Well-Arranged Porous Co₃O₄ Microsheets and Its Electroanalysis toward Pb (II)

Zhong-Gang Liu and Xing-Jiu Huang

Abstract—Well-arranged porous Co₃O₄ microsheets has been successfully synthesized via a hydrothermal process and subsequent thermal decomposition. The characterization of the as-prepared product is identified with scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The results show that the as-prepared porous Co₃O₄ possesses the face-centered cubic phase structure and well single-crystallized phase. Its electrochemical performance was characterized with square wave anodic stripping voltammetry (SWASV) for the detection of Pb(II) at the porous Co₃O₄/nafion modified electrode with the good sensitivity of 48.5 μ A μ M⁻¹ and detection limited of 30 nM (3 σ method). In addition, the stability measurement is investigated under the optimized conditions.

Index Terms—Porous Co₃O₄ microsheets, hydrothermal process, heavy metal ions, electroanalysis.

I. INTRODUCTION

In recent years, the pollution of heavy metal ions in drinking-water has attracted the increasing concern because of their toxicity in direct adverse impact on human health and the environment even at trace amount [1]. Take Pb (II) for example, it can be widely found in drinking-water and known to cause health problems at very low concentrations, such as digestive, neurological, cardiac, and mental troubles [2]. In recent years, there are already many mature methods to analyze heavy metal ions, such as flame flame atomic absorption spectrometry [3], electrothermal atomic absorption spectrometry [4], [5] and inductively coupled plasma spectrometry [6].

Alternatively, opportunity for electrochemical techniques has been accepted with advantages of highly sensitive, easy to perform, and low-cost [7]-[9]. In particular, great efforts have been devoted to studying the sensing materials for developing the electrochemical methods which can remarkably improve the efficiency of electrochemical technique and has developed to be the important part for the determination of heavy metal ions. For instance, CNTs [10]-[12], metal nanomaterials [13]-[15], graphene [8], [16], [17] are common materials used for modifying electrode, whereas porous metal oxide nanomaterials are rarely reported. Considering the porous metal oxide that can provide a high surface area, a high hydrothermal stability, and surface active sites which can interact with micropollutants, e.g., heavy metal ions and organic micropollutants, a study on developing porous metal oxides as chemical sensing materials for detection heavy metal ions is of much interest and significance.

 Co_3O_4 is one of the most intriguing p-type semiconductors and has been widely applied in a wide range of fields, including lithium-ion batteries [18]-[21], supercapacitors [22]-[24], catalysts [25], and gas sensors [26], [27]. Inspired by the unique porous nature and special surface active sites of Co_3O_4 , we would expect that the porous Co_3O_4 as sensing material to modify electrode for ultratrace metal ions detection with high sensitivity. In this study, we prepared the porous Co_3O_4 microsheets with highly uniform porosity morphology by calcining the layered precursor $Co_2(OH)_2CO_3$. A case study with Pb (II) was developed to evaluate its electrochemical performance with square wave anodic stripping voltammetry (SWASV).

II. MATERIAL AND METHODS

A. Chemical Reagents

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and were of analytical grade. 0.1 M acetate buffer (NaAc-HAc, pH 5.0) solution was prepared using NaAc and HAc. Ultrapure fresh water was obtained from a Millipore water purification system (MilliQ, specific resistivity >18 M Ω cm, S.A., Molsheim, France) and used in all runs.

B. Synthesis of porous Co₃O₄ Microsheets

Porous Co_3O_4 was synthesized using a modified strategy that has been used previously [23]. In brief, 1.455 g $Co(NO_3)_2$ 6H₂O (5 mM) was dissolved in 25 mL deionized water, which was dropped into 25 mL of 0.025 mM polyvinyl pyrrolidone (PVP, K-30) aqueous solution. After stirring for 1 h, 10 mM urea was added to the solution under stirring for additional 3 h. The resulting solution was then sealed in a 60 mL Teflon-lined autoclave, followed by hydrothermal treatment at 120 °C for 24 h. After treatment, a light pink, solid precipitate was collected by centrifugation, washed repeatedly with deionized water and absolute ethanol, and dried at 60 °C in a vacuum. Finally, the precursor was heated to 600 °C for 2 h in air. Layered Co₃O₄ was prepared by calcination of the precursor at 300 °C for 2 h as a comparison.

C. Apparatus

Electrochemical experiments were recorded using a CHI

Manuscript received November 13, 2013; revised January 6, 2014. This work was supported by the National Key Scientific Program-Nanoscience and Nanotechnology (No. 2011CB933700), and National Natural Science Foundation of China (No. 61102013 and 21377131).

