Int. J. Electrochem. Sci., 13 **(2018)** 7696 – 7705, doi: 10.20964/2018.08.43

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

AgNPs Modified Glass Carbon Electrode Prepared with Gelatin as an Additive for Hydrogen Peroxide Sensor

Yuepeng Guan[1,&], *Xiaogang Sun*[1,&], *Li Yin*[1], *Xianghui Hao*[2], *Shangwei Guo*[2,*], *Yaqin Huang*[1,*]

[1] State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical University of Chemical Technology
Beijing 100029, People's Republic of China.
[2] Dong E E Jiao Co.,Ltd., E-Jiao Street NO.78, Dong'e County, 252201 Shandong province, People's Republic of China.
[*] E-mail: huangyq@mail.buct.edu.cn; guosw@dongeejiao.com
[&] These authors contributed equally to this work and should be considered co-first authors.

Received: 19 August 2017 / *Accepted:* 6 November 2017 / *Published:* 5 July 2018

A method which was simple, cost effective and environmental friendly was employed for the synthesis of Ag nanoparticle (AgNP) with gelatin as a multifunctional additive. The hydrogen peroxide (H_2O_2) non-enzyme sensor was further fabricated using the mixture of the AgNPs with gelatin and fish-scale-based hierarchical lamellar porous carbon(FHLC). And its electrochemical behavior and stability was analyzed by CV, electrochemical impedance spectroscopy and amperometric I-t curve. In the result, the sensor exhibited an excellent response to the H_2O_2, and the detection limit was 0.6 μM with the linear response ranging from 0.2 mM to 12.3 mM (R^2=0.999). In addition, it exhibited good long term stability and anti-interference capability.

Keywords: Gelatin, Ag nanoparticle, Hydrogen peroxide, Electrochemical non-enzyme sensor

1. INTRODUCTION

Hydrogen peroxide (H_2O_2) is a by-product of several selective oxidases and significant mediator in chemical, biological, food, and environmental processes[1,2]. The accurate and sensitive determination of H_2O_2 is therefore critical[3-5]. By now, many analytical methods have been developed for determination of H_2O_2, among which enzyme based electrochemical sensors are especially promising due to the high sensitivity and inspection speed[6]. The utilization of enzyme-modified electrode is, however, limited by its environmental instability and high cost[7,8].

To overcome these problems, the applications of noble nanoparticles in sensors for construction of non-enzymatic sensors have been witnessed a significant growth in the past few years[9-14].

Among these sensors, Ag nanoparticle(AgNP)-based sensors have shown extremely sensitive amperometric response, low detection limit and wide linear range toward samples. Many researchers have found that the electro-catalytic performance of AgNP-based sensors strongly depended on the size and distribution[15-19]. Hence, the major challenge is to develop effective methods for the preparation of AgNPs with well-controlled size and distribution.

In this paper, gelatin was adopted as a multifunctional material for the preparation of AgNPs, which largely benefits the fabrication process of non-enzymatic hydrogen peroxide sensor from the following aspects[20-23]. Firstly, as a strong dispersion agent, gelatin is widely applied in food, photographic and medicine industry. Here, it is expected to control the size and distribution of AgNPs. Secondly, with having high adhesion ability, gelatin could directly act as the binder after the synthesis of AgNPs. Thus, the separation process which is complicated and energy consuming can be eliminated and the fabrication procedure can be simplified. Thirdly, gelatin is commercially available, cheap and degradable agent. Here, we will report a modified glassy carbon paste electrode based on Gel/AgNPs-FHLC to determine the H_2O_2. It was found that the Gel/AgNP-FHLC sensor displayed good electro-catalytic activity and high stability to the reduction of H_2O_2 by electrochemical analysis.

