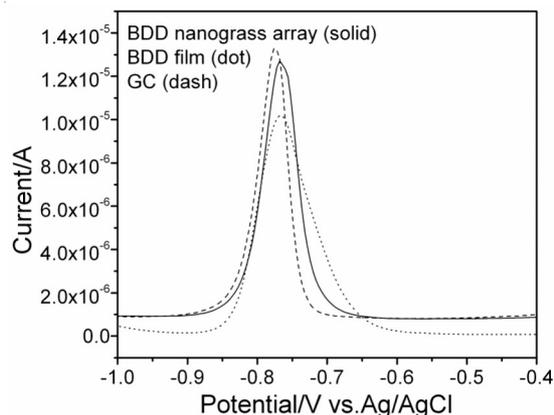


Fig. 1. DPSV curves for the stripping of Cd from 0.1 M acetate buffer solution (pH 4.7) containing 50 μM Cd²⁺ on BDD nanograss array (solid line), BDD film (dot line) and GC (dash line) electrodes. Experimental conditions as in Table-1

Electrode	Number	Potential/V vs. Ag/AgCl	Current (10 ⁻⁶ A)
BDD nanograss array	1	-0.768	12
	2	-0.772	11.99
	3	-0.772	11.98
	4	-0.772	11.95
	5	-0.772	11.93
	6	-0.772	11.93
	7	-0.772	11.91
	8	-0.772	11.91
	RSD (%)	—	0.3001
BDD film	1	-0.78	10.57
	2	-0.784	10.45
	3	-0.784	10.44
	4	-0.784	10.39
	5	-0.78	10.31
	6	-0.78	10.26
	7	-0.78	10.2
	8	-0.78	10.15
	RSD (%)	—	1.3678
GC	1	-0.768	12.16
	2	-0.776	11.75
	3	-0.772	11.96
	4	-0.776	12.02
	5	-0.776	11.84
	6	-0.78	11.64
	7	-0.78	11.38
	8	-0.78	10.5
	RSD (%)	—	4.5099

electrodes, the peak potentials changed and the peak currents dropped to varying degrees due to the fouling of the electrodes, which occurred as a result of the formation of a passive film by the continuous adsorption of the products. The peak potential shifted by *ca.* 0.004 V on BDD nanograss array and BDD film electrode whereas *ca.* 0.012 V on the GC electrode. On BDD nanograss array electrode, the peak currents dropped from 12 × 10⁻⁶-11.91 × 10⁻⁶ A and the response reproducibility was 0.3001 % (RSD). On BDD film electrode, the peak currents dropped from 10.57 × 10⁻⁶-10.15 × 10⁻⁶ A and the response reproducibility was 1.3678 % (RSD). On GC electrode, the peak currents changed from 12.16 × 10⁻⁶-10.5 × 10⁻⁶ A and the response reproducibility was 4.5099 % (RSD). These results

demonstrated that BDD nanograin array electrode had favourable quality about low tendency for adsorption and was superior to BDD film and GC electrode.

Detection of the mixture of Cd^{2+} , Pb^{2+} , Cu^{2+} on BDD nanograin array, BDD film and GC electrode: Fig. 2 shows DPSV curves for determination of the mixture containing Cd^{2+} , Pb^{2+} , Cu^{2+} with concentration of 10 and 50 μM in 0.1 M acetate buffer solution (pH 4.7) obtained on BDD nanograin array, BDD film and GC electrodes. It can be seen that BDD nanograin array electrode had the best ability toward the detection of Cu (ca. -0.055 V versus Ag/AgCl) and then BDD film electrode. However, there was no characteristic peak of Cu observed on GC electrode. For the stripping of Cd, the stripping peaks (ca. -0.8 V versus Ag/AgCl) were well-defined with concentration of 50 μM whereas ill-defined with concentration of 10 μM on the three electrodes. The characteristic peak for the stripping of Pb became various at different concentrations: In the presence of 10 μM , there occurred single distinct stripping peak of Pb on BDD nanograin array electrode (ca. -0.5 V versus Ag/AgCl) and BDD film electrode (ca. -0.55 V versus Ag/AgCl) whereas both a primary peak (ca. -0.57 V versus Ag/AgCl) and a minor one (ca. -0.47 V versus Ag/AgCl) on GC electrode. In the presence of 50 μM , there are both a primary peak and a minor one observed in the potential range from -0.6 V to -0.4 V on the three electrodes. The formation of double peaks may have to do with the inactivity of electrode surface. From the above results, it can be concluded that BDD nanograin array was a more efficient electrode material towards the detection of the mixture with less surface adsorption and higher resolution.

