



Fabrication of a novel nonenzymatic hydrogen peroxide sensor based on Se/Pt nanocomposites

Ye Li, Jing-Jing Zhang, Jie Xuan, Li-Ping Jiang*, Jun-Jie Zhu*

Key Lab of Analytical Chemistry for Life Science (MOE), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

A novel nonenzymatic hydrogen peroxide sensor was successfully fabricated based on the Se/Pt nanocomposites. The nanocomposites were constructed via a simple solvothermal method, and were confirmed by X-ray diffraction (XRD), energy-dispersive X-ray spectrometry (EDS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Cyclic voltammetry (CV) was used to evaluate the electrochemical performance of the nanocomposites at glassy carbon electrode (GCE). The results indicated that the Se/Pt nanocomposites exhibited excellent electrocatalytic activity to the reduction of H₂O₂ and could be used to construct a hydrogen peroxide amperometric sensor with a low detection limit and wide responding range.

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1. Introduction

The detection of hydrogen peroxide plays a significant role in many fields including clinic, food, pharmaceutical and environmental analyses [1]. Thus, several analytical methods have been developed for the detection of H₂O₂, such as fluorescence, chemiluminescence, and electrochemical methods [2–5]. Among these methods, electrochemical detection of H₂O₂ is distinctive for its low detection limit as well as low costs [6,7]. However, most sensors based on enzymes or proteins may result in limited lifetime, stability problem and complex procedures in the fabrication process. Thus, the development of enzyme-free H₂O₂ sensors with low detection limit and wide responding range has become a trend. Nowadays, nanomaterials have been investigated extensively in the fabrication of enzyme-free H₂O₂ sensors [8,9]. However, only a few reports have been found on the nonenzymatic sensors based on nanocomposites [10].

Recently, nanocomposites especially semiconductor and metal core-shell nanocomposites draw more and more attentions for their potential applications in catalysis, electronic and optoelectronic devices [11,12]. Platinum with unique catalytic properties has been used in the catalysis of methanol, glucose et al. [13,14]. As an important semiconductor, selenium has many properties such as high photoconductivity and catalytic activity [15]. Therefore, it is reasonable to expect that Se and Pt nanocomposites have both good electro-conductivity and enhanced catalytic activity. Some references

reported the fabrication of hollow Pt nanostructures by using Se as template [16]. However, no reports have been found on the solvothermal synthesis of Se/Pt nanocomposites and the application in electrocatalysis.

In this work, we developed a facile solvothermal method to synthesize Se/Pt nanocomposites. The nanocomposites modified GCE has a larger current to the reduction of H₂O₂ than the single-component Pt nanotubes and can be used to construct a nonenzymatic H₂O₂ sensor. To our best knowledge, it is the first time that Se/Pt nanocomposites are used to fabricate a sensor with a low detection limit and a wide responding range.

2. Experimental section

2.1. Materials

H₂O₂ (30%), ascorbic acid (AA) and sodium selenite (Na₂SeO₃) were purchased from Sinopharm Chemical Reagent Co., Ltd. Platinum dichloride (PtCl₂) was purchased from Shanghai Yiyang Chemical Co. All other chemicals were used without further purification. Phosphate buffer solution (PBS, 0.1 M pH 7.0) was prepared by mixing stock standard solutions of Na₂HPO₄ and NaH₂PO₄.

2.2. Synthesis of the Se/Pt nanocomposites

In order to synthesize the Se/Pt nanocomposites, the Se nanowires were first prepared as follows: 1 mmol of Na₂SeO₃ and 2 mmol of AA were first dissolved in 10 mL aqueous solution, and then stirred for 2 h at 90–95 °C. The precipitates were washed with water, ethanol,

* Corresponding authors. Tel./fax: +86 25 83594976.

E-mail address: jjzhu@mail.nju.edu.cn (J.-J. Zhu).

