

Synthesis of Silver Nanoparticles Using Cefoperazone as a Stabilizing Reagent and Its Catalysis for Sodium Sulfide

Yuan-zhi Song^{1,*}, Kui-rong Ma¹, Feng-xia Zhu¹, Zhi-peng Cheng¹, Yan Song^{2,*}, Ben-lin Dai¹, Jiang Xu³

¹ Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry & Chemical Engineering, Huaiyin Normal University, Huai An 223300, People's Republic of China

² College of Materials Science and Engineering, Beijing University of Chemical Technology, Peking 100029, People's Republic of China

³ Department of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People's Republic of China

*E-mail: singyuanzhi@sina.com; songyan@mail.buct.edu.cn

Received: 11 April 2012 / Accepted: 13 January 2013 / Published: 1 March 2013

Cefoperazone as a stabilizing reagent was used for electrochemical synthesis of the AgNPs on the surface of glassy carbon electrode and preparation of AgNPs in aqueous solution. The silver nanoparticles were characterized by scanning electron microscopy, transmission electron microscopy, cyclic voltammetry, spectrophotography and powder X-ray diffraction spectra. The oxidation peak of sodium sulfide at cefoperazone@AgNPs was found at -0.529V, and the reduction peak was observed at -0.640V. The peak potentials for sodium sulfide at cefoperazone@AgNP/GCE are less than that of sodium sulfide at AgNP/GCE, and its currents increase; both cefoperazone and AgNPs catalyze the redox reaction of sodium sulfide due to the forming bond of Ag-S and the hydrogen bonds between cefoperazone and sulfide.

Keywords: Electrodeposition, Composite materials, Nanoparticles, Thin films

1. INTRODUCTION

Among the nanomaterials reported silver nanoparticles (AuNPs) are the most frequently used for the modification on electrode surface in the fabrication of biosensor, which exhibit many advantages such as good biocompatibility, easy synthesis, high conductivity and long stability[1-3]. The reduction of AgNO₃ is the most used methods for the preparation of AgNPs in aqueous solution, the reductants such as ascorbic acid [4, 5], citrate [6-8], and borohydride [9, 10] have been

used in this reaction. However, it is difficult to control the size of AgNPs using this method, and the prepared process is time consuming. Electrochemical deposition of metal nanoparticles on the surface of electrode has been found as better alternatives because of their flexibility in controlling the size and coverage of the metal nanoparticles[11-12]. In present work, cefoperazone as a stabilizing reagent (an antibiotic) was used for electrochemical synthesis of the AgNPs on the surface of glassy carbon electrode (GCE) and preparation of AgNPs in aqueous solution, and the electrochemical catalysis of AgNPs for sodium sulfide was demonstrated.

2. EXPERIMENTAL

2.1. Materials

All reagents were of analytical grade. Double-distilled water was used throughout. 0.1 mol.L⁻¹ phosphate buffer solution (PBS) was prepared by dissolving 0.1 mol NaCl and 0.1 mol Na₂HPO₄ in the double-distilled water of 1000 mL and adjusted desired pH values with 6 M HCl or 1 M NaOH.

2.2. Preparation of AgNPs

The GCE with a diameter of 3mm was polished with 0.05 μ m alumina slurry on a polishing cloth, rinsed thoroughly with water, and then sonicated in ethanol and water for 10 min, sequentially. The AgNPs were deposited at a voltage of -0.2 V for 30 s on the surface of GCE that was immersed in the mixture of 2.5 mg.mL⁻¹ AgNO₃, 0.5 mol. L⁻¹ H₂SO₄ and 0.4 mg.mL⁻¹ cefoperazone sodium, then washed in doubly distilled water. In the typical synthetic process of AgNPs in aqueous solution, 0.150 g of NaBH₄ were dissolved the mixture of 2.5 mg.mL⁻¹ AgNO₃, 0.5 mol. L⁻¹ H₂SO₄ and 0.4 mg.mL⁻¹ cefoperazone sodium.

