Rectangular flake-like mesoporous NiCo_2O_4 as enzyme mimic for glucose biosensing and biofuel cell

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ABSTRACT The rectangular flake-like mesoporous NiCo_2O_4 (meso- NiCo_2O_4) catalysts were first used in glucose bio-sensing and glucose biofuel cell (GBFC) as an enzyme mimic simultaneously. The meso- NiCo_2O_4 displayed excellent catalytic capability to glucose including a super-fast response time (within 1 s), a super-high sensitivity ($662.31 \mu\text{A} (\text{mmol L}^{-1})^{-1} \text{cm}^{-2}$), and a super-low detection limit (0.3 nmol L^{-1} at $\text{S/N} = 3$) on the sensor. On the other hand, meso- NiCo_2O_4 provided great values in GBFC as anode material with an open circuit voltage of 0.63 V, a maximum power density of 0.092 mW cm^{-2} , and a limiting current density of 1.3 mA cm^{-2} , respectively. The preeminent catalytic abilities may be attributed to the large specific surface area resulting from the mesoporous structure and the surpassing intrinsic catalytic activity of NiCo_2O_4 itself. These significant findings may promote the development of the supersensitive detection of glucose and will undoubtedly widen the catalytic materials for biofuel cell electrodes.

Keywords: flake-like, mesoporous NiCo_2O_4 , glucose, electrochemical sensor, fuel cells

INTRODUCTION

Nowadays, rapid catalytic oxidation of glucose is of great significance in the fields of clinical medicine and energy conversion. It is crucial to fabricate glucose biosensor for monitoring the blood glucose level accurately for diabetics. On the other hand, fuel cells, especially glucose biofuel cells (GBFCs), with the help of catalyst, can produce electric energy in an efficient and steady way and are considered as the promising next-generation energy devices due to their available and easy capability to harvest electrical energy from glucose fuel [1]. Generally, glucose

biosensors and GBFCs can be classified into two categories according to the types of catalysts, namely enzyme-based and nonenzyme-based ones [2–4]. Research findings demonstrate that enzymatic catalysts exhibit high activity and excellent selectivity, but the unstable operating environment and fragile stability greatly hinder their practical applications [5,6]. To overcome these drawbacks, non-enzymatic catalysts (such as precious metal nanoparticles or alloys [7–10], composite materials [11,12], polymers [13,14] and transition metal oxides [15–18]) as enzyme mimics show higher performance than enzymatic ones. Among these non-enzymatic catalysts, transition metal oxides play important roles due to their high intrinsic catalytic performances, low cost, and environmental friendliness.

In the family of transition metal oxides and mixed transition metal oxides, notably cobalt-based metal oxides (MCo_2O_4 , $\text{M} = \text{Ni, Mn, Cu, Fe, etc.}$) with spinel structure are considered as promising candidates for the catalytic oxidation of glucose. They exhibit more excellent electrochemical activities due to the synergetic effect of the complex chemical compositions than that of the mono-metallic counterparts [19–22]. Among these cobalt-based metal oxides, NiCo_2O_4 possesses more advantages than other Co-based metal oxides owing to the existence of Ni and Co ions. Up to now, NiCo_2O_4 has been fabricated with many different morphologies including hollow nanorods [23], nanoneedles [22,24] as well as nanosheet arrays [25]. However, it is still necessary and meaningful to synthesize new structures with different morphologies for enhancing the catalytic activities of NiCo_2O_4 in glucose oxidation.

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The catalytic capability of the catalyst is not only associated with the intrinsic catalytic activity but also is related to the morphology and structure. Recent theoretical and experimental results showed that two-dimensional (2D) flake-like mesoporous structures exhibited much surpassing properties than that of other structures [25,26]. Unlike zero- or one-dimensional structures, the 2D flake-like structures can effectively inhibit the self-agglomeration of nano- or micro-materials on the electrode surface [27,28]. Moreover, the catalytic reactions are generally performed on the catalysts surface, and the reaction rates depend on the molecule quantities that reached the surface of catalyst and the intrinsic catalytic properties of the catalyst itself [29]. Interestingly, the mesoporous structure with higher porosity and more available electroactive sites will provide much more guest molecules (i.e., glucose) than other structures, enhancing the catalytic performances subsequently [30].

