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Fabrication of NiOOH/Ni(OH)$_2$@C Electrode for Detecting Blood Glucose by Composited Plating Method

Huining Cheng[1], *Mingxiao Wang*[2], *Yang Tang*[1], *Yanzhi Sun*[1], *Yongmei Chen*[1,*], *Pingyu Wan*[1]

[1] National Fundamental Research Laboratory of New Hazardous Chemicals Assessment & Accident Analysis,
Institute of Applied Electrochemistry, Beijing University of Chemical Technology, 100029, Beijing, P. R. China.
[2] China Meitan General Hospital, 100028, Beijing, P. R. China
[*]E-mail: chenym@mail.buct.edu.cn

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A sensor of NiOOH/Ni(OH)$_2$@C electrode was fabricated by the following process: metallic Ni and carbon powder was simultaneously electroplated onto Ni wire by the composite plating method with the help of cationic surfactant, then followed by electrochemically oxidation of Ni to Ni(OH)$_2$ in alkali medium. SEM and XRD characterization results showed that shell-core structure of Ni@C could be formed by simply control the ratio of Ni^{2+} and carbon powder. The high electrochemical activity and high specific surface area of the fabricated NiOOH/Ni(OH)$_2$@C electrode make it good performance in detecting glucose: sensitivity of 10.81 $mAcm^{-2}mM^{-1}$, good linearity (R^2=0.99995) in range of 5μM~10mM with detection limit of 10^{-6}M. The specific structure of the electrode also made the sensor display good selectivity to glucose when uric acid and ascorbic acid co-existed in the simulated serum sample.

Keywords: blood glucose, sensor, non-enzyme, NiOOH/Ni(OH)$_2$, composited plating

1. INTRODUCTION

A sensor for detecting glucose in body fluid (blood[1] or urine[2]) based on electrochemically oxidation of glucose[3] is desired for the routine surveillance of the diabetics[4]or the on-line monitoring of peritoneal dialysis[5], since the concentration of glucose could be easily transferred to digital information[6]. Although the competition between enzymatic and non-enzymatic glucose sensor has been last for decades, an ideal sensor with high sensitivity, wide linearity range and excellent selectivity is final target for all of these sensor studies[7].

The remarkable shortcoming of non-enzymatic sensor is its poor selectivity, especially when it is used in practical blood samples. Taking a NiOOH/$Ni(OH)_2$ electrode as an example, all of $Ni(OH)_2$ is electrochemically controlled to transform to NiOOH, and because NiOOH would react with glucose in electrolyte once it is formed, the current due to the re-oxidation of $Ni(OH)_2$ to NiOOH is proportional to the concentration of glucose in electrolyte[8]. However, ascorbic acid[9] and uric acid[10] which are co-existed in blood can also react with NiOOH like glucose, which is the reason for the deviation of non-enzymatic sensor in practical samples analysis[11]. Fortunately, the kinetics studies shown that the electro-oxidation of ascorbic acid or uric acid on electrode is a diffusion-controlled process[12], while the electrocatalytic oxidation of glucose is dynamic controlled relatively. That provides a way to improve the detection selectivity by a well-designed electrode with rough and porous structure.

The another problem is that not all of electrochemical active material (i.g. $Ni(OH)_2$) in non-enzymatic sensors is utilized during the detection[13]. For example, in an electrode made by powder press method parts of $Ni(OH)_2$ are non-electrochemical active if they did not contact with carbon powder or the substrate electrode and they will never be transferred to NiOOH. These “died” material in the electrode lowered the electrochemical active of the sensor.

Here we reported the fabrication of NiOOH/$Ni(OH)_2$@C electrode started from composited electroplating of Ni particles and carbon particles together with the aid of cationic surfactant followed Ni particles being electrochemically activated to Ni(OOH), which guarantee the electrochemical activity of the deposited coating. The performance of the electrode for detecting glucose in simulated serum sample was then tested.

2. EXPERIMENTAL PART

2.1. Chemicals

Nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), boric acid (H_3BO_3), cetyl trimethyl ammonium bromide (CTMAB), sodium dodecyl sulfate (SDS), potassium hydroxide (KOH), hydrochloric acid (HCl, 12mol/L), nitric acid (HNO_3, 8mol/L), absolute ethyl alcohol, glucose, urea were purchased from Beijing Chemical Works,(GR); Uric acid(UA), creatinine(Cr) and ascorbic acid(AA) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Aetylene black powder (with a diameter of 50nm) was purchased from Elliott (Henan Power). All the solutions were prepared using the water of 18 MΩ·cm purified by a Milli-Q purification system.