Z. G. Liu and X. J. Huang are with University of Science and Technology of China, Department of Chemistry, Hefei 230026, PR China (e-mail: xingjiuhuang@iim.ac.cn (X.J.H)).

Z. G. Liu and X. J. Huang are with Research Center for Biomimetic Functional Materials and Sensing Devices, Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, PR China.

660D computer-controlled potentiostat (ChenHua Instruments Co., Shanghai, China). A conventional three-electrode system consisted of a glassy carbon working electrode (GCE, 3 mm diameter), an Ag/AgCl reference electrode, and a platinum wire counter electrode. The scanning electron microscopy (SEM) images were taken by a FEI Quanta 200 FEG field emission scanning electron microscope

D. Preparation of Modified Electrode

Before each modification, the bare glassy carbon electrode was sequentially polished with 0.3 μ m and 0.05 μ m alumina power slurries to a mirror-shiny surface and then sonicated with HNO₃ solution (v:v 1:1), absolute ethanol and deionized water, respectively. The porous Co₃O₄/nafion film on the surface of glassy carbon electrode was performed in the following manner: 2.0 μ L of Co₃O₄ ethanol (0.1 mM) solution was dripped onto the surface of a freshly polished glassy carbon electrode was allowed to dry, and then 2.0 μ L of 0.5% w/w nafion solution was prepared in the same way.

E. Electrochemical Measurements

Square wave anodic stripping voltammetry (SWASV) was used for Pb(II) detection in 0.1 M NaAc-HAc solution under optimized conditions. A deposition potential of -1.2 V was applied for 180 s to the working electrode with stirring. SWASV responses were recorded between -1.0 and -0.2 V with a step potential of 5 mV, amplitude of 20 mV, and frequency of 25 Hz. A desorption potential of 0 V for 210 s was performed to remove the residual metal ions under stirring conditions. All experiments were performed at room temperature under air atmosphere.

III. RESULTS AND DISCUSSIONS

A. Morphology Characteristics of Porous Co₃O₄ Microsheets

Fig. 1a-Fig. 1b show SEM images of the porous Co_3O_4 microsheets (in different magnifications) with calcination of the precursor at 600 °C. It can be clearly seen that the product exhibits well-arranged multilayered structure composed of many microsheets. The further insight of the porous Co_3O_4 microsheets was characterized with HRTEM. It is observed that the sample not only has highly apparent porous morphology with pore size approximately 200 nm (Fig. 1c), but also clearly shows that the lattice fringes with a lattice spacing of about 0.468 nm corresponding to the (111) plane [28], [29]. Furthermore, it appears that the integrated porous architecture is fabricated by small nanocrystals growing in an oriented manner (Fig. 2d). The selected area electron diffraction (SAED) (Inset in Fig. 2d) also clearly shows the highly single-crystalline structure.

Generally, the porous Co_3O_4 obtained involved two process, formation of $Co_2(OH)_2CO_3$ in hydrothermal conditions and subsequent thermal decomposition in air ambient. In aqueous solution, the reactant urea can generate



Fig. 1. a-b) SEM images of the porous Co_3O_4 microsheets under different magnifications obtained at 600 °C. c) TEM images of the porous Co_3O_4 microsheets obtained at 600 °C. d) Corresponding EDS result. d) HRTEM image. Insert is the selected area electron diffraction (SAED).



Fig. 2. SEM images of a) the precursor and the product after calcination at different temperatures b) 200 \mathbb{C} , c) 300 \mathbb{C} , d) 500 \mathbb{C} and e) 600 \mathbb{C} . (d) XRD patterns of the precursor Co₂(OH)₂CO₃ and the product after calcination at 300 \mathbb{C} and 600 \mathbb{C} .