Herein, rectangular flake-like meso-NiCo₂O₄ catalysts are successfully synthesized by a simple hydrothermal method with following calcination process. Afterward, the as-prepared meso-NiCo₂O₄ catalysts are applied in glucose sensor and GBFC simultaneously. The sensor exhibits super-fast response time (within 1 s), ultra-high sensitivity (662.31 $\mu\text{A} (\text{mmol L}^{-1})^{-1} \text{cm}^{-2}$) and an extremely low detection limit (0.3 nmol L^{-1}) toward glucose compared to the previous reports. Besides, similar results showing high performance of glucose oxidation are also obtained on the GBFC.

EXPERIMENTAL SECTION

Reagents and apparatus

Ascorbic acid (AA), glucose, uric acid (UA), tryptophane (Trp), glycocholic acid (Gly), dopamine (DA), carbon paper, Pt/C, nafion, *N*-methylpyrrolidinone (NMP), polyvinylidene fluoride (PVDF), Ni(NO₃)₂·6H₂O, KOH and Co(NO₃)₂·6H₂O were purchased from Sigma Chemical Co., Ltd. Galactose, mannose, lactose, acetaminophen, epinephrine, H₃BO₃, acetic acid and H₃PO₄ were supplied by Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). All of these reagents were analytical grade and used directly. Double distilled water (18.2 M Ω cm) was used for all experiments.

Electrochemical measurements of the as-obtained samples were measured by the electrochemical workstation (CHI 842B) with a traditional three-electrode mode including a Pt foil counter electrode, a saturated calomel reference electrode and a conventional or meso-NiCo₂O₄ modified carbon paste electrode as a working

electrode in 0.2 mol L⁻¹ KOH electrolyte. The output currents and voltages of the GBFC were monitored by a digital multimeter.

The composition of the product was investigated by X-ray diffractions (XRD, Bruker, D8 Advance diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$)). The morphology of the products was examined by field emission scanning electron microscopy (FESEM; JSM-6700F, 15.0 kV), transmission electron microscopy (TEM; JEM-200CX at 160 kV and JEM-2010F at 200 kV). Nitrogen adsorption-desorption isotherms were tested at liquid nitrogen temperature (77 K) with micrometric ASAP 2020 sorptometer.

Fabrication of meso-NiCo₂O₄ and conventional NiCo₂O₄

Rectangular flake-like meso-NiCo₂O₄ was synthesized by a simple hydrothermal method according to the previous literature [31]. In brief, Co(NO₃)₂·6H₂O (2.34 g), Ni(NO₃)₂·6H₂O (1.16 g) and urea (4.8 g) were dissolved in 60 mL double distilled water with ultrasonic agitation for 30 min. Afterward, the mixture solution was transferred into a 100-mL Teflon-lined stainless steel autoclave and heated to 160°C for 12 h in the oven. After finishing the hydrothermal treating, the autoclave was cooled to room temperature, and the following processes including vacuum filtration and washing with double distilled water were employed to remove the impurities. Finally, the sample was calcined at 400°C for 4 h at the heating rate of 1°C min⁻¹ in a muffle furnace.

For comparison, the conventional NiCo₂O₄ was synthesized by a simple sol-gel method. Briefly, Co(NO₃)₂·6H₂O (2.34 g) and Ni(NO₃)₂·6H₂O (1.16 g) were dissolved in 60 mL double distilled water. The solution was heated at 60°C until total evaporation under a continuous stirring environment. The as-prepared sample precursor was calcined at 400°C for 4 h to obtain the final products.

Preparation of meso-NiCo₂O₄/carbon paste electrode

Beforehand, a carbon paste electrode (CPE) was fabricated following the previous literature [32]. Then appropriate conventional NiCo₂O₄ or meso-NiCo₂O₄ powders were dispersed in 1 mL double distilled water, ultrasonically treated for 1 h for obtaining a well-distributed suspension. Finally, the CPE surface was covered by 10 μL of the suspension.