The solution was stirred with a magnetic stirrer for 10min to ensure that the NaBH₄ completely dissolved; the black AgNPs were soon produced, and followed by centrifugal separation, washing with absolute alcohol and drying in vacuum at 40 °C for 6 h.

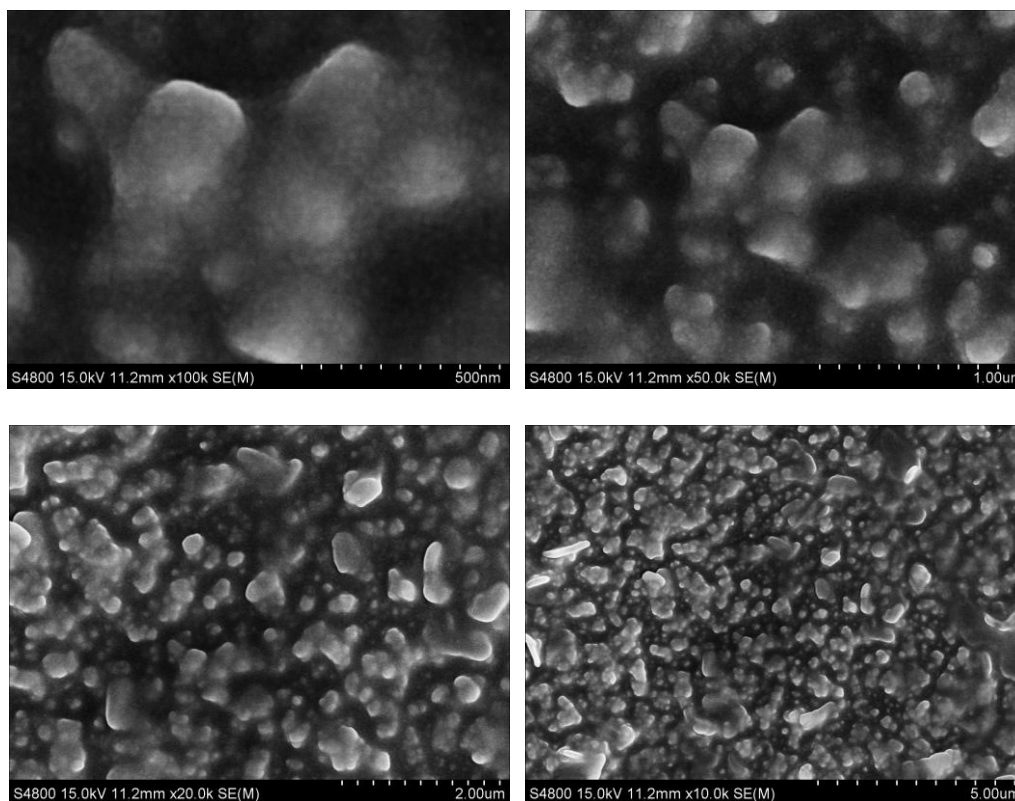
2.3. Characterization

For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The AgNP modified glassy carbon electrode (GCE) was used as working electrode, a platinum wire served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode.