 OH^{-} and CO_{3}^{2-} after decomposition and hydrolyzation, which can in situ combine with Co²⁺ to form cobalt hydroxide carbonate precipitation. More information on the formed structures can be observed with a series of SEM images (Fig. 2). Fig. 2a shows the SEM image of precursor Co₂(OH)₂CO₃, which is multilayered morphology with well-arranged two-dimension microsheets. The hypothesis of the formation mechanism is proposed. As we know, the solvent, inorganic additives and surfactant can have a significant influence on the crystal growth of nanomaterials by modifying the surface energies, which can regulate or control certain crystallographic planes. In addition, it can make the nanoparticles growth into different shapes by the selective adsorption of ions onto different crystal planes [23]. Herein, the PVP we introduced is a common and typical neutral surfactant, which can efficiently modulate the OH^{-} and CO_{3}^{2-} combining with Co^{2+} . It can further induce the nanocrystals growth in certain direction and generate the layered structure under hydrothermal conditions that can provide better advantage in controlling the structure and crystallization. Fig. 2a shows the SEM image of precursor Co₂(OH)₂CO₃, which is multilayered morphology with well-arranged two-dimension microsheets. Fig. 2a-Fig. 2e show the SEM images of precursor after thermal decomposition in different temperature. No remarkable change with the layered structure after calcinations could be observed. As increasing the temperature, the surface of the layered structure gradually becomes rougher and the pores become much larger and more apparent, which may lead to the aggregation and re-crystallization of the nanoparticles during the calcination process. Fig. 2f depicts the typical XRD patterns of the precursor, layered Co_3O_4 and porous Co_3O_4 . The precursor as the monoclinic Co₂(OH)₂CO₃ (JCPDS Card no. 29-1416) can be well indexed. The XRD patterns of Co₃O₄ at 300 °C and 600 °C have identical peaks, which can be perfectly indexed to face-centered cubic phase (JCPDS Card no. 43-1003 space group: Fd3m). The peaks represent the Bragg reflections of the (111), (220), (311), (222), (400), (422), (511), and (440) planes and no peaks from other phase have been dedicated, revealing the high purity of the synthesized sample. As expected, with increasing calcining temperature, the peak intensity increases, indicating the the significantly improvement of the crystallinity.

B. Optimization of Electrochemical Experimental Conditions

In order to gain the high sensitive electrochemical performance with the porous Co_3O_4 /nafion modified electrode to heavy metal ions, the effect of experimental parameters (deposition potential, deposition time, pH, etc.) were first discussed.

It is known that the application of appropriate deposition potential is very important to achieve the best sensitivity. Therefore, the effect of the deposition potential was investigated after 180 s accumulation in 0.1 M NaAc-HAc solution at pH 5.0. Fig. 3a depicts the peak currents of 0.15 μ M Pb(II) with deposition potential ranged from -0.8 V to -1.4 V. When the potential shifts negatively from -0.8 V to -1.2 V, the peak currents increase significantly, which is the fact that Pb(II) can be more easily reduced at more negative deposition potential because of enhanced kinetics. The peak current reaches a maximum at deposition potential of -1.2 V. However, the peak currents decrease when the deposition potential is beyond -1.2 V, which is due to the interference of the hydrogen evolution. Therefore, deposition potential of -1.2 V is selected as the optimum.

The dependence of the deposition time was also investigated from 30 s to 210 s. Fig. 3b shows the relationship between the peak currents and deposition time for 0.15 μ M Pb(II) at -1.2 V in 0.1 M NaAc-HAc solution at pH 5.0. As depicted in Fig. 3b, the peak currents increase with the increase of the deposition time. Note that the adsorption equilibrium of Pb(II) and Co₃O₄ is strongly related to interaction time. In order to detect Pb(II) more sensitively, longer deposition time could be applied. But considering that the upper detection may be limited due to the surface saturation at high Pb(II) concentrations. Therefore, to achieve lower detection limit and wider response range, a deposition time of 180 s is chosen.

The effect of pH ranged of 4.0-7.0 was investigated in 0.1 M NaAc-HAc solution containing 0.15 μ M Pb(II). As displayed in Fig. 3c, the peak currents firstly increase versus pH and the maximum current is observed at 5, which may be ascribed to the leakage of the modifier at rather acid condition.

However, peak currents reduce significantly when pH exceeds 5, due to the formation of metal hydroxide complexes $(Pb(OH)^+, Pb(OH)_2)$ that may be partially soluble. As a result, a pH of 5.0 is selected for further measurements.



Fig. 3. Effect of a) deposition potential; b) deposition time; and c) pH value on the SWASV on porous $Co_3O_4/nafion$ modified electrode in 0.1 M NaAc-HAc solution containing 0.15 μ M Pb(II).

