“Dry” NiCo$_2$O$_4$ Nanorods for Electrochemical Non-enzymatic Glucose Sensing

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A rod-like NiCo$_2$O$_4$ modified glassy carbon electrode was fabricated and used for non-enzymatic glucose sensing. The NiCo$_2$O$_4$ was prepared by a facile hydrothermal reaction and subsequently treated in a commercial microwave oven to eliminate the residual water introduced during the hydrothermal procedure. Structural analysis showed that there was no significant structural alteration before and after microwave treatment. The elimination of water residuals was confirmed by the stoichiometric ratio change by using element analysis. The microwave treated NiCo$_2$O$_4$ (M-NiCo$_2$O$_4$) showed excellent performance as a glucose sensor (sensitivity 431.29 µA·mmol/L$^{-1}$·cm$^{-2}$). The sensing performance decreases dramatically by soaking the M-NiCo$_2$O$_4$ in water. This result indicates that the introduction of residual water during hydrothermal process strongly affects the electrochemical performance and microwave pre-treatment is crucial for better sensory performance.

Key words: Glucose sensor, Electrochemical, NiCo$_2$O$_4$, Hydrothermal

I. INTRODUCTION

Glucose sensing is a great demand for modern living due to the significant growing population of diabetics. In 2015, 1.6 million deaths were caused by diabetes according to World Health Organization (WHO) data [1]. Since the first generation of enzymatic glucose electrochemical biosensor was introduced by Clark et al. [2], there have been tremendous efforts on the development of efficient and accurate enzymatic glucose sensors [3]. The enzyme-based electrochemical sensor offers high sensitivity and selectivity, as well as low detection limit, they still have some serious drawbacks such as low thermal stability, low chemical stability, and limited working conditions (temperature, pH value, oxygen partial pressure, etc.) [4]. Therefore, the enzyme-free electrode is considered as an alternative solution to solve the drawbacks of enzymatic sensors.

Similar to the traditional enzymatic electrochemical sensor, enzyme-free sensors also rely on the glucose oxidation reaction promoted by electrocatalysis at the non-enzymatic electrode surface. The catalytic glucose oxidation on the electrode surface could cause increased Faradic current that should be detectable by the sensor. This working mechanism requires the electrode to be high conductive for efficient sensing. Transition metal oxide based non-enzymatic electrodes are the most intensively investigated electrocatalysts for electrochemical glucose sensing, as a consequence of the low costs, ease of fabrication, high abundance, and high electrochemical catalytic activities [5]. For instance, transition metal oxide based electrocatalysts, such as Co$_3$O$_4$ [6], CuO [7, 8], Cu$_2$O [9], NiO [10, 11], ZnO [12, 13], MnO$_2$ [14, 15], Fe$_2$O$_3$ [16] etc., have been intensively studied and demonstrated excellent catalytic activities for glucose oxidation. Recently, bimetallic oxides, such as spined NiCo$_2$O$_4$ [17–25], outperformed the NiO or Co$_3$O$_4$ based electrocatalysts due to their enhanced conductivity [26]. In addition, rational design of the material structure can also boost the catalytic performance of NiCo$_2$O$_4$, such as nanosheets [19, 5, 23], hollow spheres [25, 26], and nanocages [17]. The high surface atom ratios lead to larger active surface areas and stronger current signals. In this context, lower dimensional rod-like structures would deliver higher surface atom ratios, and might further enhance the electrochemical performance for glucose oxidation.

Hydrothermal synthesis is one of the most commonly used methods to fabricate metal oxides [27]. This synthetic protocol offers numerous advantages such as fast reaction, facile preparation, and high product yields [28]. In this work, we fabricated rod-like NiCo$_2$O$_4$ by using the hydrothermal method. However, the hydrothermal based synthesis usually results in crystallized water residuals even after the annealing process. In order to eliminate the residual water in the as-prepared NiCo$_2$O$_4$, microwave post-processing was per-
formed for the NiCo$_2$O$_4$ catalyst prior to glucose electrochemical sensing. We found that the residual water dramatically hindered the electrochemical catalytic process. This result explains the performance decrease of metal oxide based glucose sensors work in environments with high humidity.