The standard serum sample is brought from Beijing Lablead Biotechnology Co., Ltd according to the national standard (GBW09174). The concentrations of glucose, creatinine, urea and uric acid in this serum sample are 4.22mmol/L, 0.0788mmol/L, 4.45mmol/L and 0.3357mmol/L, respectively (ascorbic acid is undetectable in this serum sample). More amounts of creatinine, urea, uric acid and ascorbic acid were added into the serum sample until the current response of glucose changed more than 5%.

2.2. Preparation and electrochemical tests of the electrodes

A Ni wire (with a diameter of 0.2mm) were purified by the diluted mixed acid (V_{H2O} : V_{HCl} : V_{HNO3}=2:1:1) under sonication for 5min and rinsed by water and absolute ethanol, then dried in air.

All of the electrochemical tests in this study were conducted with an electrochemical station (CHI660E). The electro-plating process was conducted $NiSO_4$ solution (adjusted to pH=4.0 by boric acid) using the Ni wire as the working electrode, a Pt plate as the counter electrode and a SCE as the reference electrode by constant current model in 15mA/cm^2 at 50℃. In order to composited plating of Ni with carbon powder, certain amount of carbon powder was added into the electrolyte together with surfactant (CTMAB or SDS). Ni@C electrodes were prepared by the constant current model in 15mA/cm^2 at 50℃in the presence of CTMAB, with the molar ratio of Ni to C of 12:2, 12:3, 12:12, and named them Ni@C_1, Ni@C_2, Ni@C_3 electrode in sequence. Then in KOH(1M) electrolyte the as-prepared electrode was acted as working electrode, a SCE as reference electrode and a platinum slice as the counter electrode. Cyclic voltamograms (CVs) in range of 0.0~0.5V with scanning rate of 20mV/s were operated several circles, to make all of Ni particles on the electrode transformed to Ni to Ni(OOH)[14].After the CV curves were well overlapped, the electrode was used as the sensor for detecting glucose by the constant potential chronoamperometery method at 0.33V.

The influence of the interfering substances on the determination of glucose by NiOOH/$Ni(OH)_2$@C electrode was tested as follows: taking the concentration of urea, uric acid, creatinine and ascorbic acid (AA) in blood of a health adult man as reference, the standard serum was added by 1,5,10,20,100 even 200 times in concentration of urea, uric acid, creatinine and ascorbic acid and certain concentration of glucose. The concentration of glucose in as-prepared simulated blood sample was test by the above method.

2.3. Structure characterization of the electrode

The morphology of the electrode was characterized by scanning electron microscopy (SEM) on ZEISS SUPRA 55, operated at an accelerating voltage of 20 kV. The chemical compositions of the prepared coating were determined by Energy Dispersive Spectrometer (EDS). The coating was characterized in powdered form after repeatedly ultrasonic treatment using X-ray diffraction (XRD) carried out in Bruker D8 Advance with a Cu anticathode (40 kV, 200 mA) at a scan rate of 10° min^{-1} from 5° to 90°.

3. RESULTS AND DISCUSSION

3.1 Composited plating of Ni and carbon powder on Ni wire electrode

Electrochemical deposition of Ni particles together with carbon particles onto Ni wire cathode in present of ionic or cationic surfactant or in absent of any surfactant was done under constant current model. The potential-time (V-t) curves recorded during electro-plating were shown in Fig. 1. When

carbon powder was added into the electrolyte (green curve in Fig.1), the shape of V-t curve changed obviously comparing to that of the normal deposition of Ni (i.g. without carbon powder, yellow curve in Fig.1). The increase rate of the deposition potential in the initiate stage was slow down and the actual value of the potential became more positive. It seems that carbon powder binders the migration and deposition of Ni^{2+} onto the substrate. The situation did not changed in presence of ionic surfactant SDS (the blue curve in Fig.1), but it is improved when cationic surfactant CTMAB was added, means the presence of CTMAB compensating the blocking effect of carbon powder to the deposition of Ni^{2+}.

