Short communication

Three-dimensional nanoporous gold–cobalt oxide electrode for high-performance electroreduction of hydrogen peroxide in alkaline medium

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Highlights

- NPG film/Ni foam serves as the 3D hierarchical porous conductive scaffold.
- Co₃O₄ nanosheet arrays were hydrothermally grown on the 3D NPG/Ni foam composite.
- Co₃O₄@NPG/Ni foam exhibits superior activity and stability toward peroxide reduction.

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Abstract

Using a simple hydrothermal method combined with a post-annealing treatment, cobalt oxide (Co₃O₄) nanosheet arrays are grown on three-dimensional (3D) nanoporous gold (NPG) film supported on Ni foam substrates, in which NPG is fabricated by chemically dealloying electrodeposited Au–Sn alloy films. The morphology and structure of the Co₃O₄@NPG/Ni foam hybrids are characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical activity of the Co₃O₄@NPG/Ni foam electrode toward hydrogen peroxide electroreduction in alkaline medium is studied by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA). The results demonstrate that the Co₃O₄@NPG/Ni foam electrode possesses exceptionally high catalytic activity and excellent stability for the peroxide electroreduction, resulting mainly from the unique electrode architecture. The combined 3D hierarchical porous structures of NPG/Ni foam with the open and porous structures of Co₃O₄ nanosheet arrays facilitate the mass transport and charge transfer. Therefore, the metal oxides supported on 3D hierarchical porous NPG/Ni foam framework may hold great promise to be effective electrodes for electrocatalytic reduction of peroxide and other electrochemical reactions.

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1. Introduction

Fuel cells, which convert the chemical energy directly into electric energy, are emerging as leading alternative energy conversion devices for portable power supply [1,2]. Oxygen from ambient air is generally required as an oxidant in fuel cell devices [3], while an additional oxygen tank in the system is needed in oxygen-free environments such as underwater and outer space, which significantly decreases the energy density of fuel cells. In this context, there has been considerable interest in developing liquid-based fuel cells that use hydrogen peroxide as an alternative oxidant [4]. Examples of these types of fuel cells include metal/hydrogen peroxide fuel cell [5], direct borohydride/hydrogen peroxide fuel cell [6] and hydrazine/hydrogen peroxide fuel cell [7]. Compared with oxygen, peroxide as an oxidant offers some important advantages: higher power density, higher theoretical voltage and faster reduction kinetics [8,9]. In order to further improve the performance of these peroxide-based fuel cells, it is essential to design cathode electrocatalysts with high catalytic activities for electrochemical reduction of peroxide.Conventionally, noble metal nanoparticle electrocatalysts, such as Pt [10], Pd [11] and their alloys [12], exhibit remarkably high catalytic activity and superior stability toward peroxide electroreduction. However, the limited supply and thus relatively high cost of these noble metals severely limit their practical applications. Therefore, it is imperative to search for much cheaper alternative cathode catalysts for the peroxide electroreduction to replace the noble metal catalysts. Recently, nanostructured transition metal oxides catalysts, for example, Mn3O4 [13], Co3O4 [14] and CuO [15], have been exploited as potential candidates. Among them, Co3O4 has attracted particular attention for peroxide electroreduction owing to its excellent electrocatalytic activity and stability, as well as its earth abundance and environmental benignity. However, the intrinsically poor electrical conductivity of Co3O4 severely limits its practical application. To overcome this shortage, Co3O4 nanostructures are usually supported on various conductive substrates such as Ti foil [16] and Ni foam [17]. These conductive substrates can not only support and disperse the oxides but, more importantly, could also facilitate the electron transfer between the oxides and the conducting supports, thus improving the electrocatalytic performances.

Recently, nanoporous gold (NPG), with large surface area, excellent electric conductivity, superior chemical stability and good biocompatibility, has gained significant interest because of its unique nanostructure together with excellent optical and catalytic properties [18–20]. It has been regarded as a very promising candidate material for application in various areas such as catalysis [21], energy storage [22], metal-enhanced fluorescence [23] and sensors/biosensors [24,25]. NPG films are typically prepared by chemically dealloying commercial Au–Ag alloy leaves in a concentrated HNO3 solution. However, these free-standing thin films are brittle and difficult to handle, and thus require an extremely careful transfer method to place them onto other substrates. More recently, we have developed a facile two-step strategy for fabricating NPG films through electrodeposition followed by chemically dealloying Au–Sn alloy films, enabling the preparation of high-quality NPG films directly supported on various substrates such as copper foil, stainless steel sheet and Ni foam [26]. Among them, NPG films supported on Ni foam substrate (NPG/Ni foam) with a hierarchical porous architecture is regarded as a promising electrode material for catalytic applications, as it can facilitate fast electron and ion transport through 3D interconnected pathways. Its application for electrocatalytic reduction of peroxide in neutral [26,27] and acidic medium [28,29] have been reported. However, its application in alkaline medium has not been previously demonstrated.