Fabrication of glucose fuel cell

Initially, a fuel cell reactor was fabricated with acrylic glass, and the reactor was divided into the anodic and cathodic compartments by an exchange membrane. The

current and voltage were measured by the digital multimeter. The meso- NiCo_2O_4 modified carbon paper as an anode was designed with the following process: 20 mg meso- NiCo_2O_4 was uniformly distributed in 100 mg NMP solution containing 1 mg PVDF to form a suspension solution; proper amounts of the precursor solution and nafion were uniformly cast on the carbon paper, which was dried in the air for the next experiment. Similarly, the Pt/C modified carbon paper as a cathode was also fabricated by the same method mentioned above. In the anodic compartment, 50 mL mixed solution containing 0.1 mol L^{-1} glucose and 0.1 mol L^{-1} KOH was injected into the anodic chamber as the anodic electrolyte. On the other hand, 50 mL of acid solution was regarded as the cathodic electrolyte, in this work, 0.04 mol L^{-1} Britton-Robinson buffer (B-R, pH 5) was adopted. The active area of carbon paper was about $1 \times 1 \text{ cm}^2$. During the process of reaction, the anodic and cathodic compartments were respectively stirred with oxygen gas and nitrogen gas, and the reactor was linked with an external resistance.

RESULTS AND DISCUSSION

Morphology and structure analysis

The characteristic patterns of both the meso- NiCo_2O_4 and conventional NiCo_2O_4 catalysts were evaluated by XRD. As shown in Fig. 1, all diffraction peaks were matched with NiCo_2O_4 phase completely, compared with JCPDF card: 20-0781, indicating that NiCo_2O_4 products were successfully synthesized. The crystal structure of NiCo_2O_4 compound was displayed in the inset of Fig. 1 [33].

The purities and valence state compositions of the meso- NiCo_2O_4 catalysts were measured by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 2a, a wide-scan spectrum of the as-prepared samples was obtained, and four predominant elements (Ni, Co, O, and C) were found, indicating the chemical composition of the as-obtained samples. The binding energies of the NiCo_2O_4 were corrected by referencing the C 1s peak to 284.5 eV. Fig. 2b shows a high distinct Co 2p spectrum with two strongest peaks at around 780 and 794.7 eV, which were assigned to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively. As shown in Fig. 2c, two strongest peaks of the Ni 2p core spectrum at 873.5 and 856 eV corresponding to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ respectively were observed. The peak values of the binding energies resulting from Co and Ni are consistent with the previous literature [34]. The O 1s region exhibits the fitting doublet at 529.9 and 531.8 eV (Fig. 2d), which are ascribed to the oxygen species from the NiCo_2O_4 phase and the -OH species from the surface absorption, re-

Figure 1 XRD patterns and crystal structure of NiCo_2O_4 .

spectively. In a word, both the XPS spectrum and the XRD pattern results confirm the formation of NiCo_2O_4 .

The morphological characteristics of the as-prepared meso- NiCo_2O_4 were investigated by SEM and TEM. As shown in Fig. 3a–c, most of the as-obtained samples not only present a rectangular flake-like structure with a micron size but also display a coarse surface with about 230 nm thick (Fig. 3c). However, Fig. S1 (See supplementary information) showed that the conventional NiCo_2O_4 revealed an irregular morphology. In order to further confirm the microstructure of the as-prepared NiCo_2O_4 , TEM images were displayed in Fig. 3d, e. It is clear that the meso- NiCo_2O_4 has a rectangular flake-like morphology and the flake is composed of porous structure inter-sectioned by NiCo_2O_4 nanocrystals. The porous nature of the NiCo_2O_4 can provide more binding sites to enhance the catalytic capabilities of NiCo_2O_4 . In Fig. 3f, the lattice space of 0.24 nm corresponds to the theoretical interplane spacings of spinel NiCo_2O_4 (311) planes.

The energy dispersive X-ray (EDX) measurement of the meso- NiCo_2O_4 was also carried out so as to reveal the chemical composition of the as-prepared products. As shown in Fig. 3g, the major elements including Co, O, and Ni were found in the microstructure constitution, and the atomic ratio of Ni and Co was approximately 1:2, which further demonstrated the formation of the NiCo_2O_4 materials. All above results indicate the as-prepared NiCo_2O_4 materials with the mesoporous structure.