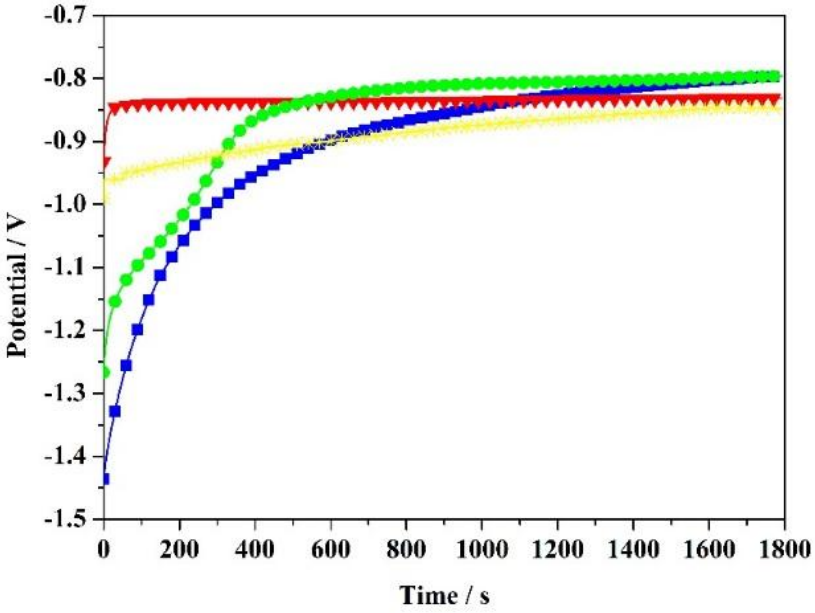

Figure 1. The recorded potential –time (E-t) curves under current-constant model in electrolyte containing Ni^{2+} (yellow); in electrolyte containing Ni^{2+} and carbon powder (green); in electrolyte containing Ni^{2+}, carbon powder and anionic surfactant SDS (blue); in electrolyte containing Ni^{2+}, carbon powder and cationic surfactant CTMAB (red)

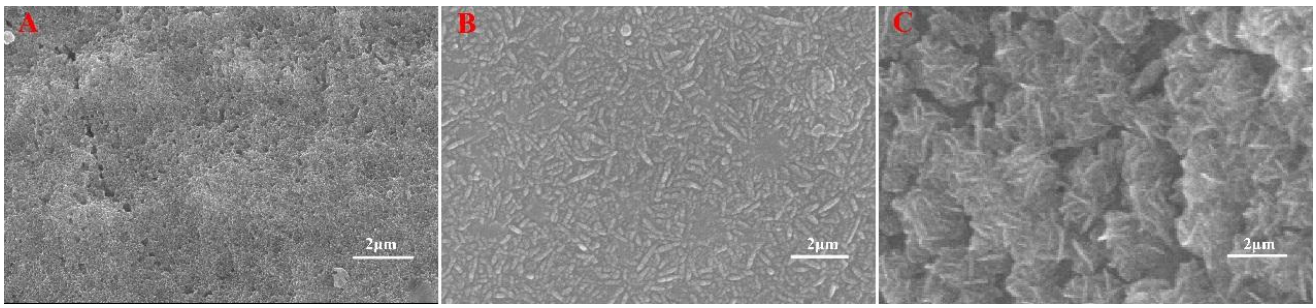

Figure 2. SEM images of the electrode surface after cathodic deposited in mixed liquid of $NiSO_4$ and carbon powder A) without any surfactant; B) with ionic surfactant SDS; C)with cationic surfactant CTMAB

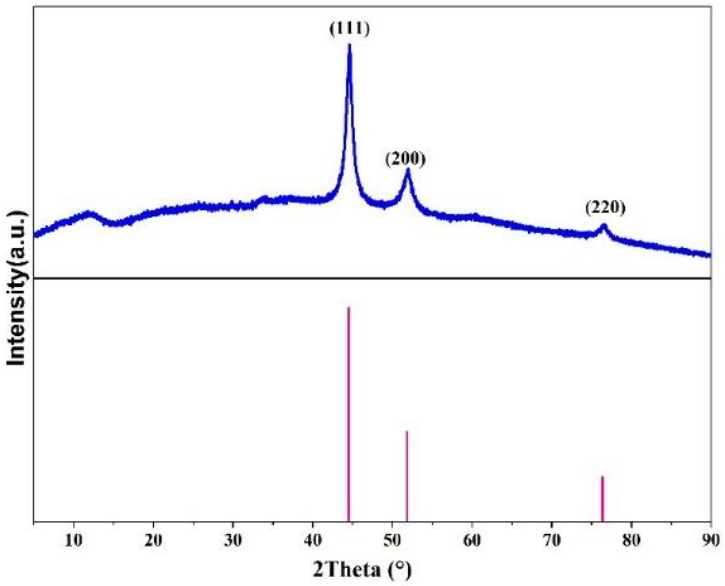

Figure 3. XRD patterns of the peeled coating deposited by the composited plating method