II. EXPERIMENTS

A. Synthesis of NiCo$_2$O$_4$ NRs

We used all reagents as received. The mixture of 0.3 mmol nickel(II) acetate tetrahydrate, 0.6 mmol cobalt acetate tetrahydrate, and 4 mmol urea were dissolved in 30 mL deionized water and transferred into a 50 mL stainless steel autoclave with Teflon coating. The autoclave was heated for 6 h at 150 °C. After cooling, the obtained Ni-Co precursor was then annealed in air for 3 h at 300 °C. For the microwave treatment, the as-prepared NiCo$_2$O$_4$ was treated in a commercial microwave oven at a power of 700 W for 1 min. The microwave-treated NiCo$_2$O$_4$ is referred as M-NiCo$_2$O$_4$ hereafter.

B. Instrumentation

The X-ray diffraction (XRD) data were collected on a Philips X’Pert diffractometer with a Cu Kα source worked at 40 kV and 40 mA. High resolution transmission electron microscopic (HRTEM) measurements were performed by using a JEM-2100HF transmission microscope (JEOL, Japan) at 200 kV. Scanning electron microscopy (SEM) measurements were performed on an S-4800 microscope (Hitachi). Elemental analysis was performed on an energy-dispersive X-ray spectroscopy (EDS Inca X-Max, UK). The X-ray photoelectron spectra (XPS) were characterized by using a VG ESCALAB Mk II spectrometer with an Al Kα (1486.6 eV) source.

C. Preparation of NiCo$_2$O$_4$/GCE and M-NiCo$_2$O$_4$/GCE

4 mg of either NiCo$_2$O$_4$ or M-NiCo$_2$O$_4$ were mixed with 10% NaCl and drop-casted on a carefully polished glassy carbon electrode (GCE).

D. Electrochemical measurement

A CHI 660E electrochemical workstation (CH Instruments, Shanghai) was used for electrochemical measurements with a standard three-electrode setup. The GCE and NiCo$_2$O$_4$ or M-NiCo$_2$O$_4$ modified GCE (5 mm in diameter) were used as the working electrode, while using Hg/HgO and a Pt plate as the reference and the counter electrodes, respectively. All the electrochemical tests were performed in 0.1 mol/L NaOH solution.

III. RESULTS AND DISCUSSION

A. Structural characterizations

Since the microwave processing of the samples would eliminate the residual water in the NiCo$_2$O$_4$ samples, we performed SEM, HRTEM, XRD, and EDS characterizations for the NiCo$_2$O$_4$ and M-NiCo$_2$O$_4$ samples to examine the variations in the morphologies, the crystalline symmetries, and the stoichiometric contents. All these measurements can be compared as depicted in FIG. 1. As shown in FIG. 1 (a) and (b), the SEM images of NiCo$_2$O$_4$ and M-NiCo$_2$O$_4$ both show a long and thin rod-like structure, and there is no significant difference in the morphologies before and after microwave treatment. This result indicates that microwave pretreatment does not affect the microscopic structure of the NiCo$_2$O$_4$ samples. The NiCo$_2$O$_4$ nanorods offer high surface atom ratio and provide a large surface area, which might result in stronger redox current signals as the glucose oxidation occurs. The HRTEM image of the NiCo$_2$O$_4$ nanorods after microwave treatment is depicted in FIG. 1(c). It is clear that the crystal lattice distances of NiCo$_2$O$_4$ are 0.25, 0.48, and 0.30 nm, and these d-spacings originate from the (311), (111) and (220) crystal plane indices, respectively. These results agree well with the XRD data shown in FIG. 1(d), where all the peaks of the NiCo$_2$O$_4$ and the M-NiCo$_2$O$_4$ samples match with the NiCo$_2$O$_4$ reference data (PDF: No.20-0781). These characterizations indicate that the microwave treatment does not vary the crystal structure of NiCo$_2$O$_4$ nanorods. FIG. 1(e) and (f) depict the EDS patterns of NiCo$_2$O$_4$ before and after the microwave treatment, respectively. The stoichiometric ratio between Ni, Co, and O changes from approximately 1:2:5 to 1:2:4 via microwave treatment. The loss of O content can be ascribed to the elimination of H$_2$O. After the microwave treatment, the stoichiometric ratio coincides with the NiCo$_2$O$_4$ formula. This suggests that NiCo$_2$O$_4$ was successfully synthesized using the facile hydrothermal synthetic procedure followed by microwave treatment. Moreover, the EDS mapping of NiCo$_2$O$_4$ confirms the co-existence of nickel, cobalt and oxygen elements in NiCo$_2$O$_4$ and they are uniformly distributed (FIG. S1 in supplementary materials).