The specific surface area and the porous nature of the samples were measured *via* Brunauer-Emmett-Teller (BET). From the nitrogen adsorption-desorption isotherm (Fig. 4), the NiCo_2O_4 manifests type-IV isotherm with an obvious hysteresis loop, which confirms the ex-

Figure 2 XPS spectra of meso- NiCo_2O_4 : full wide-scan (a), Co 2p (b), Ni 2p (c) and O 1s (d).

Figure 3 SEM (a–c), TEM (d), HRTEM (e), lattice-resolved HRTEM (f) images and EDX pattern (g) of meso- NiCo_2O_4 .

istence of mesoporous structure [31]. The specific surface area is as high as $\sim 89 \text{ m}^2 \text{ g}^{-1}$, which is larger than previous reported results [26,35]. As shown in the inset of Fig. 4, the average pore diameter of NiCo_2O_4 is centered at

$\sim 15.5 \text{ nm}$ along with a pore distribution at $\sim 2.24 \text{ nm}$, calculated by the Barrett-Joyner-Halenda (BJH) method from the adsorption branches of the isotherm, which further demonstrates that the mesoporous products are

Figure 4 Nitrogen adsorption-desorption isotherm of meso-NiCo₂O₄ catalysts; inset shows the pore size distributions of meso-NiCo₂O₄ catalysts.

successfully synthesized.

Electrochemical characterizations

Initially, the cyclic voltammetry (CV) was utilized in 0.2 mol L⁻¹ KOH electrolyte to investigate the electrochemical behaviors of the meso-NiCo₂O₄/CPE under the applied potential from 0 to 0.6 V. Meanwhile, the conventional NiCo₂O₄/CPE, and bare CPE were also performed by the same method for comparison. As shown in Fig. 5a, two pairs of apparent anodic peaks were observed at 0.31 (labeled I) and 0.47 V (labeled II), while the cathode peaks were at 0.28 (labeled III) and 0.42 V (labeled IV) for meso-NiCo₂O₄/CPE (curve 3) and conventional NiCo₂O₄/CPE (curve 2), respectively, which were ascribed to the reversible reactions of Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺ [36,37]. Whereas, no obvious redox peaks were found on the bare CPE (curve 1). In the basic electrolyte, the reaction processes of NiCo₂O₄ can be summarized as the following equations:

Moreover, both meso-NiCo₂O₄/CPE (curve 3) and conventional NiCo₂O₄/CPE (curve 2) had a larger enclosed area than the bare CPE (curve 1), which indicated that the NiCo₂O₄ had a higher chemical reactivity [38]. Additionally, the enclosed area of meso-NiCo₂O₄/CPE was larger than that of the conventional NiCo₂O₄/CPE, resulting from the large specific surface area of the mesoporous structure.

Fig. 5b and Fig. S2 show the electrochemical response of 100 μmol L⁻¹ glucose on meso-NiCo₂O₄/CPE and conventional NiCo₂O₄/CPE at a scan rate of 100 mV s⁻¹.

When the glucose was injected into the basic solution, the obvious electrochemical responses were detected (curve 2 and curve 2') compared to the blank solution (curve 1 and curve 1'). However, the current changes were larger on meso-NiCo₂O₄/CPE (labeled V and VI) than that of on conventional NiCo₂O₄/CPE (labeled V' and VI'). The phenomenon not only demonstrates that NiCo₂O₄ has the excellent catalytic capability to glucose, but also shows that mesoporous structure can efficiently enhance the catalytic capability of NiCo₂O₄. Notably, the anodic peak VI is much larger than the peak V, which can be attributed to the combined effect resulting from the oxidizing glucose by CoO₂ and NiOOH [23]. The possible reaction mechanisms of glucose oxidation are represented as followings [39,40]:

In order to further explore the electrochemical responses of glucose on different electrodes, the amperometry technology was carried out at an applied potential of +0.5 V by successive injection of glucose into 0.2 mol L⁻¹ KOH electrolyte under a stirring condition. As shown in the Fig. 5c, the response current on meso-NiCo₂O₄/CPE was larger than that on others. Meanwhile, when the current-time response was steady, the calibration curves were realized (as shown in Fig. 5d). The slope of calibration curve can reflect the sensitivity of the sensor. It was clear that a higher sensitivity to glucose was obtained on the meso-NiCo₂O₄/CPE than these on the other two samples. The chronoamperometry results are in good agreement with the CV observations. These findings reconfirm that a stronger electrochemical reaction takes place at the meso-NiCo₂O₄/CPE. The increased response current is considered to be caused by the large specific surface area of the mesoporous structure and excellent intrinsic catalytic abilities of NiCo₂O₄ [34,41]. All the above results indicate that the meso-NiCo₂O₄/CPE shows more excellent catalytic abilities to glucose than the conventional counterparts, which is promising for designing a novel sensor for the electrochemical detection of glucose.

The influence of scan rate on the electrochemical response of 400 μmol L⁻¹ glucose was well studied on the meso-NiCo₂O₄/CPE by CV in the applied potential ranging from 0 to 0.7 V. As shown in Fig. S3a, b, the oxidation peak currents (*I*_{pa}) of glucose increased linearly with the increasing of scan rate from 20 to 200 mV s⁻¹, and the oxidation and reduction peaks potential revealed a slight shift to the positive and negative directions, re-

Figure 5 (a) CVs of bare CPE (curve 1), conventional NiCo₂O₄/CPE (curve 2) and meso-NiCo₂O₄/CPE (curve 3) in 0.2 mol L⁻¹ KOH electrolyte at the scan rate of 100 mV s⁻¹. (b) CVs of meso-NiCo₂O₄/CPE in the absence of glucose (1) and with 0.1 mmol L⁻¹ glucose (2) at a scan rate of 100 mV. (c) Amperometric responses of glucose on bare CPE (curve 1), conventional NiCo₂O₄/CPE (curve 2) and meso-NiCo₂O₄/CPE (curve 3) under the successive injection of glucose from 40 to 240 μmol L⁻¹ at the applied potential of 0.5 V in 0.2 mol L⁻¹ KOH. (d) Plot of response current of glucose versus the corresponding glucose concentration (μmol L⁻¹).

spectively. The regression equation of the I_{pa} was calculated as $I_{pa} (\mu A) = 8.21 + 0.48v$ (mV s⁻¹) ($R^2 = 0.996$), indicating a surface-controlled electrochemical process.

Effect of operational parameters

To improve the electrochemical properties of the glucose sensor, three major operational parameters including the concentration of KOH electrolyte, the applied potential, and the concentration of the meso-NiCo₂O₄, were optimized by amperometry. As shown in Fig. S4a, the concentration of KOH was optimized from 0.01 to 0.3 mol L⁻¹. When the concentration value reached 0.2 mol L⁻¹, a relatively optimum current value was obtained. Similarly, the applied potential and meso-NiCo₂O₄ concentration were also optimized by the same method (Fig. S4b, c). These results show that the optimized operational parameters are 0.2 mol L⁻¹ KOH, +0.5 V applied potential, and 1.0 mg mL⁻¹ meso-NiCo₂O₄ suspensions,

which would be used in the following experiments.

Amperometric determination of glucose

Under optimized conditions, the electrochemical determination of glucose on the meso-NiCo₂O₄/CPE was carried out by amperometry. From the inset (1) of Fig. 6a, a steady-state current (99%) within 1 s was achieved after the injection of glucose, which indicated a quick recovery capability of meso-NiCo₂O₄. The phenomenon happened due to the excellent electron/mass transfer of the NiCo₂O₄ and the large specific surface area of the mesoporous structure. As shown in Fig. 6a, b, the I_{pa} of glucose increases linearly with the change of the glucose concentration from 1 nmol L⁻¹ to 1.9 mmol L⁻¹ and the linear regression equation is described as follows: $I_{pa} (\mu A) = 2.21 + 0.044c$ (μmol L⁻¹) ($R^2 = 0.996$). The detection limit of glucose was 0.3 nmol L⁻¹ (S/N = 3) and the sensitivity was 662.31 μA (mmol L⁻¹)⁻¹ cm⁻². Compared to previous

Figure 6 (a) Current-time curves of different concentrations of glucose in 0.2 mol L⁻¹ KOH electrolyte on meso-NiCo₂O₄/CPE at +0.5 V. (b) Calibration curve of glucose on meso-NiCo₂O₄/CPE.