2. EXPERIMENTS

2.1. Preparation of the H_2O_2 sensor

Synthesis of AgNPs by chemical reduction, the preparation method comprises the following steps: Put the silver nitrate($AgNO_3$) into the gelatin solution in a beaker. After the silver nitrate completely dissolves, put ascorbic acid solution into the gelatin solution with $AgNO_3$ by dripping slowly on a magnetic stirrer at room temperature(25℃). After all the ascorbic acid dissolves in the solution, keep stirring about 15 minutes. Then, mix up the prepared solution with a certain amount of FHLC uniformly by ultrasonic dispersing technology (FHLC was prepared according to the method described in a previous study[24]). Put 10μL mixture (Gel/AgNPs-FHLC) onto the surface of glassy carbon electrode(GCE) by pipette. After drying, it will form a layer on the surface of glassy carbon electrode. Put 10μL glutaraldehyde solution(0.25%) onto the surface of Gel/AgNPs-FHLC layer as a crosslinking agent. At last, store the sensor at room temperature.

2.2. Measurements and apparatus

The surface morphologies of the acquired bio-sensitive membrane were characterized by scanning electron microscopy (SEM) using HITACHI S-4700 (Hitachi, Ltd., Japan) operated at 20kV. The microstructure of AgNPs was characterized by the UV-vis spectrometer and transmission electron microscope (TEM) observed with JEM-2100 (JEOL, Ltd., Japan) at 200 kV. To characterize the AgNPs, X-ray diffraction(XRD) test was completed using a Rigaku Rint D/max 2500 type diffractometer.

All the electrochemical experiments-including CV, EIS and CA-were performed by a CHI 660C(CH instruments, Shanghai, China) electrochemical workstation with a conventional three-electrode system. A preprocessed or modified GC electrode was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and the counter electrodes.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Gel/AgNPs-FHLC film modified electrode

With gelatin as a multifunction additive, the AgNPs have been synthesized by chemical reduction method. Form the XRD patterns of the as-synthetized product (Fig.1(a)), we can observe five diffraction peaks at 38.30, 44.30, 64.20, 77.50 and 81.60, which correspond to (111), (200), (220), (311) and (222) lattice planes of silver, respectively (JCPDS No.4-0783)[25,26]. The diffraction peaks are extremely specific, which indicates the resultant is pure silver with face-centered cubic crystal structure[27-29]. To understand the particle size and morphology of the material better, UV-vis absorption spectra and TEM image were introduced here. As shown in Fig.1(b), the UV-vis absorption spectra of the as-synthetized product displays a strong absorption peak at wavelength around 450nm, which is the characteristic absorption peak of the AgNPs[30-32]. And the TEM image (Fig.1(c)) further confirms the particle size of the as-synthetized Ag, which exhibited a regular spherical with diameter from 50nm to 100nm.

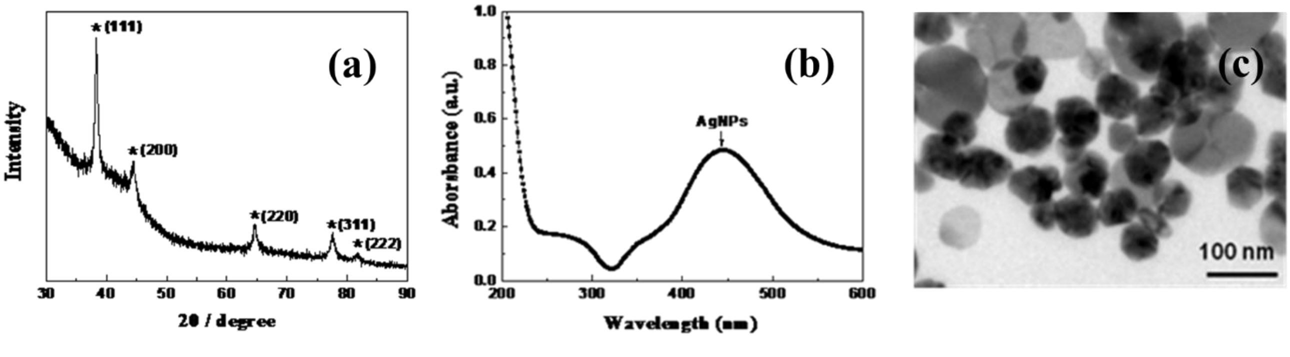

Figure 1. (a). XRD pattern of the as-synthetized product (b). UV spectra of the as-synthetized product (c). TEM images of the as-synthetized product

3.2. Electrochemical behavior of the Gel/AgNPs-FHLC film modified electrode towards H_2O_2

Here, we mainly study the direct electrochemical catalytic response to H_2O_2 of the non-enzymatic sensor. And CV was utilized to test the Gel/AgNPs-FHLC film modified GCE in 0.1M pH 7.0 PBS without or with H_2O_2.