The detailed chemical composition and corresponding electronic structures were analyzed with the help of XPS measurements. FIG. 2(a) displays a complete survey of the XPS spectrum of the as-prepared M-NiCo$_2$O$_4$, where all the element features can be clearly observed. The deconvoluted spectra in the Ni 2p region are shown in FIG. 2(b), where the peaks consisting of binding energies 853.9 and 871.6 eV are ascribed to the Ni$^{2+}$ oxidation state and those at 855.4 and 873.1 eV originate from the Ni$^{3+}$ state. FIG. 2(c) shows the
FIG. 1 SEM images of the NiCo$_2$O$_4$ before (a) and after (b) microwave treatment. (c) HRTEM image of the NiCo$_2$O$_4$ after microwave treatment. (d) XRD analysis of NiCo$_2$O$_4$ before and after microwave treatment. EDS patterns of NiCo$_2$O$_4$ before (e) and after (f) microwave treatment.

FIG. 2 XPS spectra of M-NiCo$_2$O$_4$ nanorods. (a) full spectrum, and in the Ni 2p (b), Co 2p (c), and O 1s (d) regions.
Co 2p spectrum at a higher resolution with the spin-orbit doublets has Co$^{3+}$ and Co$^{2+}$ characteristics and each is followed by a satellite feature. The peaks of 2p$_{3/2}$ and 2p$_{1/2}$ states of Co$^{3+}$ are shown at 779.7 and 794.9 eV and the Co$^{2+}$ 2p$_{3/2}$ and 2p$_{1/2}$ signals appear at 781.4 and 796.8 eV. These results indicate that the as-synthesized M-NiCo$_2$O$_4$ has mixed oxidation states both for the Co and the Ni elements, which agrees well with previous reports [29]. Moreover, the deconvoluted O 1s spectrum shown in FIG. 2(d) reveals three oxygen components at 529.4, 531.0, and 533.4 eV, these features can be attributed to the metal-bonding oxygen, hydroxyl oxygen and oxygen appearing in moisture adsorptions, respectively [30]. We also note that the XPS spectrum of NiCo$_2$O$_4$ before microwave treatment shows almost identical features with that of the M-NiCo$_2$O$_4$ (FIG. S2 in supplementary materials), indicating that microwave treatment does not alter the oxidation states and elemental compositions of NiCo$_2$O$_4$.

B. Electrochemical characterization of NiCo$_2$O$_4$ modified electrode

We first investigated the redox process of NiCo$_2$O$_4$ in 0.1 mol/L NaOH with cyclic voltammetry (CV) scanning. As depicted in FIG. 3(a), before microwave treatment, we observed the oxidation and cathodic peaks appear at +0.58 V and +0.43 V vs. Hg/HgO, respectively. The corresponding Randles-Sevick plot (FIG. 3 (b)) shows that the peak current is linearly correlated with the square root of the scan rate. This result indicates that the electrode processes are diffusion controlled. In comparison, after microwave treatment, the CV curves of M-NiCo$_2$O$_4$ show two anodic peaks at +0.51 and +0.63 V and one cathodic peak at +0.35 V. The anodic peak at +0.51 V can be attributed to the redox process of Ni$^{2+}$/Ni$^{3+}$, whereas the oxidation peak at +0.63 V originates from the redox process of Co$^{2+}$/Co$^{3+}$. The corresponding Randles-Sevick plot also indicates a diffusion controlled electrode process. The fact that only one oxidation peak was observed before microwave treatment suggests that the residual water in NiCo$_2$O$_4$ might hinder the redox kinetics of Ni$^{2+}$/Ni$^{3+}$. It is worth noting that for both of NiCo$_2$O$_4$ samples, the increasing scan rates leads to apparent shifting in peak potentials, indicating rather a sluggish electrode kinetics. This suggests a rather slow surface diffusion process of OH$^-$ or the semiconducting behavior of NiCo$_2$O$_4$.