C. Electrochemical Determination of Pb(II) at Co_3O_4 Modified Electrode

In comparison with other different electrodes (bare GCE, nafion/GCE, layered Co_3O_4 /nafion), the performance of porous Co_3O_4 /nafion modified electrode toward Pb(II) was evaluated by the square wave stripping voltammograms (SWASV) response in the presence of 0.20 μ M Pb(II) in 0.1 M NaAc-HAc (pH 5.0) There is no obvious peak at bare GCE and a small stripping peak for nafion/GCE is observed under the same conditions However, a strong and well-defined

response at -0.55 V can be clearly obtained for porous Co_3O_4 /nafion modified GCE. The peak current is increased by nearly 5-fold than that of at nafion/GCE, 12-fold than that of bare-GCE. For layered Co_3O_4 /nafion modified GCE, the response performance is not comparable with the porous Co_3O_4 /nafion. The results demonstrate that porous Co_3O_4 is of great benefit to electrochemical sensing Pb(II) due to its adsorption behavior.



Fig. 4. a) SWASV responses of porous Co₃O₄/nafion modified electrode toward Pb(II) at different concentrations in 0.1 M NaAc-HAc solution (pH 5.0). b) The the corresponding calibration plot.

TABLE I: COMPARATIVE DATA FROM SOME STUDIES FOR DETERMINATION OF PB(II)

Methods	Sensitivity (μΑ μM ⁻¹)	LOD (µM)	Ref.
ICP-MS		0.24	[30]
AAS		0.45	[3]
SWV (MFE)		0.08	[31]
SWV (Bi-GCE)	0.476	0.05	[32]
LSV (Sb-BDD)		25.4	[33]
SWV (Co ₃ O ₄ -GCE)	48.5	0.03	This work

ICP-MS, inductively coupled plasma-mass spectrometry;

AAS, atomic absorption spectrometry;

MFE, mercury film electrode; BDD, boron doped diamond electrode; GCE, glassy carbon electrode

Subsequently, the electrochemical measurement toward Pb(II) on porous Co_3O_4 /nafion modified electrode was analyzed with SWASV under the optimal experimental conditions. The stripping voltammograms for Pb(II) at concentrations of 0.05-0.675 µM are illustrated in Fig. 4a. As seen, the peak currents increase linearly versus the Pb(II) concentrations and the linearization equation is $i/\mu A = -2.29 + 10^{-10}$

48.5 c/μ M (Fig. 4b) with the limit of detection (LOD) is 30 nM (3 σ method). These results suggest that the modifier of porous Co₃O₄ has the excellent performance to heavy metal ion (Pb(II)) with high sensitivity. The comparative data of the modified electrode to the common electrode modified with Hg, Bi, or Sb and the conditional methods are summarized in Table I. These results suggest that the modified porous Co₃O₄ is highly sensitive to heavy metal ions (Pb(II)).



Fig. 5. Measurements stability in the presence of 0.3 μ M Pb(II) in 0.1 M NaAc-HAc (pH 5.0) on porous Co₃O₄/nafion modified electrode. Data were collected from every SWASV response at about -0.55 V shown in the inset.

In addition, the stability study was investigated with the porous Co_3O_4 /nafion modified GCE to characterize the reproducibility of the electrode performance. Fig. 5 illustrates the peak currents after successive cycling for 16 times in 0.1 M NaAc-HAc (pH 5.0) solution containing 0.3 μ M Pb(II). No obvious change with the peak currents is observed with the relative standard deviation (RSD) 9.2 %, indicating that the porous Co_3O_4 /nafion modified electrode exhibits favorable stability for repetitive deposition-stripping in the experimental conditions.

ACKNOWLEDGMENT

X.-J. H. acknowledges the One Hundred Person Project of the Chinese Academy of Sciences, China, for financial support.

REFERENCES

- Z. Q. Zhu *et al.*, "Highly sensitive electrochemical sensor for mercury(II) Ions by using a mercury-specific oligonucleotide probe and gold nanoparticle-based amplification," *Anal. Chem.*, vol. 81, pp. 7660-7666, Sep. 2009.
- [2] A. Abbaspour, E. Mirahmadi, A. Khalafi-Nejad, and S. Babamohammadi, "A highly selective and sensitive disposable carbon composite PVC-based membrane for determination of lead ion in environmental samples," *J. Hazard. Mater.*, vol. 174, pp. 656-661, Feb. 2010.
- [3] H. H. Bai, Q. X. Zhou, G. H. Xie, and J. P. Xiao, "Temperature-controlled ionic liquid-liquid-phase microextraction for the pre-concentration of lead from environmental samples prior to flame atomic absorption spectrometry," *Talanta*, vol. 80, pp. 1638-1642, Mar. 2010.
- [4] E. M. Martinis, P. Berton, J. C. Altamirano, U. Hakala, and R. G. Wuilloud, "Tetradecyl(trihexyl)phosphonium chloride ionic liquid single-drop microextraction for electrothermal atomic absorption spectrometric determination of lead in water samples," *Talanta*, vol. 80, pp. 2034-2040, Mar. 2010.
- [5] A. N. Anthemidis and K. I. G. Ioannou, "Development of a sequential injection dispersive liquid-liquid microextraction system for electrothermal atomic absorption spectrometry by using a hydrophobic

sorbent material: Determination of lead and cadmium in natural waters," *Anal. Chim. Acta*, vol. 668, pp. 35-40, May 2010.