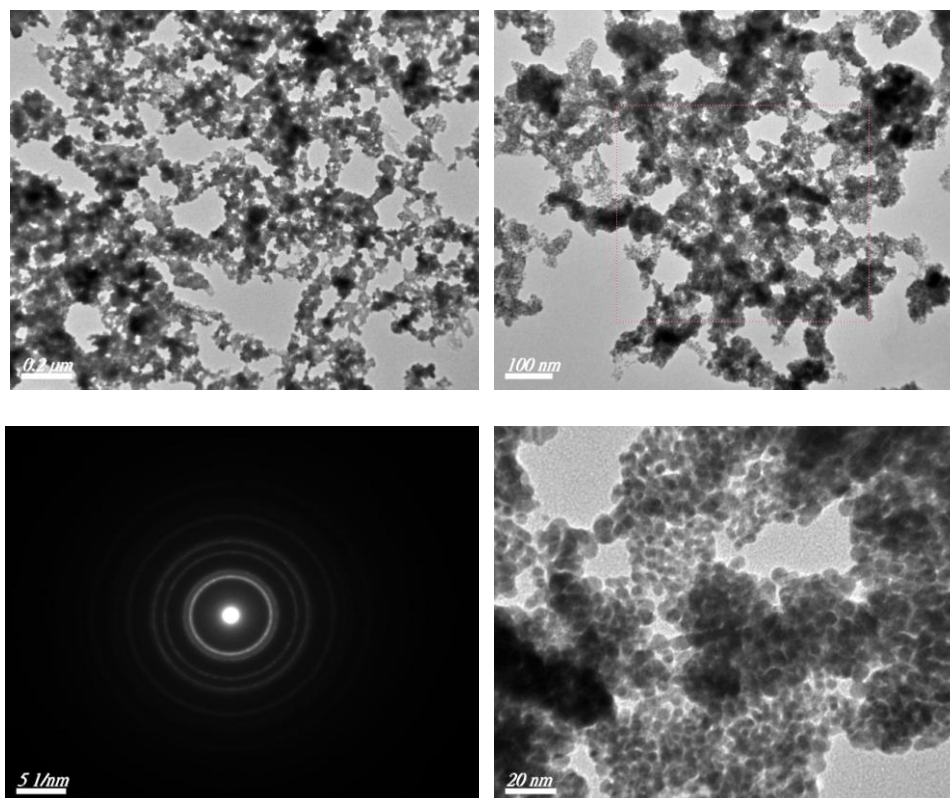
The AgNPs were characterized by scanning electron microscopy (SEM) (S-4800, HITACHI, Japan), spectrophotography (UV-1750, Shimadzu, Japan) and transmission electron microscopy (TEM) (JEM 2100, JEOL, Japan), Powder X-ray diffraction (XRD) spectra was recorded on a Switzerland ARL/X'TRA X-ray diffractometer rotating anode with Cu-K α radiation source ($\lambda = 1.54056 \text{ \AA}$).

3. RESULTS AND DISCUSSION

3.1. SEM and TEM images of AgNP



A



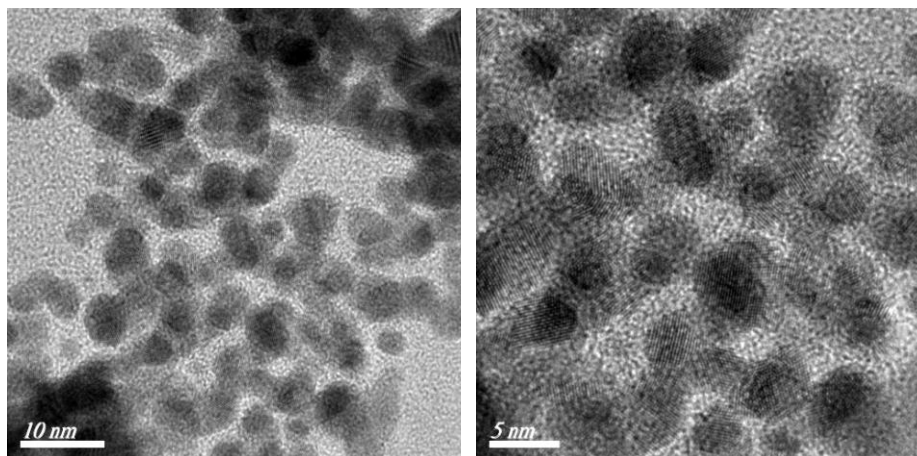


Figure1. SEM (a) and TEM (b) images of AgNPs

3.2. XRD of AgNPs

SEM images confirm the formation of a layer of AgNP on the GCE surface. Several AgNPs on the surface of GCE were observed in Fig.1 (a), indicating that the well dispersion AgNPs on the surface of GCE was obtained. The TEM of AgNPs from aqueous solution are shown in Fig.1 (b), the size of AgNPs is about 5nm. The AgNPs on the GCE surface is similar to the preparation of AgNPs in aqueous, the large nanoparticles on the GCE surface is composed of small AgNPs.