The prepared mixture of AgNPs with gelatin was directly used to mix with fish-scale-based hierarchical lamellar porous carbon(FHLC) for preparation of the slurry. And then it was dropped onto the GC electrode, which was used to prepare the non-enzymatic hydrogen peroxide sensor by glutaraldehyde crosslinking. Fig. 2 shows the first two cycles' CV curves of the prepared Gel/AgNPs-FHLC film modified GCE in pH 7.0 PBS at the scan rate of 50 mV/s. There is a pair of symmetrical peak, with reduction potential at around 0.00V and oxidation potential at 0.45V, which is corresponding to the AgNPs' electrochemical activity. By comparing the CV curves of the first two cycles, it can be easily observed that they almost overlap, which indicates that AgNPs are fixed onto the surface of the GCE and the electrode has high stability.

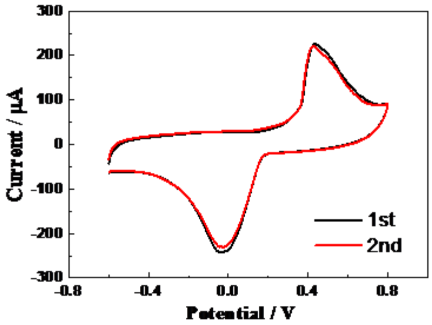

Figure 2. CVs of Gel/AgNPs-FHLC film modified GCE in pH 7.0 PBS at the scan rate of 50 mV/s

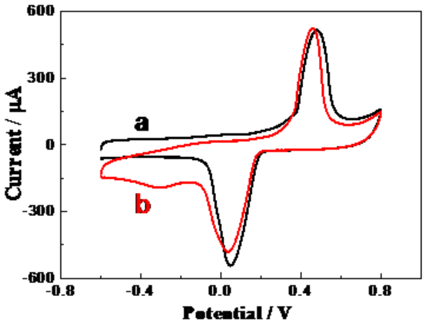

Figure 3. CVs of Gel/AgNPs-FHLC film modified GCE in pH 7.0 PBS at the scan rate of 50 mV/s in the absence (a) and presence (b) of H_2O_2.

CVs for the Gel/AgNps-FHLC film modified GCE in 0.1M pH 7.0 PBS without(a) or with H_2O_2 (b) are shown in Fig.3. Comparing the two curves (Fig.3), besides AgNPs electrochemical activity peaks, there is an obvious cathode reduction peak in the curve of the PBS solution with H_2O_2, which can illustrate that the peak current increases when adding the H_2O_2. This could be attributed to: (i) Smaller particle size of AgNPs could provide higher catalytic ability to H_2O_2 reduction. Combined with the TEM characterization of the AgNPs, the particle size has efficient catalytic ability to H_2O_2 reduction[33,34]; (ii)Gelatin and FHLC play an important role in the catalytic response to H_2O_2. Gelatin not only works as the dispersant and protective agent when preparing the AgNPs, but also helps to form membrane and maintain stability when preparing the electrode[35]. The huge specific surface area and countless active sites of the FHLC make it an excellent carrier and the AgNPs can be dispersed and fixed well on it. Gelatin and FHLC could improve the efficiency and stability of the catalytic response to H_2O_2.

