

# A Novel Tellurium Film Electrode for Simultaneous Determination of Cd(II) and Pb(II) Using Anodic Stripping Voltammetry

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Tellurium film modified glassy carbon electrode (TeFE) is presented in this paper as a promising alternative candidate for simultaneous electrochemical determination of Cd(II) and Pb(II) using anodic stripping voltammetry (ASV) analysis. Key operational parameters, including deposition potential and deposition time were investigated. Under the optimum conditions, TeFE exhibited well-defined and separated stripping peaks for Cd(II) and Pb(II) and a linear relationship existed between the currents and the concentrations of Cd(II) and Pb(II) in the range from 20 µg/L to 370 µg/L, with the detection limits of 0.50 µg/L for Cd(II) and 0.80 µg/L for Pb(II) respectively. Compared with the traditional mercury-film electrode and recently introduced bismuth film electrode, the TeFE displays wider potential window, low toxicity and better stability. The interference experiments showed that some metal ions have little influence on the ASV signals of Cd(II) and Pb(II). The proposed tellurium film-based modified electrode, a new promising type of less toxic electrode, opens new opportunities for highly sensitive determination of metal ions.

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**Keywords:** Tellurium film electrode, Anodic stripping voltammetry, Cd(II), Pb(II)

## 1. INTRODUCTION

Anodic stripping voltammetry (ASV) is the most sensitive and particularly suitable technique for the determination of trace heavy metals in different matrices [1, 2] because of the inexpensive instrumentation and portability and the ability to distinguish between the different metal oxidation states. The AVS method, when coupled with an appropriate electrode material, generally provides low detection limits for many metal ions with a wide linear dynamic range and good response to precision.

In the past, mercury has been used as an electrode material with different electrode geometries, such as static mercury or hanging mercury drop electrode, dropping mercury electrode and mercury film electrode [3], for anodic stripping voltammetry. However, the toxicity of mercury and mercury salts is the greatest drawback [4] and new alternative electrode materials that possess the same attractive properties as Hg are urgently desired. So far, some of the promising alternate electrodes have been investigated, such as different modifications of gold, antimony, carbon, silver, lead, several alloys and amalgams [5-8]. Among others, the bismuth film electrode has attracted considerable attention as a new alternative to the mercury counterpart owing to its excellent resolution of neighboring peaks and insensitivity to the dissolved oxygen in a solution and low toxicity [9-11]. However, Bi-based electrodes still have some problems to solve: difficult and time-consuming to fabricate, comparably low detection limit and toxicity [12].

Tellurium, a silvery white and a p-type semiconductor, exhibits many interesting properties, such as thermoelectricity, high piezoelectricity and photoconductivity, which have been found useful in optoelectronic and electronic devices [13-15]. The electrochemical behavior of tellurium and its compounds have been investigated for many years [16-18]. Recently, the use of tellurium as an electrode material for determination of dopamine and glucose was reported [19-20]. As far as we know, no similar study has been reported on the application of a tellurium film electrode in stripping analysis of trace metal ions.

In this work, our ultimate goal was to develop a less toxic, highly sensitive and low-cost electrochemical method for the determination of trace heavy metals by ASV using the novel in situ prepared TeFE. In addition, the optimized conditions, performance of our method and interference study in electrochemical analysis were investigated.

## 2. EXPERIMENTAL

### 2.1. Materials and apparatus

ASV measurements were performed with CHI660C electrochemical analyzer (CHI, USA) with a conventional three-electrode configuration. A tellurium film (or bismuth and mercury film) modified glassy carbon electrode was used as a working electrode. An Ag/AgCl(3 mol/L NaCl) electrode and a platinum wire were used as the reference and counter electrodes, respectively.

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and  $\text{Pb}(\text{NO}_3)_2$  were of guarantee reagent and purchased from Jinshan Chemical Reagent Co. Ltd. Stock standard solutions of cadmium (1mg/mL) and lead (1mg/mL) were prepared in accordance with Chinese National standard method [21] and diluted to standard solutions with required concentration for daily use. Other chemicals were of analytical grade and used without further purification. All solutions were made up with doubly distilled water and purged with high-purity nitrogen for at least 15 min prior to each electrochemical experiment.