The powder XRD pattern of the AgNPs is shown in Fig. 2. The major diffraction peaks can be indexed as the gold face-centered cubic (fcc) phase based on the data of the JCPDS file (JCPDS no.04-0783) [13].

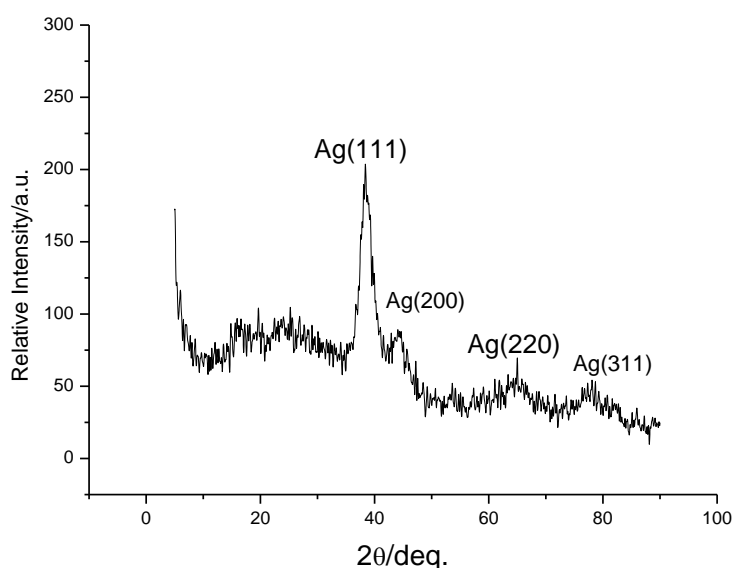


Figure 2. XRD pattern of AgNPs

The peaks of AgNPs in Fig. 2a appeared at 38.6° , 44.3° , 64.8° , and 77.7° , which can be assigned to (111), (200), (220), and (311) crystalline plane diffraction peaks of silver, respectively.

3.3. UV of AgNPs

Fig. 3 shows the UV–vis absorption spectrum of the AgNPs. A band centered at ca. 580nm appears, characteristic of surface plasmon absorption on the AgNPs.