The SEM images of the deposited coating (Fig.2) shown that there is no carbon particle was found on the electrode except for the case in presence of cationic surfactant CTMAB. Furthermore, the XRD pattern of the peeled coatings (Fig.3) confirmed that Ni metal was deposited on the substrate by the above composited plating method.

The above results indicate that cationic surfactant CTMAB plays the important role in co-deposition of Ni and carbon powder onto the electrode surface [15][16].The mechanism is descripted as follows: CTMAB-coated carbon particles become hydrophilic and could migrate to cathode together with Ni^{2+}, and then Ni nanoparticles were deposited on carbon particles as while as the substrate.

3.2 The core-shell structure Ni@C controlled by the ratio of Ni^{2+} and carbon powder

When the increased amount of carbon powder was added in the same concentration of $NiSO_4$ solution, the shape of the deposited Ni@C on the substrate changed. Compared to the original size of carbon powder (about 100nm in diameter, shown in Fig 4A), the size of the cluster increased as the ratio of carbon powder to Ni^{2+} increased (from 120nm to about 800nm, as shown in Fig.4B-D). If the amount of carbon powder is relatively low comparing to Ni, carbon particle could be coated by Ni separately but the thick of Ni coating might be more than 25nm (Fig 4B). On the other hand, if the amount of carbon powder was too much, more than one carbon particles would be agglomerated together during the deposition of Ni. Taking 4D as an example, there might be more than ten carbon particles in each cluster. So the desirable core-shell Ni/C structure could be obtained by controlling the appropriate ratio of carbon powder to Ni^{2+}, as shown in Fig.4C.

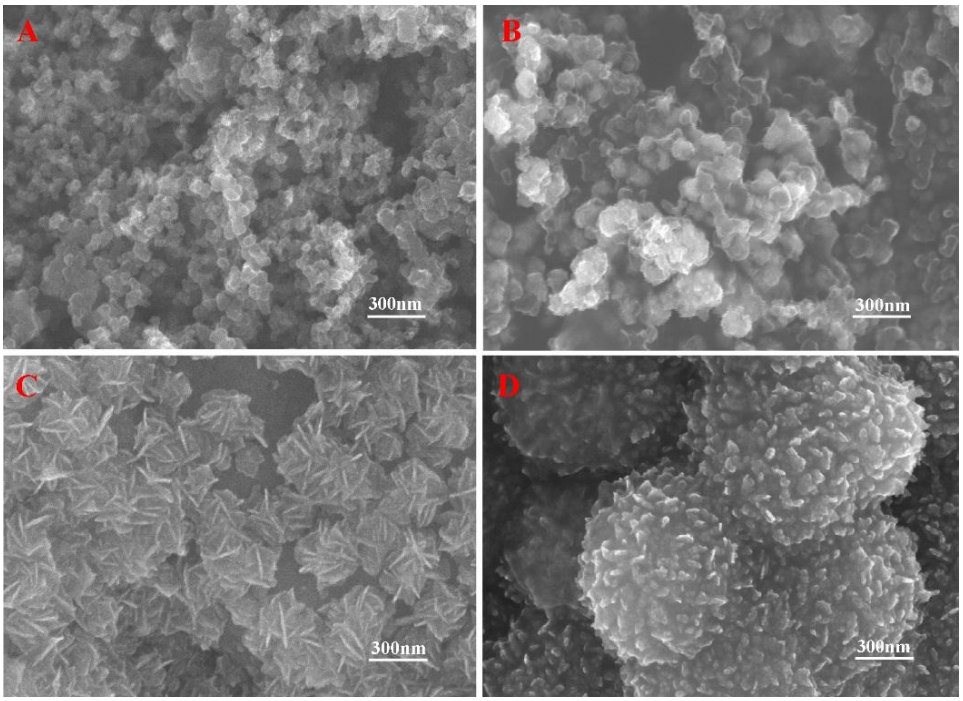

Figure 4. SEM images of the co-deposited Ni/C on Ni electrodes by the constant current model in the presence of CTMAB, with the molar ratio of Ni to C of 12:2(B, Ni@C_1), 12:3(C, Ni@C_2), 12:12(D, Ni@C_3). The image of carbon powder used in this study was shown in A.