In this work, we report Co3O4 nanosheet arrays supported on three-dimensional (3D) hierarchical porous NPG-covered Ni foam, referred to as Co3O4@NPG/Ni foam, as a binder-free electrode for high-performance electrochemical reduction of peroxide in alkaline medium. The 3D hierarchical porous NPG/Ni foam hybrid was employed as the conductive scaffold to load the Co3O4 nanostructures and improve the electrical conductivity of the overall electrode material. Such a unique electrode architecture provides not only a large electrochemical active surface area but also a fast pathway for electron transport and mass transfer. Electrochemical studies showed that the Co3O4@NPG/Ni foam electrode exhibited high electrocatalytic activity and excellent stability/durability toward the peroxide electroreduction, which makes it a promising candidate for a cathode electrocatalyst for peroxide-based fuel cells.

2. Experimental section

2.1. Materials synthesis

Ni foam (approximately 1 cm × 7 cm) was pretreated with 5 M HCl solution for 30 min in order to remove the oxide layer on the surface, and then rinsed thoroughly with deionized water. The Au–Sn alloy electrodeposition was carried out in a two-electrode system with the clean Ni foam as working electrode and a Pt plate as counter electrode. The Au–Sn alloy film was galvanostatically electrodeposited on Ni foam in an Au–Sn alloy plating solution (Huizhou Leadao Electronic Material Co., Ltd.) with a current density of 5 A dm−2 for 10 min at 45 °C. After electrodeposition, the Ni foam was rinsed with deionized water and dried in air. Then, the sample was immersed into a 5 M NaOH and 1 M H2O2 solution for 3 days at ambient conditions to selectively etch Sn away from Au–Sn alloy film, leading to the formation of an NPG film on Ni foam. After etching, the Ni foam was carefully rinsed with deionized water and dried in air. Then, the NPG/Ni foam was wrapped with a Teflon tape with exposure area of ~1 cm2, and immersed into a Teflon-lined stainless steel autoclave containing a 30 ml mixture of 0.3 mM Co(NO3)2, 0.6 mM NH4F and 1.5 mM urea. The autoclave was then sealed and heated in an electric oven at 180 °C for 35 min. After cooled down to room temperature, the samples were carefully rinsed with deionized water and then dried in the oven at 60 °C for 1 h. Finally, the samples were annealed at 300 °C for 2 h for synthesis of crystalline Co3O4. As a control experiment, the Ni foam without NPG film was employed to prepare a Co3O4/Ni foam hybrid by following the same procedure.

2.2. Characterization and electrochemical measurements

The microstructure of the samples was investigated by field-emission scanning electron microscopy (SEM, JEOL, JSM-6700F, 15 keV). X-ray diffraction (XRD) measurements were performed on a Rigaku D/max-2200/PC diffractometer using Cu Kα radiation. Electrochemical measurements were carried out on a Gamry Reference 600 electrochemical workstation in a three-electrode setup with 3 M KOH as the electrolyte. The Co3O4@NPG/Ni foam electrode, a Pt plate electrode and an Ag/AgCl electrode acted as the working electrode, counter electrode and reference electrode, respectively. The electrochemical impedance spectroscopy (EIS) measurements were conducted in a frequency range from 100 kHz to 0.1 Hz with a perturbation amplitude of 5 mV. All electrochemical measurements were performed at ambient temperature (25 ± 2 °C).

