Construction of high sensitivity non-enzymatic glucose sensor based on three-dimensional nickel foam supported Ni$_2$P/NiO/CeO$_2$ nanoflake arrays

Yongqiang Qin’, Yan Wang, Cuiping Yu, Jiewu Cui, Dongbo Yu and Yucheng Wu
School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China
E-mail: albon@hfut.edu.cn

Abstract. Three-dimensional (3D) nickel foam supported Ni$_2$P/NiO/CeO$_2$ nanoflake arrays (NFAs) were synthesized by hydrothermal, anneal and low-temperature phosphatizing processes. As-prepared samples were systematically researched by SEM, XRD, XPS, TEM, EDS and HRTEM technology. Cyclic Voltammograms and Chronoamperometry technology were used to measure the sensors performance of Ni$_2$P/NiO/CeO$_2$ NFAs. The results indicated that non-enzymatic glucose sensors based on Ni$_2$P/NiO/CeO$_2$ NFAs exhibited a high sensitivity of 28.23 mA cm$^{-2}$ mM$^{-1}$ and good anti-interference ability, suggesting that the 3D nickel foam supported Ni$_2$P/NiO/CeO$_2$ NFAs as a non-enzymatic glucose sensor is promising for practical applications.

1. Introduction
Glucose, as the most direct source of energy existed in blood for normal activities, is important for human$^{[1]}$. However, too high or too low blood sugar will cause direct or indirect harm to the health of the human body. Especially high blood sugar might cause obesity, diabetes and so on. Hence, fast and accurate detection of glucose are of great importance for human health$^{[2]}$. Electrochemical glucose sensors have received much intensive attention with advantages simplicity, fast response, high sensitivity and suitability for real-time detection$^{[3]}$. Conventional electrochemical glucose sensors can be divided into two types: enzyme glucose sensors and non-enzymatic glucose sensors$^{[4]}$. Electrochemical enzyme glucose sensors use various bio-enzyme, such as glucose oxidase and glucose dehydrogenase, with advantages of high selectivity and a lower detection limit$^{[5]}$. However, instability under extreme condition (higher temperature and very acidic/basic pH) and difficulty in preparation, purification in large quantities, complex enzyme immobilization procedures and high cost have limited their wide range application$^{[6]}$. To overcome existed disadvantages, direct oxidation of glucose using non-enzymatic sensors has been explored in recent decades. Nickel based compounds, such as oxides, hydroxides and phosphides, have received intensive research attention in the past decades based on their good electrochemical properties$^{[7]}$. Especially for phosphides, with their good electrical conductivity and high activity, have widely been researched in recent years$^{[8]}$. At the same time, CeO$_2$ is one of the promising candidates to build the glucose electrochemical sensors because of its environment friendly, biocompatibility and oxygen defect.

In this work, we have designed Ni$_2$P/NiO/CeO$_2$ NFAs grown on nickel foam by hydrothermal, anneal and phosphorization processes for nonenzymatic glucose detection. 3D nickel foam was chose as the substrate with their large surface area for growth of Ni$_2$P/NiO/CeO$_2$ NFAs. The results indicated
that the Ni$_2$P/NiO/CeO$_2$ NFAs presented a high sensitivity to glucose detection, suggesting the Ni$_2$P/NiO/CeO$_2$ NFAs were excellent substrate for nonenzymatic glucose detection.

2. Experiment

2.1 Materials

Synthesis of NiO/CeO$_2$ NFAs was carried out by the hydrothermal method\[^9\]. 173 mg Ce(NO$_3$)$_3$·6H$_2$O, 30 mg NH$_4$F and 121 mg CO(NH)$_2$ were dissolved in 40 ml Milli-Q water (18.25 M$\Omega$·cm$^{-1}$) and transferred to 50 mL Teflon stainless steel autoclave. Nickel foam (about 2 cm$\times$3 cm) was etched with 3 M HCl with ultra-sonication for 20 minutes to remove the oxide layer on the surface of nickel foam, and then rinsed with ethanol and Milli-Q water alternatively. The pre-treated nickel foam was immersed into the aforementioned mixture solution. Subsequently, the autoclave was transferred to a conventional oven at 100 °C for 12 h and the autoclave was cooled down to room temperature naturally. The samples were washed by Milli-Q water and ethanol alternatively and dried under 70 °C for 24 h. Finally, the precursors were heated in a tube furnace with a heating rate of 2 °C min$^{-1}$, maintained at 500 °C for 2 h and then cooled down naturally. Then the as-prepared NiO/CeO$_2$ NFAs in the combustion boat was placed at the downstream and 400 mg NaH$_2$PO$_2$ in the combustion boat was placed at the upstream of the tube furnace. The samples were heated at 300 °C for 2 h with a heating rate of 5 °C min$^{-1}$ in Ar atmosphere, and then cooled down to ambient temperature naturally.