FIG. 4 displays the CV curves of both NiCo$_2$O$_4$ and M-NiCo$_2$O$_4$ modified GCE in NaOH solution with a scan rate of 40 mV/s. Upon the addition of a different amount of glucose, the oxidation peak current for both electrode materials increases, suggesting both the NiCo$_2$O$_4$ coatings are responsive toward the detection
of glucose. The redox-catalyzed electrode process can be summarized as follows:

\[
\begin{align*}
\text{NiCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \rightarrow \text{NiCo}_2\text{O}_4(\text{OH})_3 + e^- \quad (1) \\
\text{NiCo}_2\text{O}_4(\text{OH})_3 + 3\text{glucose} & \rightarrow \\
& \text{NiCo}_2\text{O}_4 + 3\text{glucolactone} \quad (2)
\end{align*}
\]

It is obvious that the catalyzed oxidation process on M-NiCo\(_2\)O\(_4\) modified electrode requires lower potential than that of the NiCo\(_2\)O\(_4\) case. The lower catalytic oxidation potential is beneficial for sensitive glucose sensing at low operating potentials.

The sensing performance of the NiCo\(_2\)O\(_4\) modified electrodes was evaluated by performing amperometric studies towards glucose detection by successively adding glucose withholding the NiCo\(_2\)O\(_4\) electrode at a constant potential. The amperometric responses of the M-NiCo\(_2\)O\(_4\) modified GCE at +0.5, +0.6, and +0.7 V vs. Hg/HgO are shown in FIG. 5(a). With the increase of the glucose concentration, the current increases for all three measurements. The corresponding calibration graph is shown in FIG. 5 (b)–(d), with the linear region shown as inserts. The potential of +0.6 V is found to be optimal, with the highest sensitivity of 431.29 μA-mmol/L⁻¹-cm⁻². The limit of detection for the +0.6 V operating potential is 0.0126 mmol/L (S/N=3) and the recovery percentage of glucose lies between 95.83% (at glucose concentration of 0.24 mmol/L) and 83.73% (5.47 mmol/L) (see Table S1 in supplementary materials). The complete analytical data of the three different operating potentials are shown in Table S2 in supplementary materials. In comparison, NiCo\(_2\)O\(_4\) was also used to modify the GCE surface followed by amperometric measurements. As shown in FIG. S3 in supplementary materials, similar to that of M-NiCo\(_2\)O\(_4\) modified GCE, NiCo\(_2\)O\(_4\) also responds to the successive addition of glucose. However, the sensitivity of the electrode modified by NiCo\(_2\)O\(_4\) is much lower than that of the M-NiCo\(_2\)O\(_4\) case. Again, the +0.6 V electrode potential offers the highest sensitivity for the NiCo\(_2\)O\(_4\) modified electrode, but only 193.92 μA-mmol/L⁻¹-cm⁻² is achieved. The recovery percentage of NiCo\(_2\)O\(_4\) modified GCE was found to be much lower than that of M-NiCo\(_2\)O\(_4\), with only 66.67% recovery when glucose concentration was 0.24 mmol/L and 48.99% at 5.47 mmol/L (Table S1 in supplementary materials). Obviously, M-NiCo\(_2\)O\(_4\) offers much better electrochemical performance than NiCo\(_2\)O\(_4\), which confirms the assumption that the residual water hinders the electrochemical catalytic activity.

Since the sensing process would be interfered by other bio-organic molecules, we performed interference test for sensors with NiCo\(_2\)O\(_4\) and M-NiCo\(_2\)O\(_4\) modified electrodes. FIG. 6 depicts the response of the current density to usual interferences, such as ascorbic acid and uric acid. These interference sources were added with the concentration of 0.1 mmol/L, which preserved the concentration ratio respect to glucose in plasma [31]. It is obvious that the addition of small amount of ascorbic acid and uric acid only increases the current density slightly, whereas the addition of glucose dramatically raises the current density. This result suggests that M-NiCo\(_2\)O\(_4\) is a good inorganic catalytic material for glucose sensing with high robustness.