3. Results and discussion

The crystalline phase of the as-prepared Co3O4@NPG/Ni foam...
samples were characterized using XRD. Fig. 1 depicts the typical XRD pattern of the as-synthesized Co$_3$O$_4$ nanosheet arrays supported on NPG/ Ni foam substrate. It can be observed that the diffraction peaks can be well indexed to the pure cubic phase of Co$_3$O$_4$ (space group: Fd3m (227), JCPDS card no. 42-1467). The diffraction peaks at the 20 values of 19.0°, 31.1°, 36.7° and 59.1° can be assigned to the (111), (220), (311) and (511) planes of Co$_3$O$_4$ phase, whereas the other diffraction peaks marked by diamond and dot originate from Ni foam substrate and NPG film, respectively. The XRD result verifies the formation of Co$_3$O$_4$ on the NPG/Ni foam support. Representative SEM images under different magnifications of NPG/Ni foam and Co$_3$O$_4$@NPG/Ni foam composites are displayed in Fig. 2A–F. A bicontinuous nanoporous structure composed of interconnected gold ligaments and nanopores is uniformly distributed on Ni foam surfaces (Fig. 2A and B). A higher magnification SEM image shows that the NPG structure (Fig. 2C) has a typical ligament/nanopore size of 70 nm. After synthesis of Co$_3$O$_4$ on NPG/Ni foam, it can be seen from Fig. 2D and E that Co$_3$O$_4$ nanosheet arrays are uniformly grown on the ligaments of the NPG/Ni foam. As can be seen from the higher magnification SEM image (Fig. 2F), the growth of Co$_3$O$_4$ nanosheet does not change the basic nanoporous morphology of NPG/Ni foam support, and most of Co$_3$O$_4$ nanosheets are aligned perpendicular to the substrate, forming a highly open and porous structure. When used as an electrode in electrochemical reactions, this kind of composite material has several advantages as follows: (i) the 3D hierarchical porous structure of NPG/Ni foam allows conformal loading of Co$_3$O$_4$ and facilitates easy electrolyte penetration; (ii) NPG in the composite provides excellent interfacial contact between Co$_3$O$_4$ and NPG for fast electron transport; (iii) the vertically aligned nanosheet array architecture of Co$_3$O$_4$ offers a large electrochemical active surface area for rapid chemical reactions.

The as-prepared Co$_3$O$_4$@NPG/Ni foam composite was employed as the working electrode to evaluate its electrochemical performance toward peroxide electroreduction in alkaline medium. Fig. 3A shows the cyclic voltammograms (CVs) of the Co$_3$O$_4$@NPG/Ni foam electrode in a 3 M KOH solution at a scan rate of 20 mV s$^{-1}$ in the absence and in the presence of 0.2 M peroxide. While the CV curve (a and inset) displayed only a small background current in a 3 M KOH solution, the CV curve in the presence of peroxide (b) exhibited a large reduction current peak at −0.28 V, revealing the high electrocatalytic activity of the Co$_3$O$_4$@NPG/Ni foam electrode toward the peroxide reduction. The bare Ni foam, NPG/Ni foam and Co$_3$O$_4$/Ni foam electrodes were also examined under the same conditions for comparison, and the results of this comparison were shown in Fig. 3B. It can be observed that the background current caused by Ni foam substrate was negligible, revealing that the catalytic activity for peroxide electroreduction mainly originated from the nanomaterials grown on Ni foam substrate. The Co$_3$O$_4$/Ni foam electrode exhibited higher electrocatalytic activity, in terms of reduction peak current density, than that of the NPG/Ni foam electrode, and the Co$_3$O$_4$@NPG/Ni foam electrode showed the best performance among all the electrodes.
catalytic performance. These results indicated that the hybridization of NPG with Co3O4 nanostructures effectively improves its catalytic activity for peroxide electroreduction.

The electrochemical responses of the Co3O4@NPG/Ni foam electrode to various concentration of peroxide in 3 M KOH solution at a scan rate of 20 mV s⁻¹ were shown in Fig. 4A. It can be seen that the reduction peak current densities shifted negatively and increased with increasing concentration of the peroxide, implying that the peroxide electroreduction at the peak potential is diffusion controlled. With the increase of peroxide concentration from 0.05 to 0.5 M, the reduction current density significantly increased from −12 to −381 mA cm⁻² at −0.6 V. The comparison of peroxide electroreduction performance on Co3O4@NPG/Ni foam electrode with other previously reported nanomaterials was displayed in Table 1. As seen, Co3O4@NPG/Ni foam electrode revealed outstanding performance for peroxide electroreduction than that on those previously reported electrode materials. The superior electrocatalytic performance of the Co3O4@NPG/Ni foam electrode toward peroxide reduction could be attributed to its unique electrode architecture which combined the 3D hierarchical porous structure of NPG/Ni foam support with the open and porous structure of Co3O4 nanosheet arrays.