- [6] H. F. Hsieh, W. S. Chang, Y. K. Hsieh, and C. F. Wang, "Lead determination in whole blood by laser ablation coupled with inductively coupled plasma mass spectrometry," *Talanta*, vol. 79, pp. 183-188, Jul. 2009.
- [7] Y. Wei, Z. G. Liu, X. Y. Yu, L. Wang, J. H. Liu, and X. J. Huang, "O(2)-plasma oxidized multi-walled carbon nanotubes for Cd(II) and Pb(II) detection: Evidence of adsorption capacity for electrochemical sensing," *Electrochem. Commun.*, vol. 13, pp. 1506-1509, Dec. 2011.
- [8] Y. Wei *et al.*, "SnO₂/reduced graphene oxide nanocomposite for the simultaneous electrochemical detection of cadmium(II), lead(II), copper(II), and mercury(II): An interesting favorable mutual interference," *J. Phys. Chem. C*, vol. 116, pp. 1034-1041, Jan. 2012.
- [9] Y. X. Zhang *et al.*, "Ultra high adsorption capacity of fried egg jellyfish-like gamma-AlOOH(Boehmite) @SiO₂/Fe₃O₄ porous magnetic microspheres for aqueous Pb(II) removal," *J. Mater. Chem.*, vol. 21, pp. 16550-16557, Aug. 2011.
- [10] A. Mohadesi, Z. Motallebi, and A. Salmanipour, "Multiwalled carbon nanotube modified with 1-(2-pyridylazo)-2-naphthol for stripping voltammetric determination of Pb(II)," *Analyst*, vol. 135, pp. 1686-1690, May 2010.
- [11] J. Morton, N. Havens, A. Mugweru, and A. K. Wanekaya, "Detection of trace heavy metal ions using carbon nanotube-modified electrodes," *Electroanalysis*, vol. 21, pp. 1597-1603, Jul. 2009.
- [12] Y. Wei, L. T. Kong, R. Yang, L. Wang, J. H. Liu, and X. J. Huang, "Electrochemical impedance determination of polychlorinated biphenyl using a pyrenecyclodextrin-decorated single-walled carbon nanotube hybrid," *Chem. Commun.*, vol. 47, pp. 5340-5342, Mar. 2011.
- [13] Y. J. Kim, R. C. Johnson, and J. T. Hupp, "Gold nanoparticle-based sensing of "spectroscopically silent" heavy metal ions," *Nano Lett.*, vol. 1, pp. 165-167, Apr. 2001.
- [14] S. J. Xing, H. Xu, J. S. Chen, G. Y. Shi, and L. T. Jin, "Nafion stabilized silver nanoparticles modified electrode and its application to Cr(VI) detection," *Journal of Electroanalytical Chemistry*, vol. 652, pp. 60-65, Mar. 2011.
- [15] O. Dominguez-Renedo, L. Ruiz-Espelt, N. Garcia-Astorgano, and M. J. Arcos-Martinez, "Electrochemical determination of chromium(VI) using metallic nanoparticle-modified carbon screen-printed electrodes," *Talanta*, vol. 76, pp. 854-858, Aug. 2008.
- [16] J. Li, S. J. Guo, Y. M. Zhai, and E. K. Wang, "High-sensitivity determination of lead and cadmium based on the Nafion-graphene composite film," *Anal. Chim. Acta*, vol. 649, pp. 196-201, Sep. 2009.
- [17] J. Li, S. J. Guo, Y. M. Zhai, and E. K. Wang, "Nafion-graphene nanocomposite film as enhanced sensing platform for ultrasensitive determination of cadmium," *Electrochem. Commun.*, vol. 11, pp. 1085-1088, May 2009.
- [18] X. W. Lou, D. Deng, J. Y. Lee, and L. A. Archer, "Thermal formation of mesoporous single-crystal Co₃O₄ nano-needles and their lithium storage properties," *J. Mater. Chem.*, vol. 18, pp. 4397-4401, Aug. 2008.
- [19] X. Wang *et al.*, "Synthesis and lithium storage properties of Co₃O₄ nanosheet-assembled multishelled hollow spheres," *Adv. Funct. Mater.*, vol. 20, pp. 1680-1686, May 2010.
- [20] Y. Y. Wu, Y. G. Li, and B. Tan, "Mesoporous Co₃O₄ nanowire arrays for lithium ion batteries with high capacity and rate capability," *Nano Lett.*, vol. 8, pp. 265-270, Jan. 2008.