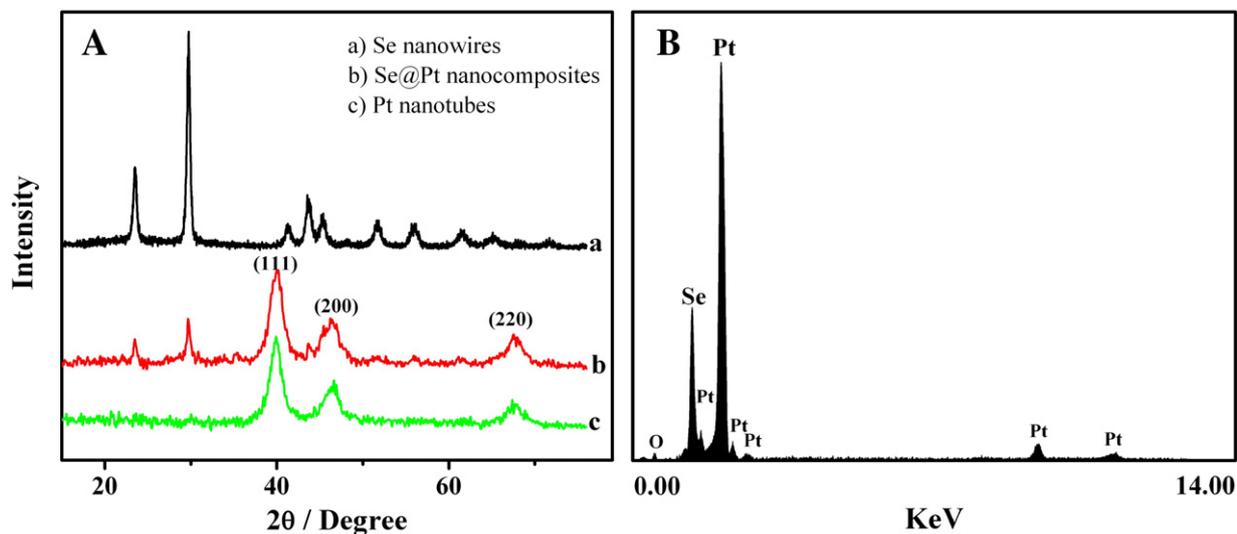


Fig. 1. A) XRD patterns of the Se nanowires (a), Se/Pt nanocomposites (b), and Pt nanotubes (c). B) EDS data for the Se/Pt nanocomposites.

and then dried in air. The Se/Pt nanocomposites were prepared using a solvothermal method. Briefly, 0.1 mmol of Se nanowires and 0.1 mmol of PtCl_2 were dispersed in 5 mL of ethanol and loaded into Teflon-lined autoclave (15 mL). After the autoclave was sealed and maintained at 70 °C for 1.5 h, the products were rinsed with dilute HCl and hot water (90 °C), then Se/Pt nanocomposites were collected. Pt nanotubes could be further obtained by soaking the Se/Pt nanocomposites in hydrazine monohydrate for 4 h.

2.3. Characterization

XRD patterns were obtained with a Philips X'pert Pro X-ray diffractometer (CuK radiation, $\lambda = 0.15418$ nm). EDS analysis was carried out by using a SEM equipped with an energy-dispersive X-ray detector (Shimadzu, SSX-550). SEM and TEM images were taken on a LEO-1530VP field-emission scanning electron microscope and a

FEI Tecnai-12 microscope with an accelerating voltage of 120 kV, respectively.

2.4. Electrochemical measurements

Electrochemical measurements were performed on a CHI 630 electrochemical workstation (Chenhua, Shanghai, China) with a conventional three-electrode system. A platinum wire was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was the reference. The nanomaterials were dispersed in water in 1.0 mL of water, then 10 μL of this suspension was dropped onto the electrode and dried in a silica gel desiccator. The working electrode was glassy carbon electrode (GCE, 3 mm in diameter) modified with Se/Pt nanocomposites, Pt nanotubes, Se nanowires or their simple mixture with the same mass respectively. Electrochemical experiments were all carried out in PBS under a high purity nitrogen atmosphere.