In order to examine the effect of residual water in NiCo\(_2\)O\(_4\) on the sensing performance, we soaked the M-NiCo\(_2\)O\(_4\) in water with various durations. As shown in FIG. 7, the M-NiCo\(_2\)O\(_4\) modified electrode shows excellent sensitivity (431.29 μA-mmol/L⁻¹-cm⁻²) towards glucose sensor when it was directly applied after microwave treatment (refer to 0 h in FIG. 7). After soaking the M-NiCo\(_2\)O\(_4\) in water for 2 h, the sensitivity dramatically decreased to 118.00 μA-mmol/L⁻¹-cm⁻², which indicates that water strongly hindered the electrochemical activity of NiCo\(_2\)O\(_4\). As the soaking time increases, the sensitivity fluctuates between 100–245 μA-mmol/L⁻¹-cm⁻², which is much lower than that of the as-prepared M-NiCo\(_2\)O\(_4\) modified electrodes. As shown in FIG. S4(a) (supplementary materials), EDS characterization confirmed the existence...
FIG. 5 (a) Amperometric analysis of M-NiCo$_2$O$_4$ modified GCE upon consecutive addition of glucose at +0.5, +0.6, and +0.7 V vs. Hg/HgO. (b–d) The linear calibration plot of (a), the insertion shows the linear region of the calibration graph.

FIG. 6 Interference test of NiCo$_2$O$_4$ and M-NiCo$_2$O$_4$ nanorod modified GCE in 0.1 mol/L NaOH (aq) at +0.6 V vs. Hg/HgO with 0.5 mmol/L glucose, 2.5 mmol/L glucose, 0.1 mmol/L ascorbic acid, and 0.1 mmol/L uric acid.

FIG. 7 The glucose sensing sensitivities after soaking the M-NiCo$_2$O$_4$ in water. 0 h denotes the M-NiCo$_2$O$_4$ was applied on the GCE directly after microwave-treatment, and post-108 denotes the microwave-retreated M-NiCo$_2$O$_4$ after soaking in water for 108 h.

of residual water in the soaked samples. In general, the residual water affects the electrochemical performance of NiCo$_2$O$_4$ dramatically. The sample was then treated with microwave again after being soaked in water for 108 h. As expected, the sensitivity recovered and reached 410.09 $\mu$A·mmol/L$^{-1}$·cm$^{-2}$. FIG. S4(b) in supplementary materials shows the EDS analysis of M-NiCo$_2$O$_4$ after soaking in water followed by annealing at 300 °C for 2 h. The molar ratio of O, Co, and Ni serves at about 5:2:1. This is interesting that even at a high annealing temperature of 300 °C, it is still unable to eliminate the residual water unless a microwave treatment is performed. This also suggests an efficient and economic approach to recover the sensor performance.
IV. CONCLUSION

We synthesized NiCo$_2$O$_4$ nanorods via hydrothermal reaction followed by annealing in air at 300 °C for 3 h. The NiCo$_2$O$_4$ was then treated in a commercial microwave oven at 700 W for 1 min to eliminate the residual water that may be introduced during the hydrothermal synthesis. The as-prepared M-NiCo$_2$O$_4$ was drop-casted on a GCE and applied for glucose electrochemical sensing. Although there is no significant structural alteration before and after the microwave treatment, the elimination of residual water was confirmed by the stoichiometric ratio change revealed by EDS analysis. The M-NiCo$_2$O$_4$ showed excellent performance towards glucose sensing with a sensitivity up to 431.29 μA·mmol/L$^{-1}$·cm$^{-2}$. By soaking the M-NiCo$_2$O$_4$ in water after various durations, the sensing performance reduced dramatically. The performance can be recovered by another microwave treatment. We found that the residual water is difficult to remove by conventional annealing process even with a temperature up to 300 °C. This result showed that the introduction of residual water during the hydrothermal procedure strongly affects the electrochemical performance. Microwave pre-treatment is crucial to eliminate the residual water and provides an efficient and economic approach to recovering the performance of the glucose sensors using NiCo$_2$O$_4$ modified electrodes.

**Supplementary materials:** SEM image and EDS mapping of M-NiCo$_2$O$_4$, XPS analysis of microwave untreated NiCo$_2$O$_4$ nanorods, glucose sensing tests for untreated NiCo$_2$O$_4$ nanorods, EDS analysis of M-NiCo$_2$O$_4$ after soaking in water, recovery test data and limit of detection data are presented in Supplementary materials.

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