3.3. Transformation of Ni@C electrode to $Ni(OH)_2$/NiOOH@C electrode

The above Ni@C electrodes were oxidized by cyclic voltammogram method in range of 0.0-0.5V in 1M KOH. As shown in Fig. 5, the intensity of the anodic peaks at 0.35V and the cathodic peaks at 0.2V increased in the first three circles, and then the curves were overlapped with the former one. Metal Ni can be easily oxidized to $Ni(OH)_2$ in alkali medium[17][18], and the anodic peaks at 0.30-0.35V are assigned to the oxidation of $Ni(OH)_2$ to NiOOH, while the cathodic peaks at 0.15-0.25V are attributed to the reduction of Ni(OOH) to $Ni(OH)_2$.

It is notable that the intensity of peaks in CV curves of the four Ni@C electrodes was different, which means the amount of NiOOH formed on the electrode was different [19]. Supporting no other cathodic reaction (such as hydrogen evolution) occurred during the composited plating, the loaded amount of Ni on the substrate should be the same since the four Ni@C electrodes were performed under the same current density for the same time[20]. It could be understood that the electrochemical activity of the deposited Ni in the four Ni@C electrodes was different.

As shown in Fig.5, the most amount of NiOOH formed on the Ni@C_2 electrode among the four electrodes, which means that the Ni@C_2 electrode as a precursor provided good structure leading most of $Ni(OH)_2$ on carbon particle be well electrochemically oxidized[21]. Too thick coating of Ni on carbon powder (i.e. Ni@C_3 electrode) or too much carbon particles in each aggregation (like Ni@C_1 electrode) made part of Ni could not be electrochemically activated.

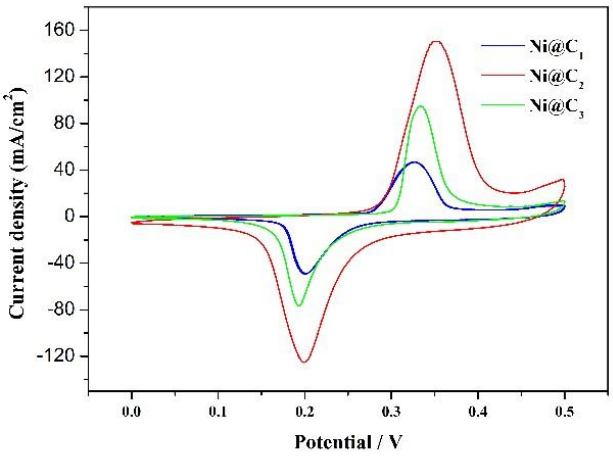

Figure 5. CV curves of Ni@C electrodes in 1M KOH after stable overlap, scanning rate 20 mV/s,

3.4. Detection of glucose

After Ni@C_2 electrode was completely transformed into NiOOH/$Ni(OH)_2$@C, it can be used to detect glucose in electrolyte. Using the three-electrode-system with the prepared NiOOH/$Ni(OH)_2$@C electrode as the working electrode, the current-time (I-t) curves were recorded at potential of 0.33V when certain amount of glucose (0.05mM 0.01mM or 1mM) was added into the electrolyte. As shown in Fig6, the current increased as the concentration of glucose in the electrolyte increased, and the relationship between the current (I) and the glucose concentration (C) is fairly linear with R^2=0.99995 in range of of 5×10^{-3} -10 mM (that is almost 4 orders of magnitude). The detection sensitivity is calculated as 164.46mA/cm^2 for 1mg glucose in concentration range of 0.05mM to 10.0mM. However, the linearity goes worse when the concentration larger than 10mM, which might be the critical value of glucose to be oxidized by NiOOH on the electrode under the described condition.