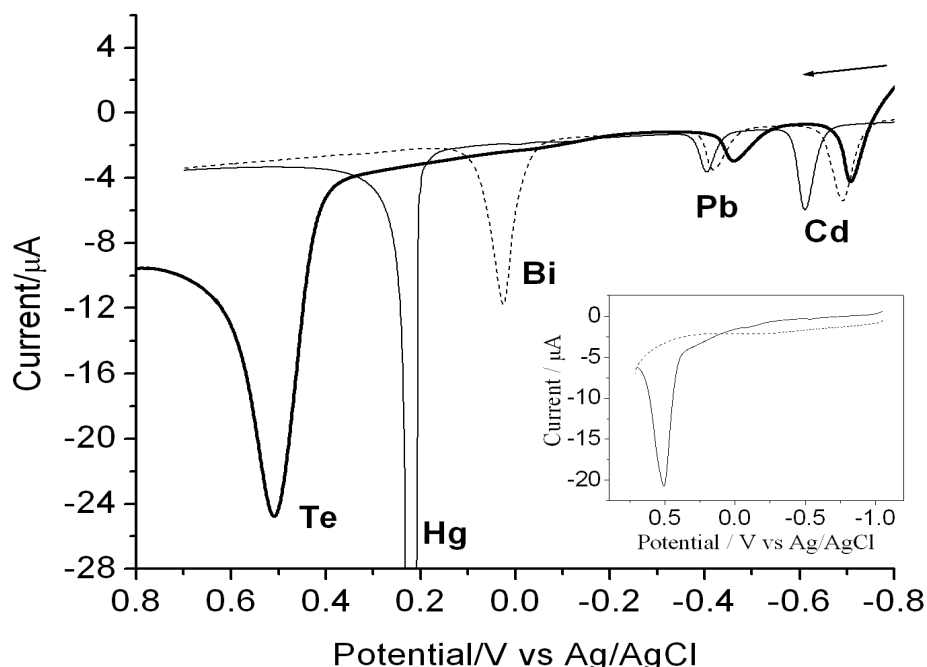
## 2.2 Preparation of the modified electrode and measurement procedures

Initially, a substrate glassy carbon electrode was polished to mirror and rinsed with doubly distilled water and ethanol in an ultrasonic bath successively, and allowed to dry at room temperature. The substrate electrode was then transferred into the KCl solution (0.1M) containing 1.2 mg/L of Te(IV) and different concentrations of Cd(II) and Pb(II), after which the TeFE was formed in situ together with electrochemical accumulation of analytes using one-step electrochemical deposition at -1.3V under a magnetic stirring. For comparison, the bismuth film electrode (BiFE) and mercury film electrode (HgFE) were prepared in the same way only replacing tellurium with bismuth or mercury.

After 10 s, linear sweep stripping voltammetry (LSSV) was performed by potential scan from -0.8 V to 0.8 V with a scan rate of  $100 \text{ mV}^{-1}$ . Differential pulse stripping voltammogram (DPSV) were also recorded by potential scan from -0.9 V to 0.2 V with amplitude of 50 mV, pulse width of 50 ms and potential step of 4 mV. After that, the electrode was cleaned at +0.7 V for 30 s. All experiments were carried out at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1 Electrochemical behavior of tellurium film electrode



**Figure 1.** LSSV of Cd(II) and Pb(II) at tellurium film (thin line), bismuth film (dash line), and mercury film (thick line) electrode. Solution: 0.1 mol/L KCl containing  $70 \mu\text{g/L}$  Cd(II) and Pb(II) together with  $1.2 \text{ mg/L}$  Bi(III) or Hg(II) or Te(IV). Deposition at -1.3V for 180s. The inset depicts LSSVs at glass carbon electrodes after deposition with (solid line) and without (dashed line)  $1.2 \text{ mg/L}$  Te(IV) in 0.1M KCl at -1.3V for 180 s.