2.2 Characterization

The as-obtained samples were characterized by X-ray diffraction (XRD, D/MAX2500V, Rigaku, Japan), field emission scanning electron microscopy (FESEM, SU8020, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The electrochemical measurements of as-obtained materials were tested by CHI760E electrochemical workstation (Chenhua, China) in a conventional three-electrode system in 0.1 M NaOH aqueous solution. A Ni foam supported active material (around 0.2 cm$^2$ in geometry area) was used as working electrode. Ag/AgCl (3 M KCl) and Pt/Ti electrode were employed as reference electrode and counter electrode, respectively. Cyclic Voltammetry (CV) was carried out in the quiescent solution and Chronoamperometry measurement was performed under continuous stirring.

3. Results and discussion

![Figure 1. XRD patterns of the as-prepared samples on Ni foam.](image)
The phase structure of as-prepared sample is characterized by XRD technique, as displayed in Figure 1. The black, red and blue curves correspond to as-prepared precursors, NiO/CeO₂ NFAs and Ni₃P/NiO/CeO₂ NFAs, respectively. The XRD pattern of precursors exhibit the diffraction peaks of Ni(OH)₂ (JCPDS 14-0117)² and Ce(OH)₃ (JCPDS 19-0284)², and the diffraction peaks of NiO/CeO₂ NFAs can be assigned to NiO (JCPDS 47-1049)¹¹ and CeO₂ (JCPDS 34-0394), which are corresponding to our previous study⁹. After phosphorization, the peaks of NiO weaken obviously compared to that of NiO in NiO/CeO₂ NFAs, at the same time, a new diffraction peak is presented around 40.8°, which is assigned to the (111) plane of Ni₃P (JCPDS 65-3544)¹², indicating the coexistence of NiP, NiO and CeO₂ in the sample.

The FESEM technology is used to observe the surface morphology of the samples. Figure 2 (a) and (b) display the FESEM images of as-obtained samples after phosphorization process with different magnifications. Apparently, the Ni foam is covered by Ni₃P/NiO/CeO₂ NFAs uniformly. It is found that the amount of pores are formed by an anneal process in air. To obtain more detailed information, the TEM and high resolution transmission electron microscopy (HRTEM) technology are adopt to measure the as-obtained samples, and the results are presented in Figure 2 (c) and (d). It can be observed that the diameter of individual nanoflake is around 300 nm. Figure 2. (d) presents the HRTEM image of nanoflake selected from the marked area in Figure 2(c), the calculated lattice spacing about 0.19 nm, 0.24 nm and 0.31 nm can be attributed the (210) plane of Ni₃P, (111) plane of NiO and (111) plane of CeO₂, respectively. The results of HRTEM is consistent with XRD pattern showed in Figure 1. And the composition distribution of the hybrid nanoflake is analyzed by energy dispersive spectroscopy (EDS), as depicted in Figure 3. It is obvious that Ni, Ce, O and P elements are distributed in individual nanoflake uniformly.

To further investigate the sensor performance of as-obtained NFAs, the nickel foam supported Ni₃P/NiO/CeO₂ NFAs are utilized as working electrode directly. Figure 4 (a) depicts the CV curves of non-enzymatic glucose sensors based on Ni₃P/NiO/CeO₂ NFAs in 0.1 M NaOH with different glucose concentrations at the scan rate of 10 mV s⁻¹ within the potential range of 0 to 0.8 V. As showed in Figure 4 (a), Ni₃P/NiO/CeO₂ NFAs shows a pair of redox peaks at about 0.55 and 0.30 V, which could be assigned to the interconversion of Ni²⁺ and Ni³⁺ [1]. The results of CV curves suggest that the current increases with the increasing of glucose concentrations. The working potential is further investigated.
by chronoamperometry technology, and the response of as-prepared sample at different working potentials are depicted in Figure 4 (b). Eventually, 0.5 V is chose as working potential and utilized in the following experiments. Furthermore, the catalytic performance of NiO NFAs, Ni$_2$P NFAs, NiO/CeO$_2$ NFAs and Ni$_2$P/NiO/CeO$_2$ NFAs are measured under the same conditions for comparison. 

Figure 3. EDX mapping of Ni$_2$P/NiO/CeO$_2$ NFAs depicted in Fig. 2(c).