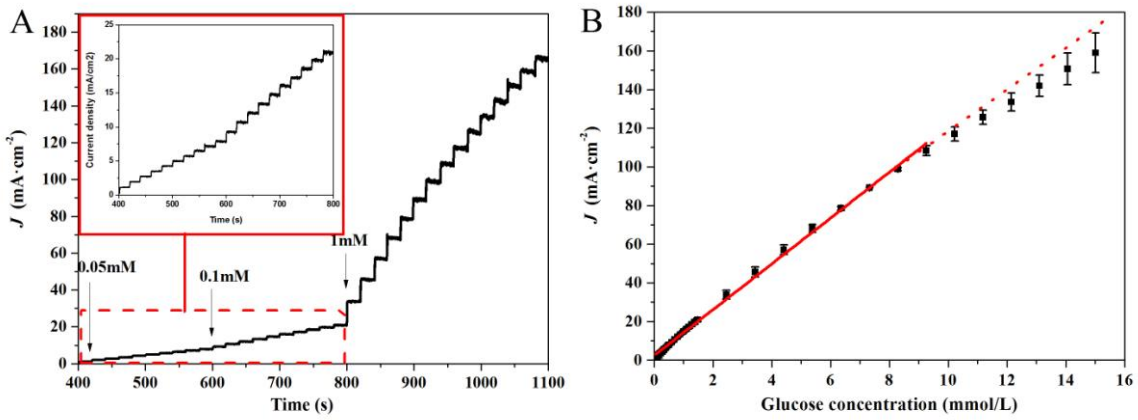

Figure 6. The typical current-time dynamic response of glucose in concentration range of 0.05mM to 1mM on NiOOH/$Ni(OH)_2$@C electrode at potential of 0.33V(A); and the linear regession of current density with the concentration of glucose(B).

On the contrast, the sensitivity for detecting glucose using other precursor Ni@C electrodes are 2.71 $mAcm^{-2}mM^{-1}$ and 6.54 $mAcm^{-2}mM^{-1}$, respectively. Thus, we can see that high sensitivity bears a relation to high specific surface area under the same test environment[22].

3.5. Influence of the co-existed substance in serum

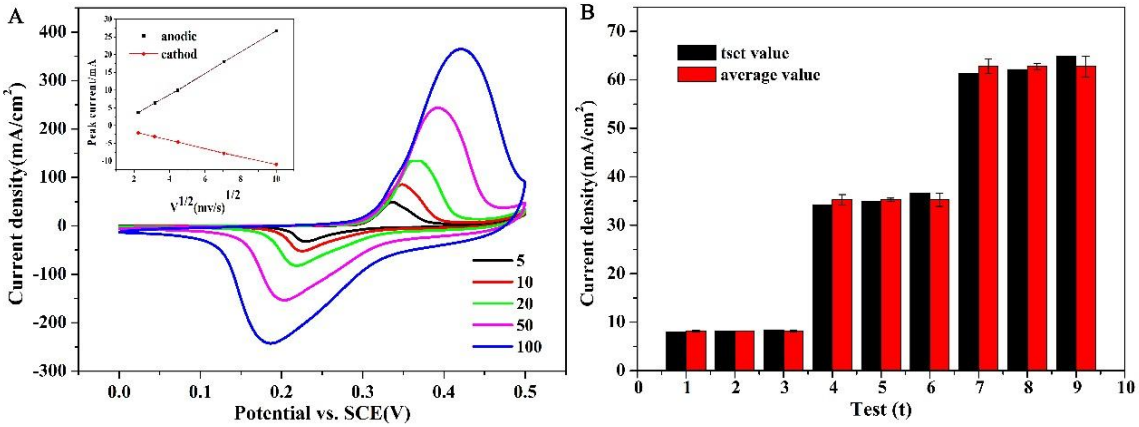

Figure 7.CV curves of NiOOH/$Ni(OH)_2$@C in 1MKOH solution with various scan rates from 5 to 100mV/s (5,10,20,50,100) (A); Parallel test at different glucose concentration (1mM, 5mM, 10mM) in the same batch (B).

Fig.7(A) gives the CV curves of NiOOH/$Ni(OH)_2$@C electrode in 1MKOH with different scan rates (v). We can see that the i-$v^{1/2}$ curves both kept an excellent linearity indicating that the electrochemical reaction on the surface of the electrode was a diffusion-controlled process [23]. The parallel test results shown in Fig.7(B) demonstrated the value of RSD ranges from 2.02% to 7.70%, and implying good parallelism.