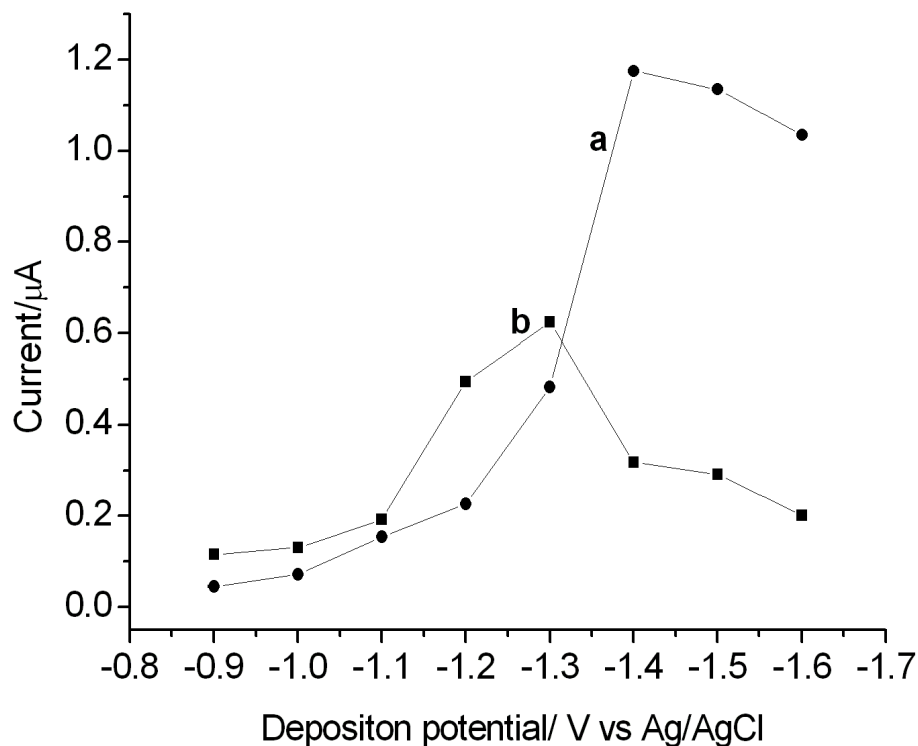
Stripping analysis has been widely recognized as a powerful tool for trace metal analysis. Its remarkable sensitivity is attributable to the combination of an effective accumulation step and a pulse measurement which generates an extremely favorable signal-to-background ratio.

For the stripping peak currents of metals were less steady at mixed solution of KCl and HCl in our experiment, we conducted the investigation in 0.1 M KCl under ASV mode. The inset of Fig.1 depicts LSSVs at glass carbon electrodes after deposition with (solid line) and without (dashed line) 1.2 mg/L Te(IV) in 0.1 M KCl at -1.3V for 180 s. The dashed line in inset of Fig.1 shows that no redox peaks were observed at the glassy carbon electrode after deposition in 0.1M KCl. While there is an obviously oxidation peak at 0.5V (solid line) at the glassy carbon electrode after deposition with 1.2 mg/L Te(IV) in 0.1 M KCl, indicating Te film has formed in the electrode surface.

The accumulation step of Cd and Pb was allowed to proceed in 0.1M KCl with 1.2 mg/L Te(IV) and at -1.3 V for 180s, which was achieved simultaneously with electrode construction. In the initial stage, we have prepared the TeFE using different Te concentration. The experiment results indicated that the stripping peak currents of Pb and Cd less steady when Te concentration is less than 1.2 mg/L. While the concentration is above 1.2 mg/L, the steadiness and reproducibility of the stripping peak currents has improved. Subsequently, the preparation of TeFE were carried out in 0.1M KCl containing 1.2 mg/L of Te(IV). Then the obtained electrode transferred to KCl solution and LSSV was recorded by potential scan from -0.8 V to 0.8 V. Fig. 1 depicts the LSSV analytical characteristics of HgFE (thin line), BiFE (dashed line) and TeFE (thick line) for Cd(II) and Pb(II) determination. The stripping peaks of Cd(II) at -0.71 V and Pb(II) at -0.48 V were presented in TeFE corresponding to the oxidation of Cd and Pb. Comparison with the HgFE and BiFE, the anodic peak also shifts to the negative potentials and gets smaller in TeFE. This implied there are similar processes associated with the formation of metal alloys but the doping reaction becomes slower in TeFE. Nevertheless, TeFE provided a wider potential window (-0.8 to 0.4V) than HgFE (-0.8 to 0.15V) and BiFE (-0.8 to 0.1V) since the oxidation potential of Te (0.51V) is more positive than Hg (0.22V) and Bi (0.01V). Therefore, TeFE still is a deserving candidate for simultaneous determination of multiple metal ions and avoiding the high toxicity associated with mercury-based electrodes.

### 3.2 Effect of deposition potential and deposition time

The performance of the developed electrochemical sensor in ASV analysis depended crucially on the deposition extent of heavy metal. Several critical factors, including deposition potential and deposition time, were investigated. The influence of deposition potential on the stripping peak current was performed in the range from -0.9 V to -1.6 V and the results were shown in Fig.2. As shown in Fig.2, it's crystal clear that the stripping peak current signals of Cd and Pb exhibited a significant upward trend with the negative shift of deposition potential. The maximal stripping peak current could be observed at -1.4 V for Cd(II) and at -1.3 V for Pb(II). When considering the increasing hydrogen evolution at more negative potentials [22], the deposition potential of -1.3 V was chosen as optimum deposition potential for two heavy metals.