Cyclic voltammograms for the Gel/AgNPs-FHLC modified GCE in PBS at different scan rates are shown in Fig.4(a). The scan rates increased from 20 mV/s to 200 mV/s with the gradient of 20 mV/s. It can be seen that the response current increases with the increasing of scan rate but the peak potential barely changes. The influence of scan rate to increasing response current is shown in Fig.4(b). We can find a linear relationship between reduction peak current and scan rates[36]. The correlation is 0.999, which means the catalytic reaction in the GCE's surface is controlled by the diffusion of hydrogen peroxide and the quantitative determination can be achieved.

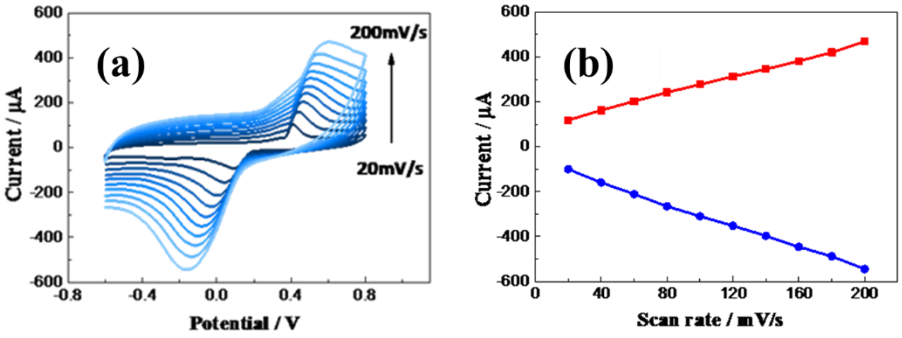

Figure 4. (a) Influence of scan rate on electrochemical responses of Gel/AgNPs-FHLC modified GCE in pH 7.0 PBS with scan rates from 20 mV/s to 200 mV/s, respectively. (b) Linear relationship of reduction peak current on different scan rates from 20 mV/s to 200 mV/s.

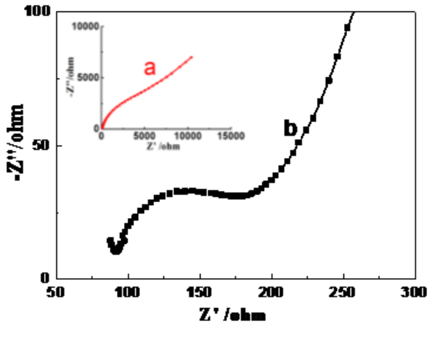

Figure 5. EIS of (a) bare GCE, (b) Gel/AgNPs-FHLC films modified GCEs in pH 7.0 PBS containing 5 mM $K_3Fe(CN)_6$ and 0.1M KCl across the frequency range from 1 Hz to 10^5 Hz. Inset:Randles equivalent circuit model

To confirm that the FHLC was fixed onto the surface of the GCE and it did work, we used the EIS to test the resistance change of bare electrode(a) and Gel/AgNPs-FHLC film modified GCEs(b) in pH 7.0 PBS containing 5mM $K_3Fe(CN)_6$ and 0.1MKCl, which are shown in Fig.5. In the equivalent circuits, R_s is the resistance of electrolyte, R_{et} is charge transfer resistance, C_{dl} represents double-layer capacitance, Z_w represents Warburg impedance.

As shown in Fig.5, a semi-circle was found with quite big arc radius with bare electrode, which indicates a very high electron-transfer resistance to the redox probe. By comparing it with Gel/AgNPs-FHLC film modified GCEs (Fig.5 b), we can find that electron-transfer resistance is largely reduced. We fitted the EIS to the equivalent circuits, which is shown in the Fig.5. The fitted charge transformation resistance (R_{et}) was 65.9Ω. Compared with the line(a), we can confirm that FHLC can facilitate the electron transportation between the AgNPs and the surface of non-enzymatic electrode. And the smaller resistance value indicates the well conductivity of FHLC and its hierarchical porous structure has positive effect on reducing the resistance of ion and electron transportation[37,38].