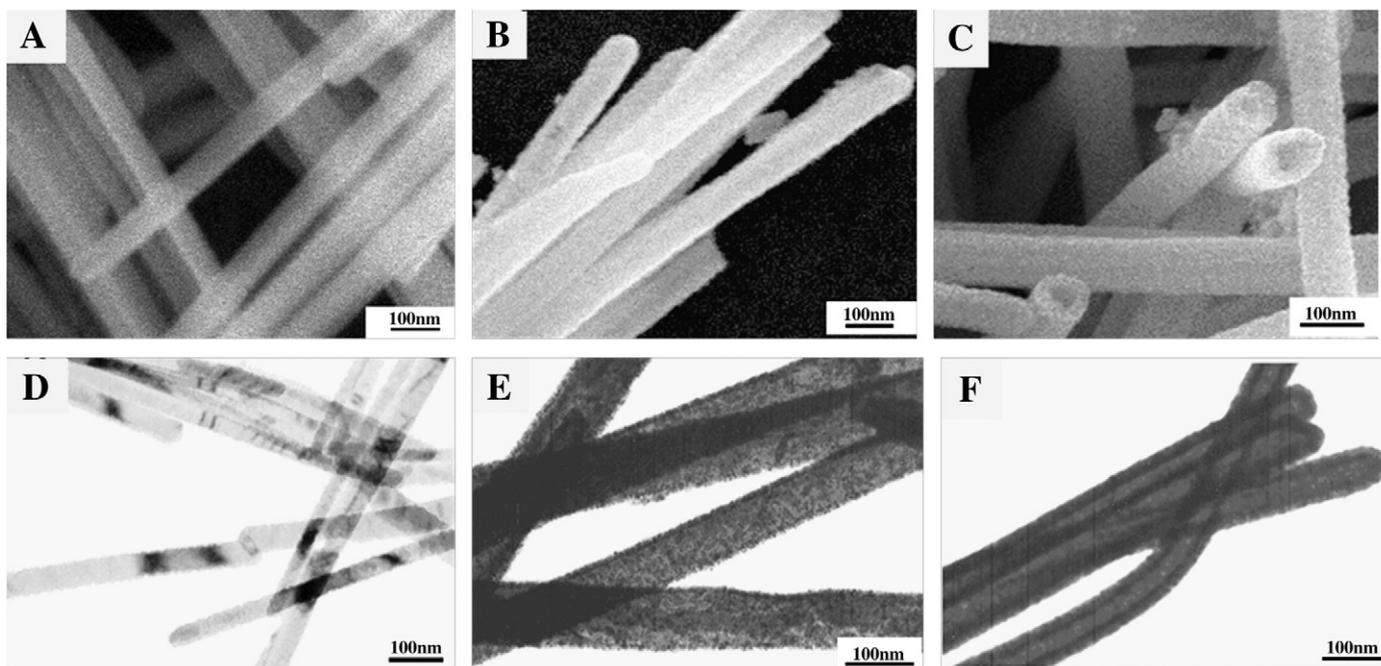


Fig. 2. SEM and TEM images of Se nanowires (A) (D), Se/Pt nanocomposites (B) (E), and Pt nanotubes (C) (F).

3. Result and discussion

3.1. Characteristics of the Se/Pt nanocomposites

XRD was used to characterize the as-prepared products. Firstly, Se nanowires were prepared by a template-free method with AA as reducing agent. All the reflections of the prepared selenium nanowires could be assigned to trigonal bulk selenium (JCPDS card No. 06-0362) (curve a in Fig. 1A). After the reaction with PtCl_2 , the newly-appeared diffraction peaks located at 39.88° , 46.38° and 67.54° , corresponded to the (111), (200) and (220) lattice planes respectively, which was in good agreement with face-centered cubic Pt (JCPDS card No.04-0802) (curve b in Fig. 1A), indicating the reduction of Pt (II). In order to study the coating shell, the template was dissolved to obtain Pt nanotubes (JCPDS card No.04-0802) (curve c in Fig. 1A). The as-prepared nanocomposites were characterized by EDS, indicating that all the samples were of high purity (Fig. 1B).

The structures of the products could be verified by the TEM and SEM images. Selenium nanowires with an average size of 80 ± 10 nm in diameter (Fig. 2A and D) could serve as both template and the reducing agent. The core-shell nanostructures, as shown in Fig. 2B and E, have a larger diameter of about 100 nm than the template, which proves that Pt has covered the surface of Se nanowires, also in agreement with the XRD result. In order to investigate the thickness of the shell, the templates were removed, and Pt nanotubes could be obtained. From curve c in Figs. 1A and 2C, F, the average thickness of the shell is about 20–40 nm, which further proves that the template is t-Se according to the trigonal tips of the nanotubes [16].