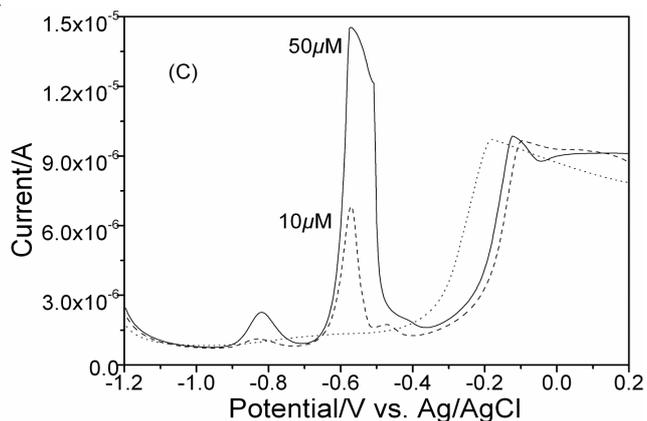
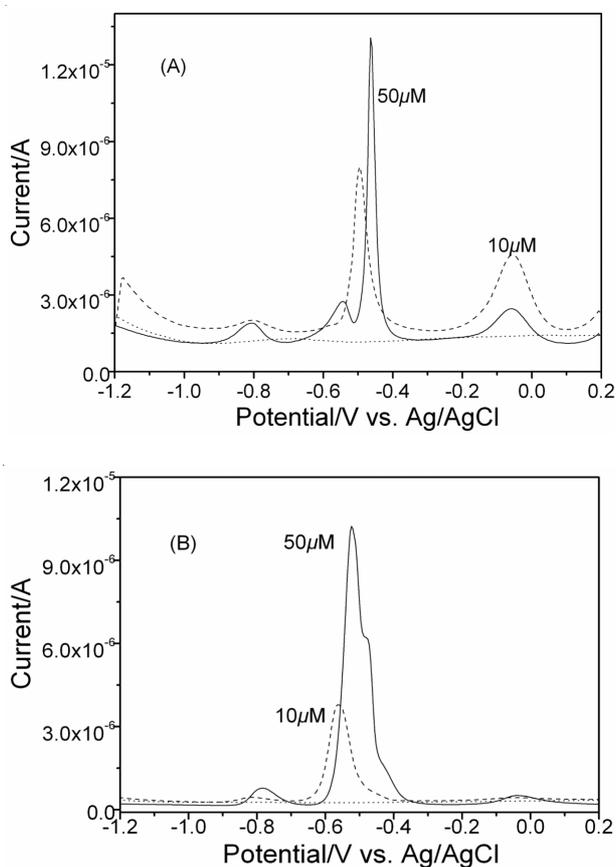


Fig. 2. DPSV curves for a mixture containing Cd^{2+} , Pb^{2+} , Cu^{2+} with concentration of 0 μM (dot line), 10 μM (dash line) and 50 μM (solid line) in 0.1 M acetate buffer solution (pH 4.7) obtained on (A) BDD nanograin array, (B) BDD film and (C) GC electrodes

Conclusion

Electrochemical technique is significant for the determination of heavy metals. The choice of working electrode is important. The results of this work demonstrated that, as a novel electrode material, the BDD nanograin array was more efficient towards the detection of heavy metal with less surface adsorption, better reproducibility and higher resolution.

ACKNOWLEDGEMENTS

This research was supported by National Natural Science Foundation of China (Grant No. 21105022) and Doctor Foundation of Henan University of Technology (2010BS019).

REFERENCES

1. E.A. McGaw and G.M. Swain, *Anal. Chim. Acta*, **575**, 180 (2006).
2. A. Manivannan, R. Kawasaki, D.A. Tryk and A. Fujishima, *Electrochim. Acta*, **49**, 3313 (2004).
3. C. Babyak and R.B. Smart, *Electroanalysis*, **16**, 175 (2004).
4. K.Z. Brainina, N.A. Malakhova and N.Y. Stojko, *J. Anal. Chem.*, **368**, 307 (2000).
5. C. Agra-Gutierrez, J.L. Hardcastle, J.C. Ball and R.G. Compton, *Analyst*, **124**, 1053 (1999).
6. I. Turyan, M. Atiya and D. Mandler, *Electroanalysis*, **13**, 653 (2001).
7. K.C. Honeychurch, J.P. Hart and D.C. Cowell, *Anal. Chim. Acta*, **431**, 89 (2006).
8. C.E. Banks, M.E. Hyde, P. Tomcik, R. Jacobs and R.G. Compton, *Talanta*, **62**, 279 (2004).
9. E. Gustafsson, *Water, Air Soil Pollut.*, **80**, 99 (1995).
10. S.C. Petrovic and H.D. Dewald, *Anal. Chim. Acta*, **357**, 33 (1997).
11. H.P. Wu, *Anal. Chem.*, **66**, 3151 (1994).
12. In *Interfacial Electrochemistry: Theory, Experiment and Applications*, R.L. McCreery, Marcel Decker, New York (1999).
13. J. Xu, M.C. Granger, Q. Chen, J.W. Strojek, T.E. Lister and G.M. Swain, *Anal. Chem.*, **69**, A591 (1997).
14. J. Xu, Q. Chen and G.M. Swain, *Anal. Chem.*, **70**, 3146 (1998).
15. M. Wei, C. Terashima, M. Lv, A. Fujishima and Z.Z. Gu, *Chem. Commun.*, **24**, 3624 (2009).
16. M. Lv, M. Wei, F. Rong, C. Terashima, A. Fujishima and Z.Z. Gu, *Electroanalysis*, **22**, 199 (2010).