The amperometric response to Gel/AgNPs-FHLC film modified GCE at -0.4V upon successive additions of H_2O_2 is shown in Fig.6(a). A certain amount of hydrogen peroxide was added into PBS in regular intervals of 50s. The reduction current rises sharply and achieves the steady-state current within 3s. The amperometric response curve to hydrogen peroxide is shown in Fig.6(b). It displays the perfect linear relationship between the concentration of hydrogen peroxide and the response current with linear ranging from 0.2 mM to 12.3 mM (R^2=0.999). Its detection limit is estimated to be 0.6 μM based on the criterion of signal-to-noise ratio of 3 and the sensitivity is 16.17 $\mu AmM^{-1}cm^{-2}$.

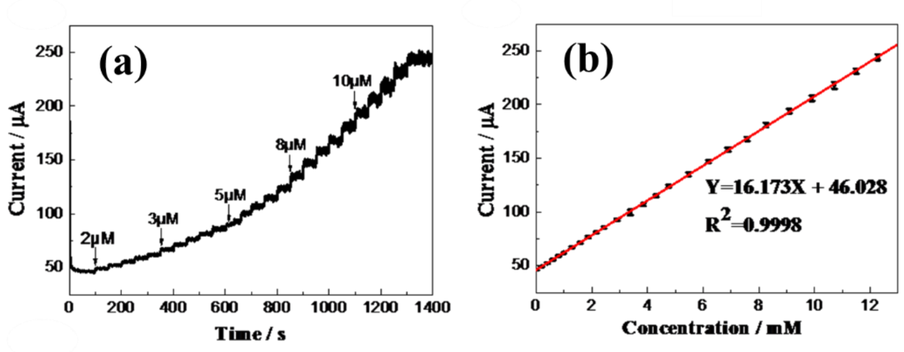

Figure 6. (a) The amperometric response of Gel/AgNPs-FHLC film modified GCE at -0.4 V upon successive additions of H_2O_2 in 0.1 M pH 7 PBS. (b) Amperometric response curve for H_2O_2

The quick response and high sensitivity could be attributed to AgNPs' catalysis to hydrogen peroxide. FPC's porous structure is not only conducive to the immobilization of AgNPs but also beneficial to the quick spread of ion and promotes the electron transfer between AgNPs and electrode surface.

3.3. Interference and stability study of the the Gel/AgNPs-FHLC film modified electrode

To inspect the anti-interference performance of the Gel/AgNPs-FHLC film modified GCE and investigate whether the hydrogen peroxide detection will be disturbed by other substance, the electrode was put in 0.1M pH 7.0 PBS at a certain stirring rate. When the initial current was stable, the change of current was recorded by current-time curve every 50s after adding 0.3mM hydrogen peroxide, ascorbic acid (AA), uric acid (UA), dopamine (DA) and glucose (Glu)[39]. The result is shown in Fig.7(b). It can be clearly seen in the diagram that there is an obvious ascend step after adding hydrogen peroxide and the response current did not show clear change after adding AA, UA, DA and Glu and at the end there is another obvious ascend step after adding hydrogen peroxide. From the result, it can be confirmed that this non-enzymatic sensor based on Gel/AgNPs-FHLC film modified GCE has excellent selectivity to hydrogen peroxide and anti-interference ability. So it can be used in actual detection.

The stability tests to the hydrogen peroxide sensor based on Gel/AgNPs-FHLC mainly include work stability and storage stability. Fig.7(a) shows the current-time curves of the hydrogen peroxide sensor based on Gel/AgNPs-FHLC in a month. From Fig.7(a), the curves are almost overlap and at the steady-state response currents are almost the same without decrease trend. After analysis and calculating, the electrochemical response value to hydrogen peroxide of the non-enzymatic sensor could remain 99.4% of the initial value after a month, which displays that it has excellent long-term storage stability. By comparing with other non-enzymatic sensors' stability which are shown in Table1, we can see that its stability is better, which can be attributed to the high stability of gelatin and FHLC's to AgNPs' fixing, AgNPs' zero-bioactivity, and low requirements to environment. So the non-enzymatic sensor has excellent advantages for development and can detect hydrogen peroxide effectively in the long-term.