Figure 4. (a) Cyclic voltammograms of Ni$_2$P/NiO/CeO$_2$ NFA-based glucose sensors in 0.1 M NaOH with different glucose concentrations. (b) Working potential optimization. (c) Comparison of different materials. (d) I-t curve of Ni$_2$P/NiO/CeO$_2$ NFA-based glucose sensor with successive injection of different concentrations of glucose. (e) Calibration curve of the as-prepared glucose sensor. (f) I-t curve of as-prepared glucose sensor with successive injection of 50 μM glucose, 5 μM UA, 5 μM AA, 5 μM L-cyst, and 50μM glucose.
as shown in Figure 4 (c). The results indicate that Ni$_2$P/NiO/CeO$_2$ NFAs is the optimum material for detect of glucose. Figure 4 (d) presents the typical amperometric response of the glucose sensor based on Ni$_2$P/NiO/CeO$_2$ NFAs with successive injection of glucose with various concentrations. The calibration curve for our glucose sensor is presented in Fig. 4 (e), which gives a linear range from 1 to 250 μM ($R^2=0.996$). The detection limit and sensitivity are calculated to be 0.5 μM and 28.23 mA cm$^{-2}$ mM$^{-1}$, respectively.

Selectivity is one of the major factors to evaluated the nonenzymatic glucose detection performance. Uric acid (UA), ascorbic acid (AA) and L-cysteine (L-cyst) are usually co-existence with glucose in human blood serum. Hence, UA, AA and L-cyst are used to check the anti-interference capability. However, the normal physiological level of glucose concentration (4.4-6.6 mM) is much higher than those of UA (~0.02 mM), AA (~0.1 mM) and L-cyst (~0.1 mM). Figure 4 (f) shows the amperometric responses of the as-prepared samples at 0.5 V in 0.1 M NaOH with successive inject of 50 μM glucose, 5 μM AA, 5 μM L-cyst and 50 μM glucose. Compared to the response of glucose, the response of UA, AA and L-cyst are negligible, suggesting good anti-interference capability of glucose sensors constructed by Ni$_2$P/NiO/CeO$_2$ NFAs.

**Conclusion**

In summary, 3D nickel foam supported Ni$_2$P/NiO/CeO$_2$ NFAs are successfully synthesized and used to fabricate the non-enzymatic electrochemical sensor for glucose detection. The results indicate that as-obtained electrodes exhibit high selectivity of 28.23 mA cm$^{-2}$ mM$^{-1}$ and good anti-interference ability. The Ni$_2$P/NiO/CeO$_2$ NFAs also shows excellent selectivity, reproducibility and long-term stability. Hence, 3D nickel foam supported Ni$_2$P/NiO/CeO$_2$ NFAs as a non-enzymatic glucose sensor is promising for practical applications.

**References**

[1] Chen T, Liu D, Lu W, Wang K, Du G, Asiri A M and Sun X 2016 Analytical chemistry, 88 7885.
[2] Fang B, Gu A, Wang G, Wang W, Feng Y, Zhang C and Zhang X 2009 ACS applied materials & interfaces, 1 2829.
[3] Xie L, Asiri A M and Sun X 2017 Sensors and Actuators B: Chemical, 244 11.
[4] Wang G, Lu X, Zhai T, Ling Y, Wang H, Tong Y and Li Y 2012 Nanoscale, 4 3123.
[5] Kang X, Mai Z, Zou X, Cai P and Mo J 2007 Analytical biochemistry, 369 71.
[6] Wei H and Wang E 2013 Chemical Society reviews, 42 6060.
[7] Yang J, Cho M and Lee Y 2016 Sensors and Actuators B: Chemical, 222 674.
[8] Bai Y, Zhang H, Fang L, Liu L, Qiu H and Wang Y 2015 Journal of Materials Chemistry A, 3 5434.
[9] Cui J, Luo J, Peng B, Zhang X, Zhang Y, Wang Y, Qin Y, Zheng H, Shu X and Wu Y 2016 Nanoscale, 8 770.
[10] Hu X, Liu S, Li C, Huang J, Luv J, Xu P, Liu J and You X 2016, Nanoscale, 8 11797.
[11] Bao M, Chen Y, Li F, Ma J, Lv T, Tang Y, Chen L, Xu Z and Wang T 2014 Nanoscale, 6 4063.
[12] Wang A, Lin J, Xu H, Tong Y and Li G 2016 Journal of Materials Chemistry A, 4 16992.

**Acknowledgments**

This work is financially supported by National Natural Science Foundation of China (Nos. 51402081, 51502071 and 51372063).