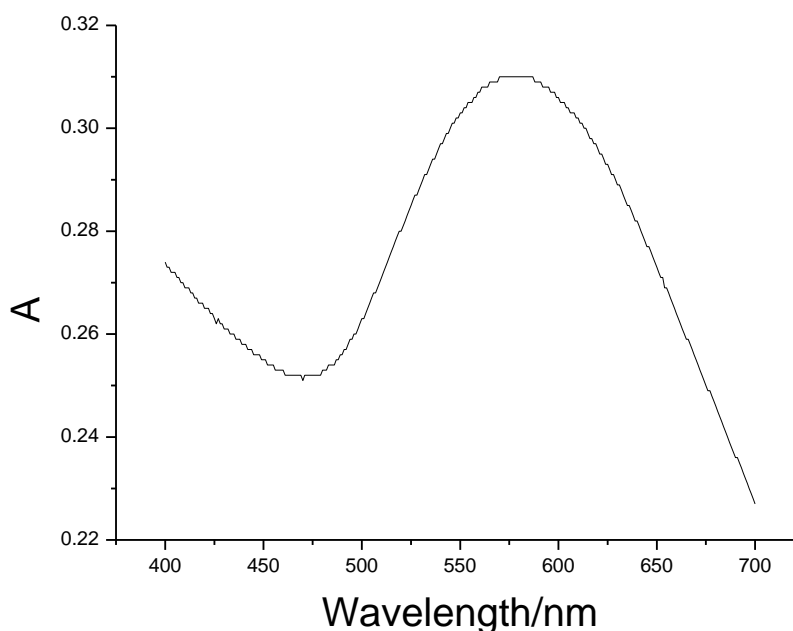
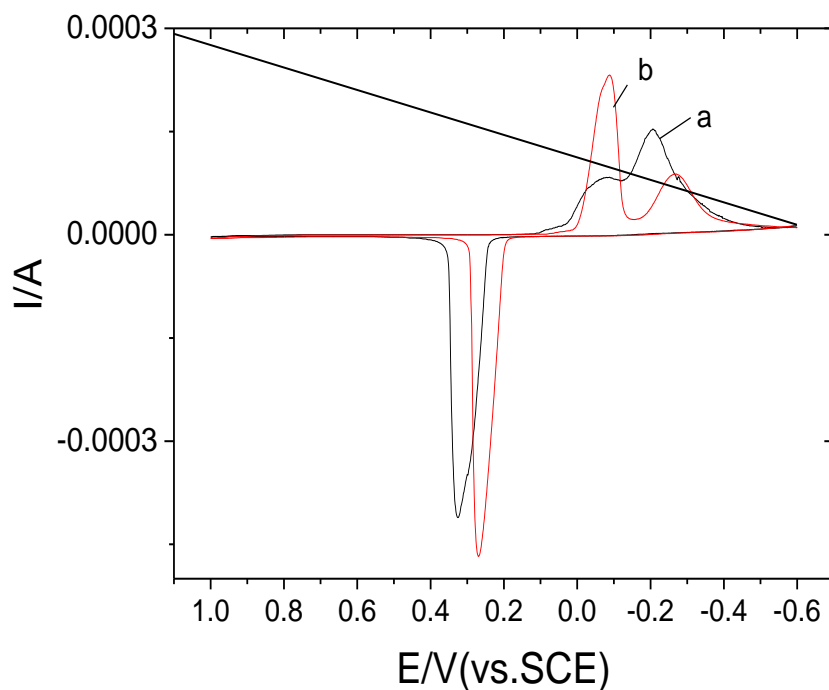


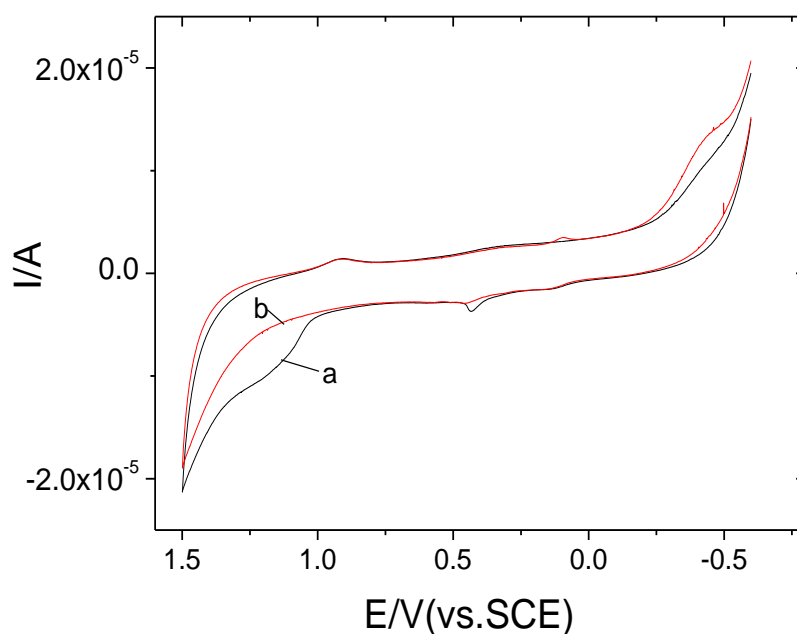
Figure 3. UV spectra of AgNPs in absolute alcohol

