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Ni foam-supported ZnO nanowires and $Co_3O_4/NiCo_2O_4$ double-shelled nanocages for efficient hydrogen peroxide detection

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ABSTRACT

Nanocrystalline transition metal oxides have attracted a great deal of attention due to their good electrochemical activity. To pursue novel active electrode materials with low detection, high sensitivity and good selectivity for the detection of H_2O_2, Ni foam-supported ZnO nanowires and $Co_3O_4/NiCo_2O_4$ double-shelled nanocages (ZnO/$Co_3O_4/NiCo_2O_4$/Ni foam) have been successful fabricated by facile and effective methods When tested as an enzymatic-free H_2O_2 electrochemical sensor, the obtained ZnO/$Co_3O_4/NiCo_2O_4$/Ni foam exhibits fast response time within 5 s, low detection limit of 0.163 μM (S/N = 3), high sensitivity of 0.388 mA•mM^{-1} cm^{-2}, wide linear range from 0.2 μM to 2.4 mM (R^2 = 0.996), exhibiting good selectivity and long-term stability. The reason is that special structure of the ZnO nanowires could provide direct electrical pathways for the fast electron transport and $Co_3O_4/NiCo_2O_4$ double-shell nanocages provide abundant mesopores and large specific surface area to enhance the catalytic activity of H_2O_2 detection. These results suggest that the ZnO/$Co_3O_4/NiCo_2O_4$/Ni foam could be considered as a promising electrode material to build electrochemical biosensor.

1. Introduction

The increasing demands for hydrogen peroxide (H_2O_2) sensor with high sensitivity, good stability and excellent selectivity have motivated researchers to explore new approach for H_2O_2 sensor applications in various fields, such as food industry [1], biopharmaceutical [2], environmental analyses [3] and clinical diagnostics [4]. So far, lots of methods have been employed to detect H_2O_2, including chemiluminescence [5], spectrophotometry [6], titration [7], fluorometry [8] and electrochemical methods [9]. Among the above mentioned methods, electrochemical method has been regarded as most promising method owing to its fast response time, low cost and high sensitivity. Based on whether having enzyme, H_2O_2 electrochemical sensor can be generally categorized as enzyme electrochemical sensor and enzymatic-free electrochemical sensor. Despite its excellent selectivity and high sensitivity, enzyme sensors suffer from the disadvantages of high cost, sensitive to the environmental conditions and complicated immobilization procedures [10]. Thus, enzymatic-free H_2O_2 electrochemical sensor has gained growing attention because it is a potential alternative method to overcome the shortcoming mentioned above of enzymatic sensors.

Nanocrystalline transition metal oxides have been widely used as electrochemical electrode materials based on their good catalytic activity for the detection of H_2O_2 and nature abundance. Among various types of transition metal oxides, Co_3O_4 has displayed excellent electrocatalytic performance towards H_2O_2. However, low conductivity restricts its use in application. $NiCo_2O_4$, as a typical binary metal oxide with spinel structure, has been reported to exhibit greater electronic conductivity and electrochemical catalytic activity than the single component cobalt oxides (two orders of magnitude higher) due to its multiple oxidation states [11–13]. Inspired by the potential applications of $NiCo_2O_4$, many research teams focus their subjects on studying and using cobalt nickel mixed oxides in glucose or H_2O_2 electrochemical sensor [14–18]. Combination of Co_3O_4 and $NiCo_2O_4$ to form $Co_3O_4/NiCo_2O_4$ nanocomposites is probably an effective way to enhance detection performance towards H_2O_2.