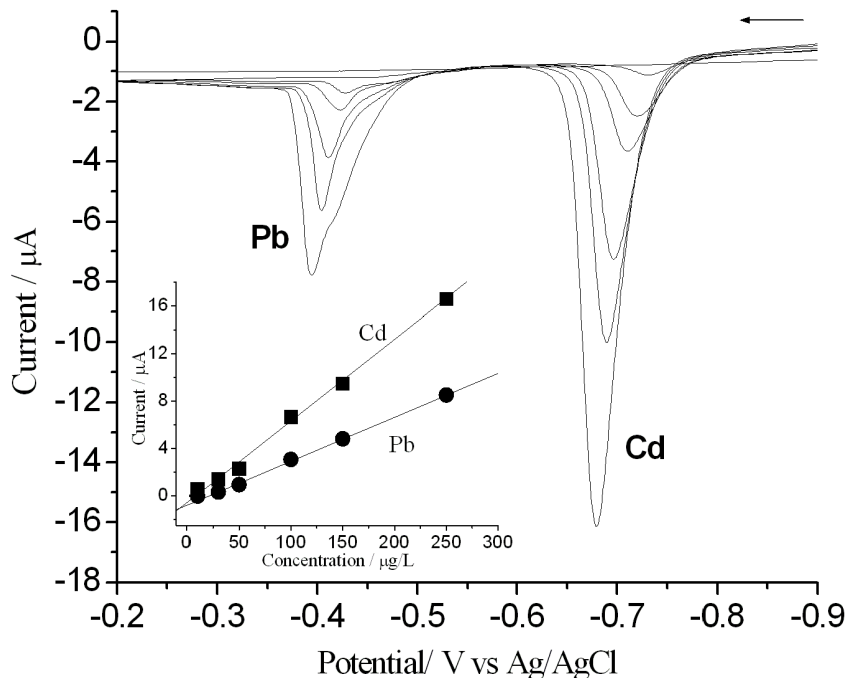


**Figure 2.** Effect of deposition potential on the stripping response of Cd(II) and Pb(II) at TeFE. Deposition for 180s. Other conditions are as in Fig. 1.

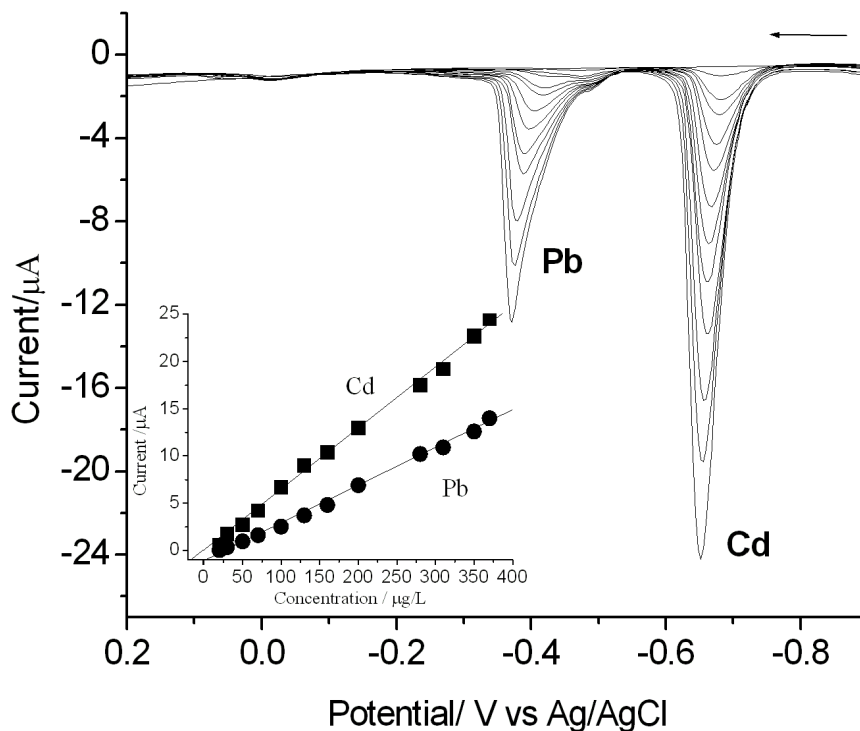
The influence of the deposition time on the anodic stripping peak currents of Cd and Pb was also studied. Obviously, the stripping peak currents of Cd and Pb increased by increasing deposition time in the range of 50-280s indicating quantity of reduced metal rose as deposition time lengthened. At higher deposition time, the peak currents reached the plateau, which may be due to the electrode surface converge towards saturation. Thus, a deposition time of 280 s was chosen for shorten the experimental time.