3.4. Cyclic voltammograms of AgNPs

The cyclic voltammograms (CVs) of cefoperazone@AgNPs on the surface of GCE in 0.1 M PBS of pH 7.3 is shown in Fig.4a. The oxidation peak of cefoperazone@AgNPs was found at 0.330V, and the reduction peaks was observed at -0.069 and -0.208 V. To remove cefoperazone on the surface of AgNPs, the AgNPs modified GCE was rinsed in $5 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ aqueous solution and doubly distilled water for 10 min, sequentially. The oxidation peak of the rinsed AgNPs was found at 0.271V, and reduction peaks were observed at -0.086 and -0.263V, which shifted to negative direction; Furthermore, the currents at 0.271 and -0.086 V increases, indicating the cefoperazone on the surface of GNPs is removed, the cefoperazone@AgNPs is more stable than AgNPs. The CVs of cefoperazone at GCE are shown in Fig.4b, two oxidation peaks were found at 0.433 and 1.158 V, which is related to two sulphur atoms in cefoperazone [14,15], indicating that cefoperazone is stable under electrochemical synthesis of AgNPs at -0.2 V.



A



B

Figure 4. a: CVs of cefoperazone@AgNPs (a) and the rinsed AgNPs (b) . Scan rate: $50.0 \text{ mV}\cdot\text{s}^{-1}$. Supporting electrolyte: $0.1 \text{ mol}\cdot\text{L}^{-1}$ PBS of pH 7.3. b: CVs of $0.4 \text{ mg}\cdot\text{mL}^{-1}$ cefoperazone. Scan rate: $100.0 \text{ mV}\cdot\text{s}^{-1}$. Supporting electrolyte: $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 .

3.5. Electrochemical catalysis of AgNPs for sodium sulfide

The CVs of for sodium sulfide at bare GCE, the cefoperazone@AgNPs and the rinsed AgNPs are shown in Fig.5, respectively. The redox peaks of sodium sulfide at cefoperazone@AgNPs were found at -0.529V and -0.640V . It can be seen that the peak potentials for sodium sulfide at

cefoperazone@AgNPs /GCE are less than that of sodium sulfide at AgNP/GCE, and the currents increase; while the oxidation peaks of sodium sulfide at bare GCE was not found, indicating that both cefoperazone and AgNPs catalyze the reaction of sodium sulfide due to the forming bond of Ag-S and the hydrogen bonds between cefoperazone and sulfide. The electrochemical process of sodium sulfide on the surface of AgNP/GCE ascribes to the reaction: $S^{2-}-2e^{-}=S$, which is similar to that of the electrochemical behavior of sodium sulfide at copper electrode [16]. The results indicated that cefoperazone@AgNPs /GCE is a well catalyzer for sodium sulfide.