3.2. The electrochemical performance of Se/Pt nanocomposites

The Se/Pt nanocomposites exhibited excellent electrocatalytic properties to H_2O_2 . Compared to the CV of GCE in PBS with H_2O_2 (curve a in Fig. 3A), the reduction current and oxidation current of Se/Pt nanocomposites modified GCE increased with the increasing concentration of H_2O_2 (curve b,c,d in Fig. 3A), indicating the electroactive property of Se/Pt nanocomposites. In contrast, the behavior of Se nanowires, Pt nanotubes and their simple mixture (1:1) was also studied. The electrochemical behavior of the Se/Pt nanocomposites modified GCE was similar to that of the Pt disk electrode and that of the Pt nanotube modified GCE. As Fig. 3B showed, a much weaker electrocatalytic response was found to H_2O_2 (curve a and inset figure) on the Se nanowires modified electrode, while a larger current signal could be observed on the Se/Pt modified GCE (curve d) compared with Pt nanotubes (curve b) and the simple mixture (curve c). In addition, the electrochemical performances of different modified GCEs in PBS containing 2 mM $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ were also studied (Fig. 3C). A larger amperometric response could be observed at the Se/Pt modified GCE than that of the Pt and simple mixture (Se:Pt = 1:1) modified GCE, indicating that Se/Pt had a larger electroactive surface area. Therefore, the larger current at the Se/Pt modified GCE could be mainly attributed to the enlarged electroactive surface areas of Se/Pt nanocomposites.

3.3. Amperometric responses to the oxidation of H_2O_2

For amperometric sensing application, the prepared electrodes are generally evaluated by measuring current response at a fixed potential with the addition of the H_2O_2 . In order to choose the suitable electrode potential, the amperometric responses of the modified GCE at the potentials of -0.3 , 0.0 and $+0.3$ V were investigated as shown in Fig. 4A. Considering both the signal-to-noise ratio and the linear range, 0.0 V was chosen as the working potential for the detection of H_2O_2 .

Fig. 4B displays the amperometric response at the Se/Pt nanocomposites and the Pt nanotube modified GCE to the successive addition of H_2O_2 in PBS. As expected from Fig. 4B, the Pt modified GCE