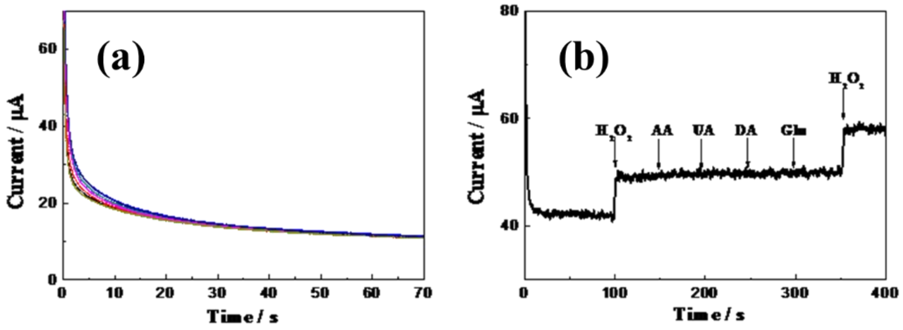

Figure 7. (a). The storage stability of the Gel/AgNPs-FHLC film modified GCE (the amperometric response of Gel/AgNPs-FHLC film modified GCE at -0.4 V in the presence of H_2O_2 in 0.1 M pH 7.0 PBS for 1 month); (b). Response of the Gel/AgNPs-FHLC film modified GCE to H_2O_2, AA, UA, DA and Glu. 0.3mM each.

To exhibit that our modified electrode has excellent performance, a comparison of amperometric response to this Gel/AgNPs-FHLC films modified GCE with other hydrogen peroxide sensors modified by AgNPs reported in the literature is shown in Table 1. We can see that the hydrogen peroxide sensor based on Gel/AgNPs-FHLC has large linear detection range, lower limit of detection and better stability, which could meet the requirement in practical detection of hydrogen peroxide.

Table 1. Comparison of performances of different non-enzyme sensors based on AgNPs for determination of H_2O_2

Sensor	LOD(μM)	LDR(mM)	Sensitivity (μAmM^{-1}cm^{-2})	Stability	Reference
Ag NPs/ATP/GCE	2.4	0.1-21.53	--	--	[2]
Ag@C@Ag/GCE	23	0.07-10	-	21 days (4℃, 96%)	[40,41]
Ag/C/GCE	1.3	0.004-25.5	8.52	21 days (96%)	[42]
MC/AgNPs/GCE	0.05	0.0001-0.041	7.067	30 days (4℃, 94%)	[43]
AgNP/rGO/GCE	3.6	0.1-100	--	--	[44]
(PDA/AgNPs)$_2$/ GCE	6.5	0.05-1.75	--	21 days (4℃)	[45]
AgPs/SWCNT/PET	2.76	0.016-18.085	10.92	--	[46]
MWNTs/Cu/Ag/GCE	2.82	0.002-0.42	--	--	[47]
Gel/AgNPs-FHLC	0.6	0.2 -12.3	16.17	30 days (25℃, 99.4%)	this work

LOD: limit of detection; LDR: linear detection range; ATP: natural nano-structure attapulgite; MC: mesoporous carbon; rGO: reduction of graphene oxide; PDA: polydopamine; SWCNT: single-walled carbon nanotube; MWNTs: multi-walled carbon nanotubes

4. CONCLUSION

A non-enzyme sensor with high stability was designed and prepared to determine hydrogen peroxide (H_2O_2). It was obtained by modifying glassy carbon electrode (GCE) with gelatin, AgNPs and fish-scale-based hierarchical lamellar porous carbon(FHLC). Using $AgNO_3$ as raw material, ascorbic as reducing agent and gelatin as dispersant, the AgNPs was synthesized. The cyclic voltammogtams at different scan rates, electrochemical impedance spectroscopy (EIS), and amperometric current time curves indicate that the non-enzyme sensor has excellent electro-catalytic activity to detection hydrogen peroxide. Its linear detection range is estimated to be from 0.2 to 12.3 mM , with a correlation coefficient(R^2) of 0.999 . The detection limit is estimated to be 0.6 μM, and the sensitivity is 16.17 μAmM^{-1}cm^{-2}. The electrochemical response value to H_2O_2 of the non-enzymatic sensor could remain 99.4% of the initial value after a month, which displays that it has excellent long-term storage stability. Therefore, this method could be a promising candidate for the preparation of non-enzyme hydrogen peroxide sensor.