Table 1 Comparison of this analytical characteristics with recent reports for determination of glucose

Electrode	Linear range (μmol L ⁻¹)	Detection limit (μmol L ⁻¹)	Ref.
Graphene-decorated MnCo ₂ O ₄	0.005–800	0.001	[42]
NiMoO ₄	10–8000	4.6	[43]
NiWO ₄	0.006–4100	0.18	[44]
Co ₃ O ₄	1–10,000	0.058	[45]
Nafion/Co ₃ O ₄ NF	3–2040	0.97	[46]
NiCo ₂ O ₄ decorated three-dimensional graphene	0.5–590	0.38	[22]
NiCo ₂ O ₄ @polyaniline	15–4735	0.3833	[41]
NiCo ₂ O ₄ nanoneedles	5–15,000	1.49	[24]
NiCo ₂ O ₄ nanosheet arrays	5–65	0.38	[25]
NiCo ₂ O ₄ hollow nanorods	0.3–1000	0.16	[23]
Meso-NiCo ₂ O ₄	0.001–1900	0.0003	This work

reports (as shown in Table 1), the proposed sensor showed excellent characteristics including a lower detection limit, higher sensitivity, and a wider linear range. The excellent intrinsic catalytic properties of NiCo₂O₄ and large specific surface area of the mesoporous structure may be the main factor for the enhanced catalytic effect of glucose.

Reproducibility, stability and anti-interference ability of the sensor

Under optimized conditions, the reproducibility of the sensor was investigated to compare the Faradic currents of five different electrodes by amperometry technology in 0.2 mol L⁻¹ KOH electrolyte including 50 μmol L⁻¹ of glucose (as shown in Fig. S5a). These electrodes were prepared in accordance with the experimental section. After five independent experiments, the relative standard deviation (% RSD) was calculated to be 4.06%, which

corresponded to the Faradic current change of glucose. The stability of the sensor was investigated through a common process, where the modified electrode was kept at 4°C for a week and then used to detect the glucose again. The result shows that the Faradic current of glucose remains similar to their initial value (as shown in Fig. S5b). In a word, the sensor has excellent reproducibility and stability.

Some possible influence factors were investigated to evaluate the anti-interference of the sensor. As shown in Fig. 7, the determination of glucose (60 μmol L⁻¹) was studied by adding 5 μmol L⁻¹ DA, UA, Trp, Gly, and AA, respectively. Moreover, another carbohydrate (galactose, mannose, and lactose) and some important electroactive species such as acetaminophen and epinephrine were also investigated (as shown in Fig. S6). The result shows that the signal change is not obvious, indicating that the NiCo₂O₄/CPE possesses a good anti-interference ability.

Figure 7 Current-time curves of $60 \mu\text{mol L}^{-1}$ glucose on meso- $\text{NiCo}_2\text{O}_4/\text{CPE}$ in the presence of $5 \mu\text{mol L}^{-1}$ different interfering species in $0.2 \mu\text{mol L}^{-1}$ KOH solution at an applied potential of 0.5 V.

Test of the non-enzymatic fuel cells

The meso- NiCo_2O_4 materials revealed excellent catalytic activity to glucose, which offered a scientific foundation for designing of GBFC. Fig. 8a shows the chronoamperometry plots for the bare, conventional, and meso- NiCo_2O_4 electrodes at an applied potential of 0.5 V in 0.1 mol L^{-1} KOH solution with 100 mmol L^{-1} glucose. It is clear that the meso- NiCo_2O_4 modified electrode exhibits much larger current density than the conventional NiCo_2O_4 modified electrode and the bare electrode, due to the superior catalytic capability of NiCo_2O_4 catalysts and