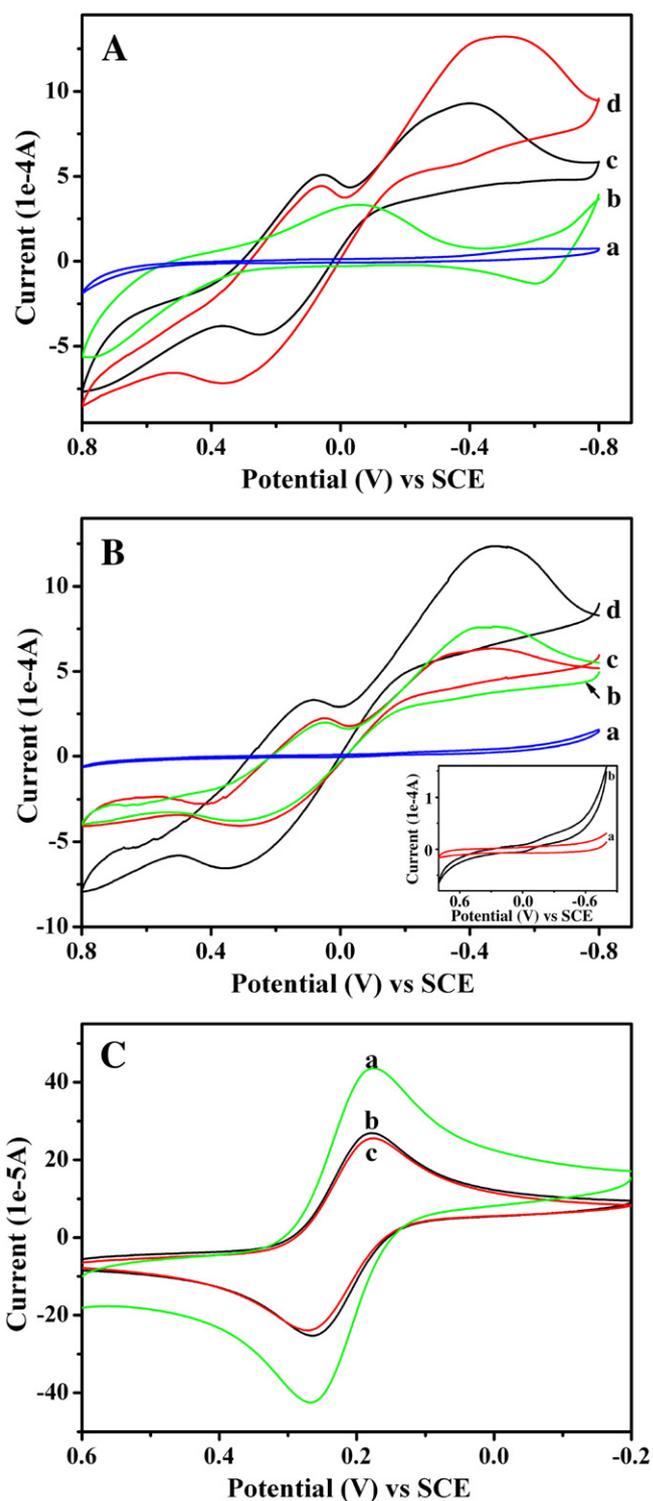


Fig. 3. A) CVs of GCE with 0.1 mM H_2O_2 (a), Se/Pt modified GCE with (b) 0 mM, (c) 0.02 mM, and (d) 0.04 mM H_2O_2 . B) CVs of the Se nanowire (a), Pt nanotube (b), Se and Pt mixture (1:1) (c), and Se/Pt (d) modified GCE in PBS (pH 7.0) with 0.03 mM H_2O_2 . (Inset: Se nanowire modified GCE in PBS with 0 mM (a) and 0.03 mM (b) H_2O_2 .) C) CVs of (a) Se/Pt, (b) Pt nanotube, and (c) Se and Pt mixture (1:1) modified GCE recorded in PBS containing 0.1 M KCl and 2 mM $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$. Scan rate: 100 mV/s.

exhibited a weaker response to the addition of H_2O_2 , while the Se/Pt nanocomposites modified GCE showed a larger catalytic current to the changes of H_2O_2 concentration (curve a in Fig. 4B).

Based on the excellent electrocatalytic activity of Se/Pt nanocomposites to H_2O_2 , a nonenzymatic sensor was constructed for the detection

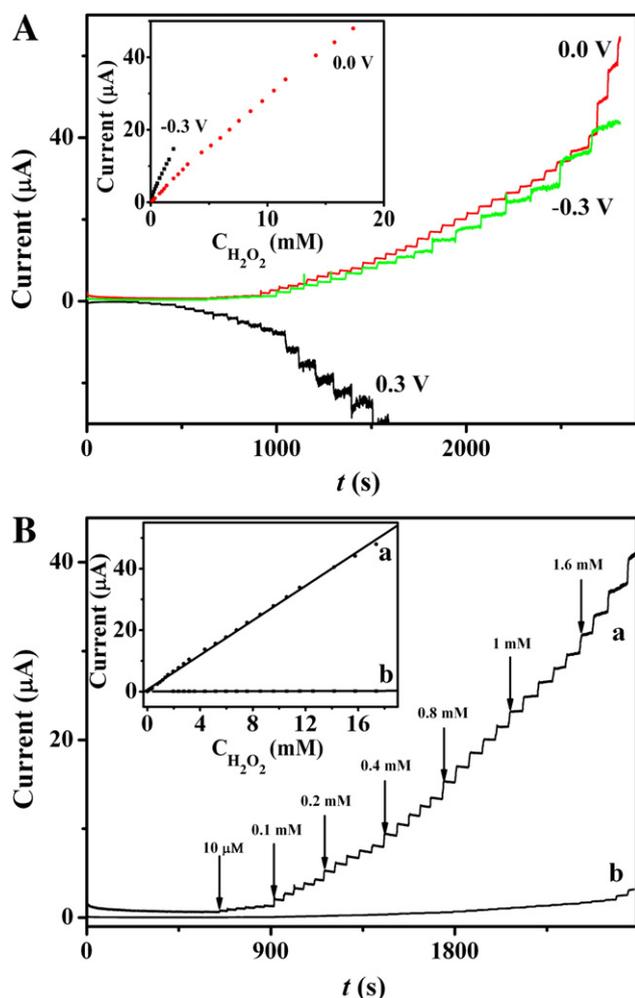


Fig. 4. Amperometric responses of (A) Se/Pt modified GCE at different working potentials of 0.3, 0.0, and -0.3 V. (B) Se/Pt (a) and Pt nanotube (b) modified GCE at working potential of 0.0 V to successive additions of H_2O_2 into PBS (H_2O_2 was added at the points indicated by arrows to the concentrations mentioned in (B) curve a). Inset (A) and (B): linear relation between the amperometric response and H_2O_2 concentration.

of H_2O_2 . Upon addition of H_2O_2 , the sensor responded rapidly to the substrates and could achieve 90% of the steady-state current within 4 s, indicating a fast amperometric response to the reduction of H_2O_2 . The sensor had a linear relationship with the concentration of H_2O_2 from $10 \mu\text{M}$ up to 15 mM with a correlation coefficient of 0.9991 (Fig. 4B inset), which was wider than the previous H_2O_2 sensors [7,10,17,18]. The regression equation was $I (\mu\text{A}) = 2.82c + 0.59$ (Where the c is the concentration of H_2O_2 in mM) with a detection limit of about $3.1 \mu\text{M}$ ($S/N=3$). The sensor showed lower detection limit and wider

responding range, indicating that the fabricated sensor could be potentially used for monitoring the concentration of H_2O_2 .