In recent years, a novel approach for synthesis of $Co_3O_4/NiCo_2O_4$ nanocomposites using ZIFs (Zeolite imidazole frameworks) as template has been presented [19,20]. ZIFs, as a kind of new coordination compounds with a large surface and well defined structures, consisting of metal ion and bridging organic linkers can synthesize porous metal oxides by direct annealing ZIFs [21]. Although ZIFs derived $Co_3O_4/NiCo_2O_4$ nanocomposites have been applied in the fields of catalysis, gas sensing and Supercapacitors [19,20,22], their application in H_2O_2 sensor is still limited. Herein, a simple method based on using of ZIF-67 as template has been adopted

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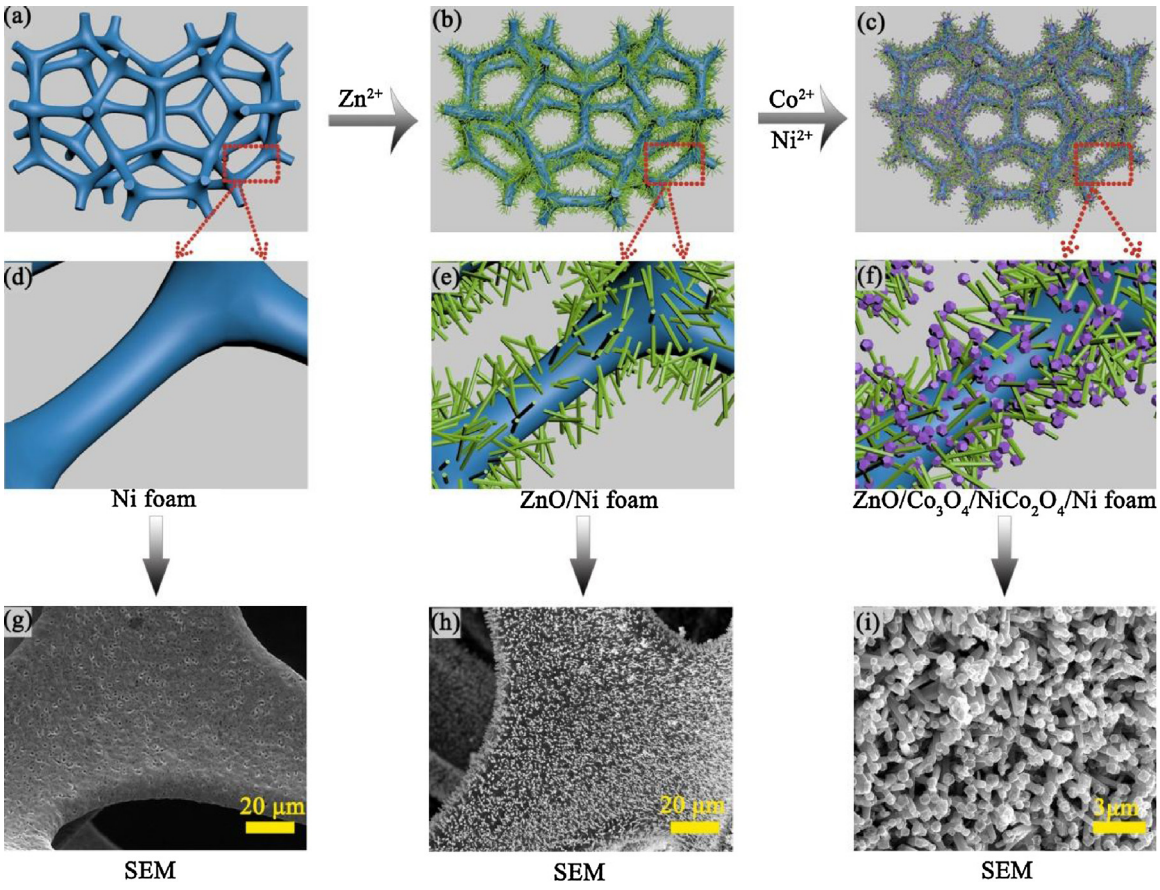

Scheme 1. Scheme of the formation process of $ZnO/Co_3O_4/NiCo_2O_4$/Ni foam.

to prepare ZIFs derived $Co_3O_4/NiCo_2O_4$ double-shelled nanocages ($Co_3O_4/NiCo_2O_4$ DSNCs) for H_2O_2 sensor.