their large specific surface area resulting from the mesoporous structure. Moreover, the stable and parallel signal line of meso- NiCo_2O_4 within a certain time indicate the stability of this electrode in the basic electrolyte. Hence, an H-type GBFC (named GBFC I) was fabricated by modifying meso- NiCo_2O_4 materials with carbon paper as an anode and commercial Pt/C with carbon paper as a cathode, respectively. Meanwhile, for comparison, another GBFC (named GBFC II) was also designed with the same method in which the meso- NiCo_2O_4 was replaced by the conventional NiCo_2O_4 . As depicted in Fig. 8b, the polarization curves and power density curves were obtained from these two GBFCs, which were summarized in Table 2. It is clear that the slope of the linear region of the polarization curve derived from GBFC II (line 1) is larger than that of GBFC I (line 2), which indicates the internal resistance of GBFC I is much lower [47]. Moreover, as shown in Table 2, the cell properties of GBFC I are superior to those of GBFC II. These findings reveal that meso- NiCo_2O_4 displays better catalytic properties to glucose than previous reports including the non- and enzyme fuel cells [48,49]. In short, the meso- NiCo_2O_4 with large specific surface area is a promising anode material for the practical fabrication of GBFC.

CONCLUSIONS

In summary, the meso- NiCo_2O_4 catalysts were successfully synthesized by a simple hydrothermal method with

Figure 8 (a) Chronoamperometry curves of bare conventional NiCo_2O_4 and meso- NiCo_2O_4 in 0.1 mol L^{-1} KOH with 100 mmol L^{-1} glucose. (b) Power output and polarization curves of the GBFCs. Experiment conditions: mixture solution containing 100 mmol L^{-1} glucose and 0.1 mol L^{-1} KOH in the anode chamber and 0.04 mol L^{-1} B-R (pH 4) solution in the cathode chamber.

Table 2 Data of GBFC I and GBFC II

GBFC	Open circuit voltage (V)	Maximum power density (mW cm^{-2})	Limiting current density (mA cm^{-2})
GBFC I	0.64	0.08	1.32
GBFC II	0.43	0.04	0.41

following calcination process. The electrochemical sensor based on meso-NiCo₂O₄ catalysts exhibits super-fast response time (within 1 s), ultra-high sensitivity (662.31 $\mu\text{A (mmol L}^{-1})^{-1} \text{ cm}^{-2}$) and extremely low detection limit (0.3 nmol L⁻¹ at S/N = 3) to the glucose concentration, which favors the electrochemical detection of glucose. The excellent electrocatalytic performance of meso-NiCo₂O₄ for glucose detection inspires us to explore the new application in non-enzymatic glucose fuel cell. The meso-NiCo₂O₄ catalysts possess an open circuit voltage of 0.63 V, a maximum power density of 0.092 mW cm⁻², and a limiting current density of 1.3 mA cm⁻² when applied as anode materials. The present research not only provides a novel meaningful exploration for fabricating a super-sensitive and non-enzymatic glucose sensor but also promotes the development of anode materials of the glucose fuel cells. Meanwhile, the meso-NiCo₂O₄ catalysts are also expected to be applied in other fields in the future.

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Supplementary information Supporting data are available in the online version of the paper.

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基于矩形片状介孔 NiCo_2O_4 用于非酶葡萄糖生物传感器和葡萄糖生物燃料电池的研究

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摘要 矩形片状介孔 NiCo_2O_4 催化剂被首次同时用于非酶葡萄糖传感器和非酶葡萄糖燃料电池中. 结果表明: 在传感器上, 介孔 NiCo_2O_4 催化剂对葡萄糖具有优异的传感特性, 如超快的响应时间(小于1 s), 超高的灵敏度($662.31 \mu\text{A} (\text{mmol L}^{-1})^{-1} \text{cm}^{-2}$)以及超低的检测限(0.3 nmol L^{-1} at $\text{S/N} = 3$); 在燃料电池上, 介孔 NiCo_2O_4 催化剂作为负极材料展示出了良好的应用前景, 包括0.63 V的开路电压, 0.092 mW cm^{-2} 的最大输出功率和 1.3 mA cm^{-2} 的极限电流密度. 该材料对葡萄糖优异的催化能力归因于介孔结构引起的巨大比表面积能够提供更多的活性位点和 NiCo_2O_4 本身具有的良好催化能力. 本研究为促进非酶葡萄糖超敏感检测和丰富非酶葡萄糖燃料电池负极催化材料的发展提供了有利的依据.