### 3.3 Determination of Cd(II) and Pb(II)

A series of LSSV of Cd(II) and Pb(II) were investigated by increasing the metal ion concentrations from 10 to 250  $\mu\text{g/L}$  under the optimum conditions described above. The well-defined sharp current peaks could be observed in Fig. 3 and the peak currents were increased with positive shifts of peak potentials when the concentration of Cd(II) and Pb(II) were enhanced. The resulting calibration plots were linear with concentration from 10 to 250  $\mu\text{g/L}$ , with a high correlation coefficients of 0.9979 and 0.9975 for Cd(II) and Pb(II), respectively. Limits of detection (LODs,  $3\sigma$ ) of 0.7  $\mu\text{g/L}$  for Cd(II) and 0.9  $\mu\text{g/L}$  for Pb(II) are worked out under the optimum conditions. These results have indicated the favorable electroanalytical characteristics of tellurium electrode for measuring Cd(II) and Pb(II) in combination with LSSV.



**Figure 3.** LSSV for successive additions of Cd(II) and Pb(II) at TeFE. The inset depicts the corresponding calibration plot. Solutions: 0.1M KCl containing increasing Cd(II) and Pb(II) from 10 to 250  $\mu\text{g/L}$ , along with 1.2 mg/L Te(IV). Deposition at -1.3V for 280s



**Figure 4.** DPSV for successive additions of Cd(II) and Pb(II) at TeFE. The inset depicts the corresponding calibration plot. Solutions: 0.1 mol/L KCl containing increasing Cd(II) and Pb(II) from 20 to 370 $\mu\text{g/L}$ , along with 1.2 mg/L tellurium. Deposition at -1.3V for 180s

To obtain better electroanalysis performance, simultaneous detection of Cd(II) and Pb(II) was performed using the DPSV. As shown in Fig. 4, the peak currents of Cd(II) and Pb(II) increased with increasing the concentration of the two metal ions from 20 to 370  $\mu\text{g/L}$ . The calibration plots for the Cd(II) and Pb(II) determination were constructed, with a high correlation coefficients of 0.9965 and 0.9919 for Cd(II) and Pb(II), respectively. Limits of detection (LODs,  $3\sigma$ ) of 0.5  $\mu\text{g/L}$  for Cd(II) and 0.8  $\mu\text{g/L}$  for Pb(II) are worked out with a 180 s deposition step. The Cd(II) and Pb(II) detection performance of the proposed sensor was compared with other previously reported metal modified electrodes and results are listed in Table 1. One can find that the proposed electrochemical sensor had low determination limits and wide linear ranges, indicating a very good alternative to determine these metals. The obtained result showed that our method is usefulness for the simultaneous determination of Cd(II) and Pb(II) with low detection limits and fast analysis.

**Table 1.** Comparison of analytical performance of some metal modified electrodes for measurements of Cd(II) and Pb(II).

Electrode	Analytical technique	Linear range ( $\mu\text{g/L}$ )		Detection limit ( $\mu\text{g/L}$ )		Reference
		Cd(II)	Pb(II)	Cd(II)	Pb(II)	
GC/Bi-xerogel-S1/Nafion electrode	ASV	0.56–11.2	1.04–20.72	0.37	1.3	[1]
photolithographically fabricated Bi-sputtered electrode	SWASV	10–90	5–45	1	0.5	[2]
BiFE–electroplated	ASV	500–5000	500–5000	2.3	1.2	[3]
Sb oxide–modified electrode	ASV	500–5000	500–5000	2.5	0.9	
Bi oxide–modified electrode	ASV	500–5000	500–5000	1.7	1.1	
Bi-CNT electrode	ASV	2–100	2–100	0.7	1.3	[4]
mercury film electrode	ASV	----	4.14–20.72	---	0.6	[5]
TeFE	ASV	20–370	20–370	0.50	0.80	This work

The interference study was performed by adding various foreign substances into a standard solution containing 20  $\mu\text{g/L}$  Pb(II) and 1.2 mg/L tellurium under optimized conditions. It was found that 100-fold of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and 50-fold of  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$  caused no obvious change of ASV signals for Cd(II) and Pb(II).