- [21] Z. Y. Yuan, B. Guo, and C. S. Li, "Nanostructured Co₃O₄ materials: Synthesis, characterization, and electrochemical behaviors as anode reactants in rechargeable lithium ion batteries," *J. Phys. Chem. C*, vol. 114, pp. 12805-12817, Jul. 2010.
- [22] S. L. Xiong, C. Z. Yuan, M. F. Zhang, B. J. Xi, and Y. T. Qian, "Controllable synthesis of mesoporous Co₃O₄ nanostructures with tunable morphology for application in supercapacitors," *Chem. Eur. J.*, vol. 15, pp. 5320-5326, Apr. 2009.
- [23] G. R. Rao and S. K. Meher, "Ultralayered Co₃O₄ for high-performance supercapacitor applications," *J. Phys. Chem. C*, vol. 115, pp. 15646-15654, Aug. 2011.
- [24] G. X. Wang *et al.*, "Hydrothermal synthesis and optical, magnetic, and supercapacitance properties of nanoporous cobalt oxide nanorods," *J. Phys. Chem. C*, vol. 113, pp. 4357-4361, Mar. 2009.
- [25] L. H. Hu, Q. Peng, and Y. D. Li, "Selective synthesis of Co3O4 nanocrystal with different shape and crystal plane effect on catalytic property for methane combustion," *J. Am. Chem. Soc.*, vol. 130, pp. 16136-+, Dec. 2008.
- [26] L. J. Wan *et al.*, "Hierarchically structured cobalt oxide Co₃O₄: The morphology control and its potential in sensors," *J. Phys. Chem. B*, vol. 110, pp. 15858-15863, Aug. 2006.
- [27] N. Hoa and S. A. El-Safty, "Meso- and macroporous Co₃O₄ nanorods for effective VOC gas sensors," *J. Phys. Chem. C*, vol. 115, pp. 8466-8474, May. 2011.
- [28] W. Y. Li, L. N. Xu, and J. Chen, "Co₃O₄ nanomaterials in lithium-ion batteries and gas sensors," *Adv. Funct. Mater.*, vol. 15, pp. 851-857, May. 2005.
- [29] L. A. Archer, X. W. Lou, D. Deng, J. Y. Lee, and J. Feng, "Self-supported formatnion of needlelike Co₃O₄ nanotubes and their application as lithium-ion battery electrodes," *Adv. Mater.*, vol. 20, pp. 258-+, Jan 2008.
- [30] C. D. Palmer, M. E. Lewis, C. M. Geraghty, F. Barbosa, and P. J. Parsons, "Determination of lead, cadmium and mercury in blood for assessment of environmental exposure: A comparison between inductively coupled plasma-mass spectrometry and atomic absorption spectrometry," *Spectroc. Acta Pt. B-Atom. Spectr.*, vol. 61, pp. 980-990, Aug. 2006.
- [31] E. Fischer and C. M. G. van den Berg, "Anodic stripping voltammetry of lead and cadmium using a mercury film electrode and thiocyanate," *Anal. Chim. Acta*, vol. 385, pp. 273-280, Apr 5. 1999.
- [32] J. Wang, J. M. Lu, S. B. Hocevar, P. A. M. Farias, and B. Ogorevc, "Bismuth-coated carbon electrodes for anodic stripping voltammetry," *Anal. Chem.*, vol. 72, pp. 3218-3222, Jul 15. 2000.
- [33] K. E. Toghill and R. G. Compton, "Metal nanoparticle modified boron doped diamond electrodes for use in electroanalysis," *Electroanalysis*, vol. 22, pp. 1947-1956, Sep. 2010.



Zhong-Gang Liu was born in Linyi, Shandong province, China on 20 September, 1986. He received his bachelor's in applied chemistry in Shandong Agricultural University(SDAU), China. He is presently a master's student at the University of Science and Technology of China, Anhui, China. The field of research is nanomaterials and environmental electrochemical detection.