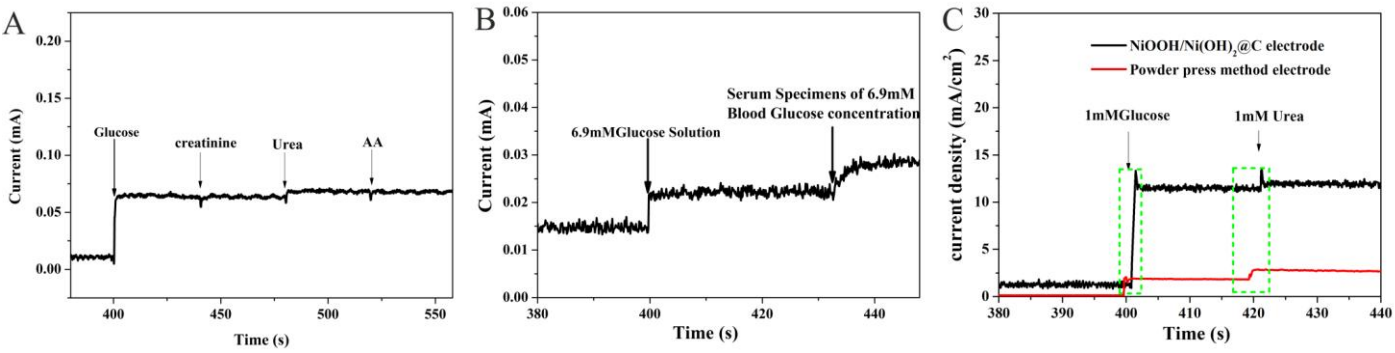

Figure 8. The current response on NiOOH/$Ni(OH)_2$@C in 0.5MKOH at 0.33V to 5mM glucose interfered by addition of 0.1mM creatinine, urea and uric acid (A); The comparison of current response of 6.9mM glucose in solution (without interferences) and in the serum solution (with interferens) (B); Effect of urea with the same additive as glucose on the response of NiOOH/$Ni(OH)_2$@C and electrode made by powder press method respectively in 0.5MKOH at 0.33V (C).

The interference of current response due to glucose by creatinine, urea, uric acid and ascorbic acid (AA) was studied by the addition of these interferences in same concentration into the electrolyte. As shown in Fig. 8A, urea gives more obvious change in the current response than other substance because urea could also be oxidized like glucose by NiOOH on the electrode. Fig.8B shows the comparison of the current response of glucose in the same concentration in solution or in the serum sample, the different in current response was within 5% although the respond of the serum sample was delayed by about 400s. As shown in Fig.8C, the anti-urea performance was also tested on the as-prepared NiOOH/$Ni(OH)_2$@C electrode and an electrode prepared by powder press method (PPM). It is obvious that the NiOOH/$Ni(OH)_2$@C electrode has better selectivity than the PPM electrode due to its larger specific surface area.

Table 1. The anti-interference performance testing results of glucose on NiOOH/$Ni(OH)_2$@C

The concertation (mM)	Glucose	Creatinine	Urea	uric acid	ascorbic acid
the standard serum	4.22	0.0788	4.45	0.3357	/
the interfering concentration	/	3.80	1.65	1.91	1.14

The anti-interference performance of glucose on NiOOH/$Ni(OH)_2$@C was tested by addition of the interferring substance untill the current response due to glucose changed more than 5%. As shown in Tab.1, the concentration might cause interference for creatinine, urea, uric acid and ascorbic acid is 3.80mM, 1.65mM, 1.91mM and 1.14mM, respectively. Comparing to the common cencetration in normal serum sample, the interference of urea is the most notable substand. So urea should be avoided by adjusting the working potential during the blood glucose concentration determination.

4. CONCLUSION

This research prepared Ni@C composite coating by cathode electro-codeposition, and the result shows that wonderful core-shell structure can be obtained and behaved good electrochemical properties (with sensitivity of 10.81$mAcm^{-2}mM^{-1}$, a linear concentration range of 5μM~30mM and the limit of 10^{-6}M (S/N=3) when CTMAB was added as well as the nickel carbon quality ratio reached 12:3. We can conclude that the obtained electrode could be effectively resisted to interference under the condition of 0.5MKOH according to the comparison of real serum sample and glucose solution.