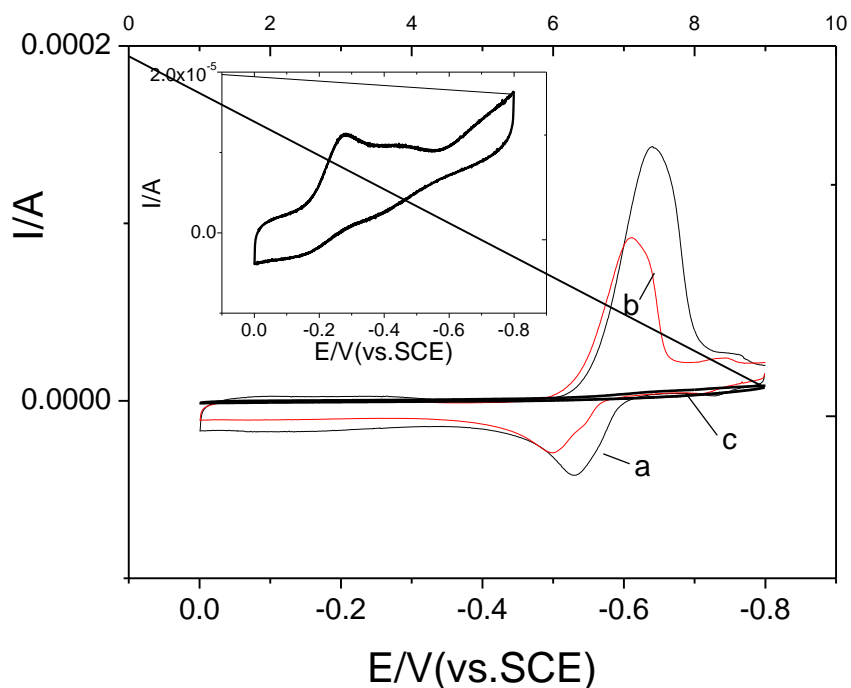


Figure 5. CVs of $0.020 \text{ mmol.L}^{-1} \text{ Na}_2\text{S}$ at cefoperazone@AgNPs /GCE (a) and the rinsed AgNP/GCE (b), and bare GCE(c). Insert Fig.: CVs of AgNP/GCE. Scan rate: 100.0 mV.s^{-1} . Supporting electrolyte: $0.1 \text{ mol.L}^{-1} \text{ PBS}$ of pH 7.3.

4. CONCLUSIONS

Electrochemical synthesis of silver nanoparticles on the surface of glassy carbon electrode and preparation of AgNPs in aqueous solution is described in this paper. The silver nanoparticles were characterized by scanning electron microscopy, cyclic voltammetry, transmission electron microscopy, and powder X-ray diffraction spectra. The electrochemical catalysis of cefoperazone@AgNPs and AgNPs for sodium sulfide was demonstrated.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the National Science Foundation of China (Grant No. 51175245), the Science Foundation of Education of Jiangsu Province of China (Grant No.

JH10-48), the Open Science Foundation for Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials (grant no. JSKC11091), and the Science Foundation for Huaiyin Normal University (grant no. 11HSGJBZ13).

References

1. L. Wang, H. Zhu, Y. Song, L. Liu, Z. He, L. Wan, S. Chen, Y. Xiang, S. Chen, J. Chen, *Electrochim. Acta* 63 (2012) 312.
2. C. Mao, X. Chen, H. Niu, J. Song, S. Zhang, R. Cui, *Biosens. Bioelectron.* 31 (2012) 544.
3. B. Karthikeyan, M. Murugavelu, *Sensor. Actuat. B* 163 (2012) 216.
4. K.P. Velikov, G.E. Zegers, A.V. Blaaderen, *Langmuir.* 19 (2003) 1384.
5. I. Sondi, D.V. Goia, E. Matijevic. *J. Colloid Interface Sci.* 260(2003)75.
6. Z.S. Pillai, P.V. Kamat. *J. Phys. Chem. B* 108 (2004) 945.
7. J. Turkevich, P.C. Stevenson, J. Hillier, *Discuss. Faraday Soc.* 11 (1951) 55.
8. P.C. Lee, D. Meisel, *J. Phys. Chem.* 86 (1982) 3391.
9. T.S. Ahmadi, Z.L. Wang, T.C. Green, A. Henglein, M.A. El-Sayed, *Science* 272 (1996) 1924.
10. J.A. Creighton, C.G. Blatchford, M.J. Albrecht, *Chem. Soc. Faraday Trans.* 75 (1979) 790.
11. Y.Z. Song, Y. Song, H. Zhong, *Gold Bull.* 44 (2011)107.
12. Y. Song, A. Zhu, H. Zhong, Y. Song, F. Wu, W. Yang, H. Huang, *Mater. Lett.* 65 (2011) 3612.
13. Joint Committee on Powder Diffraction Standards, Diffraction Data File: JCPDS International Center for Diffraction Data. Swarthmore PA, 1991.
14. N.A. El-Maali, A.M.M. Ali, Ma.A. Ghandour, *Electroanal.* 5(1993) 599.
15. D. Burcu, G., Aysegul, D. Mustafa; O. Sibel A. *Curr. Pharm. Anal.* 5(2009)179.
16. I. Zaafarany, H. Boller. *J. Saudi Chem.Soc.* 14(2010)183.