ACKNOWLEDGEMENTS
Financial support from the National Natural Science Foundation of China (no. 51672020 and 51432003) is gratefully appreciated.

References

1. H. Kivrak, O. Alal and D. Atbas, *Electrochimica Acta*, 176 (2015) 47.
2. H. Chen, Z. Zhang, D. Cai, S. Zhang, B. Zhang, J. Tang and Z. Wu, *Talanta*, 86 (2011) 266.
3. Y. Miao, S. He, Y. Zhong, Z. Yang, W. W. Tjiu and T. Liu, *Electrochimica Acta*, 99 (2013) 117.

4. L. Xiong, L. Zheng, J. Xu, W. Liu, X. Kang, Y. Wang, W. Wang, S. Yang and J. Xia, *ECS Electrochemistry Letters*, 3 (2014) 26
5. Z. Wang, L. Zhang and Y. Tia, *Analyst*, 140 (2015) 3788.
6. A.J.S. Ahammad, *Journal of Biosensors and Bioelectronics*, 2013, S9:001.
7. Y. Wang, B. Gu, X. Li, J. Wang, F. Jia, B. Ding, L. Zhang, Z. Cheng and H. Zhang, *Materials Review*, 27 (2013) 44.
8. H. Zhao, P. Zhang, S. Li and H. Luo, *Chinese Journal of Analytical Chemistry*, 45 (2017) 830.
9. M. Amiri, S. Nouhi and Y. Azizian-Kalandaragh, *Materials Chemistry and Physics*, 155 (2015) 129.
10. M. Shamsipur, Z. Karimi, M and A. Tabrizi, *Materials Science and Engineering C*, 56 (2015) 426.
11. S. Palanisamy, C. Karuppiah, S. Chen, R. Emmanuel, P. Muthukrishnan and P. Prakash, *Sensors and Actuators B*, 202 (2014) 177.
12. S. N. Azizi, S. Ghasemi, A. Samadi-Maybodi and M. Ranjbar-Azad, *Snsor and Actuators B*, 216 (2015) 271.
13. H. Chen, X. Wang, G. Liu, A. Lin, Y. Wen and H. Yang, *Science China Chemistry*, 58 (2015) 1585.
14. J. Yoon, T. Lee, B. Bapurao G., J. Jo, B.-K. Oh and J.-W. Cho, *Biosensors and Bioelectronics*, 93 (2017) 14.
15. A.D. Bonis, A. Galasso, N. Ibris, M. Sansone, A. Santagata and R. Teghil, *Surface & Coatings Technology*, 207 (2012) 279.
16. G. Kawamura, M. Nogami and A. Matsuda, *Journal of Nanomateials*, 1 (2013) 257.
17. A. Liang, Q. Liu, G. Wen and Zh. Jiang, *Trac-Trends in Analytical Chemistry*, 37 (2012) 32.
18. G. Wang, M. Li, Y. Gao and B. Fang, *Sensors*, 4 (2004) 147.
19. P. Yang, W. Wei and C. Tao, *Analytica Chimica Acta*, 585 (2007) 331.
20. S.M. Naghib, M. Rahmanian, K. Majidzadeh-A, S. Asiaei and O. Vahidi, *International Journal of Electrochemical Science*, 11 (2016) 10256.
21. P.K. Srivastava, A.M. Kayastha and Srinivasan, *Biotechnol. Appl. Biochem*, 34 (2001) 55.
22. B. Thirumalraj, S. Palanisamy, S. Chen and K.D. Wael, *Journal of The Electrochemical Society*, 163 (2016) B265.
23. Y. Bagbi, A. Sharma, H,B. Bohidar and P.R. Solanki, *International Journal of Biological Mcromolecules*, 82 (2016) 480.
24. Z. Huang, H. Shao, B. Huang, C. Li, Y. Huang, Xiao Chen. *RSC Advances*. 4 (2014) 18737.
25. J. Yin, X. Qi, L. Yang, G. Hao, J. Li and J. Zhong. *Electrochimica Acta*. 56 (2011) 3884.
26. B. Habibi and M. Jahanbakhshi. *Sensors and Actuators B: Chemical*. 203 (2014) 919.
27. M. M. Khan, S. A. Ansari, J. Lee and M. H. Cho, *Materials Science and Engineering C*, 33 (2013) 4692.
28. X. Lou, H. Pan, S. Zhu, C. Zhu, Y. Liao, Y. Li, D. Zhang and Z. Chen, *Catalysis Communications*, 69 (2015) 43.
29. Y. Li, Y. Zhang, Y. Zhong and S. Li, *Applied Surface Science*, 347 (2015) 428.
30. W. Benjamin, S. Yugang and X. Younan, *Acc. Chem. Res*, 40 (2007) 1067.
31. H. E. Emam, M.H. El-Rafie, H.B. Ahmed and M.K. Zahran, *Fibers and Polymers*, 16 (2015) 1676.
32. E.E. Khoury, M. Abiad, Z.G. Kassaify and D. Patra, *Colloids and Surfances B:Biointerfaces*, 127 (2015) 274.
33. A. S. Rad, A. Mirabi, E. Binaian and H. Tayebi. *International Journal of Electrochemical Science.* 6 (2011) 3671.
34. S. Chairam, W. Sroysee, C. Boonchit, C. Kaewprom, T. G. N. Wangnoi, M. Amatatongchai, P. Jarujamrus, S. Tamaung and E. Somsook. *International Journal of Electrochemical Science.* 10 (2015) 4611.
35. Y. Chang, A. P. Periasamy and S. Chen. *International Journal of Electrochemical Science.* 6 (2011) 4188.
36. Y. Yao, Y. Wen, L. Zhang, J. Xu, Z. Wang and X. Duan. *International Journal of Electrochemical*