ZIFs derived $Co_3O_4/NiCo_2O_4$ DSNCs have been used in chemically modified electrodes usually prepared through slurry-coating method with the presence of binder for electrochemical sensing [23]. However, powdered $Co_3O_4/NiCo_2O_4$ DSNCs generally suffer from the disadvantage of agglomeration during the electrode modification, decreasing the effective contact area between the electrolyte and the active site, thereby may lead to low catalytic activity. In addition, the existence of binder in modified electrodes materials would decline the electrical conductivity, preventing their potential application in high-properties electrochemical sensing [24]. Hence, to obtain good dispersibility, good adhesion and high electrical conductivity for improving the catalytic properties of the sensor, there was urgent need to directly grow porous $Co_3O_4/NiCo_2O_4$ DSNCs to a conductive substrate such as Ni foam. Meanwhile, ZnO nanowires (ZnO NWs) have been adopted for adhesion and dispersion of $Co_3O_4/NiCo_2O_4$ DSNCs on the surface of Ni foam. ZnO NWs, as one-dimensional nanomaterials, provided fast electron transfer path between the Ni foam and the $Co_3O_4/NiCo_2O_4$ DSNCs to reach the excellent electrochemical performance aim [25,26].

Herein, we have adopted a simple method to grow ZnO NWs and porous $Co_3O_4/NiCo_2O_4$ DSNCs on Ni foam. Subsequently, the Ni foam-supported ZnO NWs and $Co_3O_4/NiCo_2O_4$ DSNCs ($ZnO/Co_3O_4/NiCo_2O_4$/Ni foam) were used as an electrode, which exhibited high catalytic activity to H_2O_2. The synthesis of $ZnO/Co_3O_4/NiCo_2O_4$/Ni foam involves the growth of ZnO NWs on Ni foam (ZnO/Ni foam), the growth of Ni-Co layered double hydroxides nanocages (Ni-Co LDHs) on ZnO/Ni foam (ZnO/Ni-Co LDHs/Ni foam) and then thermal transformation to $ZnO/Co_3O_4/NiCo_2O_4$/Ni foam. The advantages of the designed electrode can be listed as follows: (i) the bind-free electrode not only provides good dispersibility but also exposes amount effective active site to electrolyte, enhancing the catalytic activity; (ii) the ZnO NWs not only provides direct electrical pathways for fast electron transport but also can serve as scaffolds for the adhesion and dispersion of the $Co_3O_4/NiCo_2O_4$ DSNCs; (iii) $Co_3O_4/NiCo_2O_4$ DSNCs possess abundant mesopores and large specific surface area favoring the enhancement of H_2O_2 sensing performance.

2. Experimental

2.1. Reagent and materials

Ni foams were purchased from Shenzhen Kejing Star Technology Co. Ltd. $Zn(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and 2-methylimidazole (2-mIM) were purchased from Aladdin Industrial Co. Ltd. Hydrogen peroxide (H_2O_2, 30%, w/w), methanol and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. All other reagents used were of analytical reagent grade and used without further treatments.

2.2. Preparation of ZnO/Ni foam

Scheme 1 shows the synthesis diagram of $ZnO/Co_3O_4/NiCo_2O_4$/Ni foam. ZnO/Ni foam was synthesized by galvanostatic electrodepodition method [27]. The electrochemical deposition of ZnO/Ni foam was performed in two-electrode electrolytic cell, using platinum plate as the counter electrode (1×1 cm) and Ni foam as the working electrode (1×1 cm). Before experiment, Ni foam substrate was ultrasonically washed in turn by ethanol and deionized water for 30 min and dried at 60 °C for 8 h. ZnO/Ni foam was prepared by electrodeposition in the 500 ml