The sensor exhibited good reproducibility in the detection of H_2O_2 with a relative standard deviation (RSD) of about 5% at 0.1 mM hydrogen peroxide for more than 10 times measurements. The RSD for six sensors prepared at the same conditions was less than 5%. The long-term stability of the prepared sensor was also investigated by amperometric measurements and the current response of sensor retained about 90% of its original response after 3 month's storing.

4. Conclusion

Se/Pt nanostructures have been prepared via a facile solvothermal method and could be used to fabricate a novel nonenzymatic amperometric sensor for the detection of H_2O_2 . The electrochemical results showed that the nanocomposites modified GCE had a larger current to the reduction of H_2O_2 than the single-component nanomaterials with wide responding range and low detection limit which might be attributed to the enlarged surface areas. Therefore the Se/Pt nanocomposites provide a promising platform for the study of the application of semiconductor/metal nanocomposites in electrocatalysis and the construction of attractive nonenzymatic amperometric sensor in the future.

Acknowledgements

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References

- [1] S. Yao, J. Xu, Y. Wang, X. Chen, Y. Xu, S. Hu, *Anal. Chim. Acta.* 557 (2006) 78.
- [2] Z. Rosenzweig, R. Kopelman, *Anal. Chem.* 68 (1996) 1408.
- [3] L. Luo, Z. Zhang, *Anal. Chim. Acta.* 580 (2006) 14.
- [4] R. Santucci, E. Laurenti, F. Sinibaldi, R.P. Ferrari, *Biochim. Biophys. Acta.* 1596 (2002) 225.
- [5] J.J. Zhang, Y.G. Liu, L.P. Jiang, J.J. Zhu, *Electrochem. Commun.* 10 (2008) 355.
- [6] S. Xu, B. Peng, X. Han, *Biosens. Bioelectron.* 22 (2007) 1807.
- [7] Y.Y. Wang, X.J. Chen, J.J. Zhu, *Electrochem. Commun.* 11 (2009) 323.
- [8] L. Zhang, H. Li, Y. Ni, J. Li, K.M. Liao, G.C. Zhao, *Electrochem. Commun.* 11 (2009) 812.
- [9] M.R. Guascito, E. Filippo, C. Malitesta, D. Manno, A. Serra, A. Turco, *Biosens. Bioelectron.* 24 (2008) 1057.
- [10] X.L. Cui, Z.Z. Li, Y.C. Yang, *Electroanalysis* 20 (2008) 970.
- [11] P.X. Gao, C.S. Lao, Y. Ding, Z.L. Wang, *Adv. Funct. Mater.* 16 (2006) 53.
- [12] M.K. Lee, T.G. Kim, W. Kim, Y.M. Sung, *J. Phys. Chem. C* 112 (2008) 10079.
- [13] E. Formo, Z. Peng, E. Lee, X. Lu, H. Yang, Y. Xia, *J. Phys. Chem. C* 112 (2008) 9970.
- [14] F. Jia, C. Yu, K. Den, L. Zhang, *J. Phys. Chem. C* 111 (2007) 8424.
- [15] H. Zhang, D. Yang, Y. Ji, X. Ma, J. Xu, D. Que, *J. Phys. Chem. B* 108 (2004) 1179.
- [16] B. Mayers, X. Jiang, D. Sunderland, B. Cattle, Y. Xia, *J. Am. Chem. Soc.* 125 (2003) 13364.
- [17] Y.H. Li, X.Y. Liu, X.D. Zeng, Y. Liu, X.S. Liu, W.Z. Wei, S.L. Luo, *Microchim. Acta.* 165 (2009) 393.
- [18] C. Batchelor-McAuley, Y. Du, G.G. Wildgoose, R.G. Compton, *Sensor. Actuat. B-Chem.* 135 (2008) 230.