Science. 8 (2013) 9348.
37. Z. Wang, M. Li, P. Su, Y. Zhang, Y. Shen, D. Han, A. Ivaska and L. Niu. *Electrochemistry Communications*. 10 (2008) 306.
38. A. S. Rad, M. Jahanshahi, M. Ardjmand and A.-A. Safekordi. *International Journal of Electrochemical Science*. 7 (2012) 2023.
39. Y. Xia, W. Li, M. Wang, Z. Nie, C. Deng and S. Yao. *Talanta*. 107 (2013) 53.
40. N. Pourreza, H. Golmohammadi, T. Naghdi and H. Yousefi, *Biosensors and Bioelectronics*, 74 (2015) 353.
41. Q. Wang, H. Niu and C. Mao, *Electrochimica Acta*, 127 (2014) 349.
42. D. Jiang, Y. Zhang and M. Huang, *Journal of Electroanalytical Chemistry*, 728 (2014) 26.
43. B. Habibi and M. Jahanbakhshi, *Sensors and Actuators B:Chemical*, 203 (2014) 919.
44. Q. Li, X. Qin and Y. Luo, *Electrochimica Acta*, 83 (2012) 283.
45. F. Wang, R. Han, G. Liu, H. Chen, T. Ren, H. Yang and Y. Wen, *Journal of Electroanalytical Chemistry*, 706 (2013) 102.
46. M.-P. N. Bui, X. Pham, K. N. Han, C. A. Li, Y. S. Kim and G. H. Seong. Sensors and Actuators B: Chemical. 150 (2010) 436.
47. J. Xu, X. Wei, X. Song, X. Lu, C. Ji, Y. Ni and G. Zhao. *J Mater Sci*. 42 (2007) 6972.