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Reference

1. H. C. Wang, A. R. Lee, *Journal of Food and Drug Analysis*, 23 (2015) 191-200.
2. H. J. Jang, D. H. Min, *RSC Advances*, 5 (2015) 14330-14332.
3. C. Chen, Q. J. Xie, D. W. Yang, H. L. Huang, Y. C. Fu, Y. M. Tan and S. Z. Yao, *RSC Advances*, 3 (2013) 4473–4491.
4. M. H. Yang, B. G. Choi, H. S. Park, W. H. Hong, S. Y. Lee and T. J. Park, *Electroanalysis*, 22 (2010) 1223-1228.
5. J. K. Leypoldt, C. M. Hoff, A. Akonur and C. J. Holmes, *Journal of the International Society for Peritoneal Dialysis*, 35 (2015) 428-435.
6. L. M. Lu, L. Zhang, F. L. Qu, H. X. Lu, X. B. Zhang, Z. S. Wu, S. Y. Huan, Q. A. Wang. G. L. Shen and R. Q. Yu, *Biosensors and Bioelectronics*, 25 (2009) 218–223.
7. T. G. Satheesh Babu, T. Ramachandran, *Electrochimica Acta*, 55 (2010) 1612-1618.
8. Z.B. Chen, J. W. Nai, M. He and Z. Q. Li, *Electrochimica Acta*, 116 (2014) 258-262.
9. P. J. H. J. van Os, W. P. van Bennekom and A. Bult, *Analytica Chimica Acta*, 305 (1995) 18-25.
10. A. L. Rinaldi and R. Carballo, *Sensors and Actuators B: Chemical*, 228 (2016) 43-52.
11. Z. Tang, X. Du, R. F. Louie and G. J. Kost, *American Journal Of Clinical Pathology*, 113 (2000) 75-86.
12. B. N. Chandrashekara, B. E. Kumara Swamya, M. Pandurangacharb, T. V. Sathishaa and B. S. Sherigaraa, *Colloids and Surfaces B:Biointerfaces*, 88 (2011) 413-418.
13. L. N. Wang, Y. Tang, L. Wang, H. B. Zhu, X. D. Meng, Y. M. Chen, Y. Z. Sun, X. J. Yang and P. Y. Wan, *Journal of Solid State Electrochemistry*, 19 (2015) 851-860.
14. N. N. Phong, N. T. A. Tuyet, D. C. Linh, N. V. Hue, S. C. Kwon, M. Kim and J. Y. Lee, *Metals And Materials International*, 12 (2006) 493-496.
15. N. Nwosu, A. Davidson, C. Hindle, and M. Barker, *Industrial & Engineering Chemistry Rrsearch*, 51 (2012) 5635-5644.
16. N. K. Shrestha, M. Masuko, and T. Saji, *Wear*, 254 (2003) 555-564.
17. W. Liu, H. X. Zhang, B. Yang, Z. J. Li, L. C. Lei, and X. W. Zhang, *Journal of Electroanalytical Chemistry*, 749 (2015) 62–67.
18. Y. F. Yuan, X. H. Xia, J. B. Wu, J. L. Yang, Y. B. Chen, and S. Y. Guo, *Electrochimica Acta*, 56 (2011) 2627-2632.
19. P. Lu, J. Yu, Y. T. Lei, S. J. Lu, C. H. Wang, D. X. Liu and Q. C. Guo, *Sensors and Actuators B:Chemical*, 208 (2015) 90–98.
20. Y. S. Jeon, J. Y. Byun and T. S. Oh, *Journal of Physics and Chemistry of Solids*, 69 (2008) 1391-1394.
21. Z. Z. Cui, H. Y. Yin, and Q. L. Nie, *Journal of Alloys and Compounds*, 632 (2015) 402–407.
22. H. L. Mo, Y. Tang, X. Z. Wang, J. Liu, D. D. Kong, Y. M. Chen, P. Y. Wan, H. N. Cheng, T. Q. Sun, L. Y. Zhang, M. Zhang, S. Y. Liu, Y. Z. Sun, N. Wang, L. X. Xing, L. Wang, Y. Jiang, X. Xu, Y. Y. Zhang, X. D. Meng, *Electrochimica Acta*, 176 (2015) 1100–1107.
23. E. S. Bucher, R. M. Wightman, *Annual Review of Analytical Chemistry*, 8 (2015) 239-261.