#### 4. CONCLUSIONS

In this work, we have demonstrated the application of tellurium film electrode in determination of trace heavy metals using anodic stripping voltammogram method. The parameters for accumulation time and deposition potential were optimized. The TeFE displayed favorable electroanalytical

performance similar to that of bismuth-based electrodes, with some advantages of low toxicity, well-defined stripping peak and wider potential window. Besides, the electrode exhibited satisfied sensitivity and reproducibility under the optimized conditions. Hence, the tellurium film modified electrode holds great promise in electrochemical stripping analysis as another type of “mercury-free” electrode.

## References

1. Kh. Brainina, E. Neyman, *Electroanalytical Stripping Methods*, John Wiley, New York, 1993.
2. E. Czop, A. Economou, A. Bobrowski, *Electrochim. Acta* 56 (2011) 2206.
3. S. B. Hocevar, I. Svancara, B. Ogorevc, K. Vytras, *Anal. Chem.* 79 (2007) 8639.
4. K. Tyszczyk and M. Korolczyk, *Anal. Chim. Acta* 624 (2008) 232.
5. A. M. S. Georgina, J. M. C. S. Magalhães, R. Tauler, H. M. V. M. Soares, *Electroanal.* 25 (2013) 1895.
6. J. Shokoofe, A. T. Mohammad, F. Hamid, S. Iran, *Microchim. Acta* 180 (2013) 347.
7. C. Kevin, Y. Hone, *Adv. Anal. Chem.* 3 (2013) 28.
8. Z. Li, L. Chen, F. He, L.J. Bu, X.B. Luo, S.L. Luo, *Talanta* 122 (2014) 285.
9. L. Chen, Z.h. Su, X.h. He, Y. Liu, C. Qin, Y.p. Zhou, Z. Li, S.Z. Yao, *Electrochem. Commun.* 15 (2012) 34.
10. K. C. Armstrong, C. E. Tatum, R. N. Dansby-Sparks, J. Q. Chambers and Z.L. Xue, *Talanta* 82 (2010) 675.
11. D.L. Lu, J. Wang, C.L. Ninivin, S. Mabic and T. Dimitrakopoulos, *J. Electroanal. Chem.* 651 (2011) 46.
12. R. Dansby-Sparks, J.Q. Chambers, Z. Xue, *Anal. Chim. Acta* 643 (2009) 19.
13. Z.H. Wang, L.L. Wang, J.R. Huang, H. Wang, L. Pan, X.W. Wei, *J. Mater. Chem.* 20 (2010) 2457.
14. F.X. Liang, H.S. Qian, *Mater. Chem. Phys.* 113 (2009) 523.
15. J.W. Liu, J.H. Zhu, C.L. Zhang, H.W. Liang and S.H. Yu, *J. Am. Chem. Soc.* 132 (2010) 8945.
16. H. Jung and N. V. Myung, *Electrochim. Acta* 56 (2011) 5611.
17. D. Pinisetty, M. Gupta, A.B. Karki, D.P. Young, R.V. Devireddy, *J. Mater. Chem.* 21 (2011) 4098.
18. Y.A. Ivanova, D.K. Ivanou and E.A. Streltsov, *Electrochim. Acta* 52 (2007) 5213.
19. H.Y. Tsai, Z.H. Lin and H.T. Chang, *Biosens. Bioelectron.* 35 (2012) 479.
20. M.R. Guascito, D. Chirizzi, C. Malitesta, M. Siciliano, T. Siciliano and A. Tepore, *Electrochem. Commun.* 22 (2012) 45.
21. Ministry of Chemical Industry of the People's Republic of China, Chemical fertilizer products--standard volumetric, standard, reagent and indicator solutions for chemical analysis, HG/T 2843-1997.
22. A. Afkhami, H. Ghaedi, T. Madrakian. M. Rezaeivala, *Electrochim. Acta* 89 (2013) 377.
23. P.A. Dimovasilis, M.I. Prodromidis. *Analytica Chimica Acta* 769 (2013) 49.
24. C. Kokkinos, A. Economou, I. Raptis, C.E. Efstathiou. *Electrochim Acta* 53 (2008) 5294.
25. M. Maczuga, A. Economou, A. Bobrowski, M.I. Prodromidis. *Electrochim Acta* 114 (2013) 758.
26. G.H. Hwang, W.K. Han, J.S. Park, S.G. Kang. *Talanta* 76 (2008) 301.
27. L.C. Martiniano, V.R. Abrantes, S.Y. Neto, E.P. Marques. *Fuel* 103 (2013) 1164.