The stability of the Co3O4@NPG/Ni foam electrode for peroxide electroreduction was investigated by chronoamperometric measurements. As shown in Fig. 4B, the current density obtained at −0.2 V was very stable, demonstrating that the Co3O4@NPG/Ni foam electrode possessed good stability for peroxide electroreduction. However, the reduction currents fluctuated and gradually decreased with time at −0.3 V and −0.4 V, which was probably due to the decrease of peroxide concentration near the electrode surface caused by fast consumption of the peroxide at more negative potentials. Furthermore, in order to investigate the durability of the Co3O4@NPG/Ni foam electrode, a potential cycling at a scan rate of 100 mV s⁻¹ between −0.6 and 0 V was applied to the electrode in 3 M KOH solution containing 0.2 M peroxide. Linear sweep voltammetry experiments were carried out at a scan rate of 10 mV s⁻¹ before and after the potential cycling. As shown in Fig. 4C, the current loss after 2500 potential cycles was negligible, confirming the long-term durability of the Co3O4@NPG/Ni foam electrode for peroxide electroreduction.

EIS is an effective technique for probing the charge transfer characteristics of the electrode. In this study, EIS was used to investigate the charge transfer resistance of different hybrid electrodes. As shown in Fig. 4D, the NPG/Ni foam electrode displayed a linear part at low frequency region which associated with the diffusion process and a small semicircle at high frequency region which indicated a very low charge transfer resistance at the NPG/Ni foam electrode/electrolyte interface. When the Co3O4 nanostructures were directly supported on the Ni foam surface, the EIS showed a large increase in diameter of the semicircle which could be attributed to the intrinsically poor electric conductivity of the Co3O4 nanostructures. However, when Co3O4 nanostructures were loaded onto the NPG-covered Ni foam surface, the charge transfer resistance decreased apparently, demonstrating that the hybridization of highly conductive NPG with Co3O4 nanostructures significantly accelerated the charge transfer kinetics. Such results revealed that the charge transfer process proceeded more efficiently on the Co3O4@NPG/Ni foam electrode, which is beneficial for its electrocatalytic performance for the peroxide reduction in comparison with the NPG/Ni foam and Co3O4/Ni foam electrodes.

Table 1

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Performance (mA cm⁻²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Co, Mn)₃O₄ nanowires/Ni foam</td>
<td>224 (3 M KOH + 0.4 M peroxide)</td>
<td>[13]</td>
</tr>
<tr>
<td>Co3O4 nanowires/Ni foam</td>
<td>256 (3 M KOH + 0.4 M peroxide)</td>
<td>[14]</td>
</tr>
<tr>
<td>Cu foils</td>
<td>20.3 (3 M KOH + 0.4 M peroxide)</td>
<td>[15]</td>
</tr>
<tr>
<td>Pd/Cu3O4/Ti foil</td>
<td>145.8 (3 M KOH + 0.4 M peroxide)</td>
<td>[16]</td>
</tr>
<tr>
<td>Co3O4 nanowires/Ni foam</td>
<td>105 (3 M NaOH + 0.4 M peroxide)</td>
<td>[17]</td>
</tr>
<tr>
<td>Co3O4@NPG/Ni foam</td>
<td>286 (3 M KOH + 0.4 M peroxide)</td>
<td>This work</td>
</tr>
</tbody>
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Fig. 4. CV curves of the Co3O4@NPG/Ni foam electrode for electrochemical reduction of peroxide over a concentration range from 0.05 to 0.5 M at a scan rate of 20 mV s⁻¹ (A). Chronoamperometric curves for electrocatalytic peroxide reduction on the Co3O4@NPG/Ni foam electrode at different potentials in a 3 M KOH solution containing 0.2 M peroxide (B). Polarization curves for the Co3O4@NPG/Ni foam electrode in 3 M KOH + 0.2 M peroxide at a scan rate of 10 mV s⁻¹ before and after 2500 cycles at a scan rate of 100 mV s⁻¹ between −0.6 V and 0 V (C). Nyquist plots of EIS in 3 M KOH solution containing 0.2 M peroxide for NPG/Ni foam (square), Co3O4/Ni foam (dot) and Co3O4@NPG/Ni foam (triangle) (D).
4. Conclusions

In summary, we report here an electrode fabrication method using a combination of electrodeposition, chemically dealloying, hydrothermal synthesis and post-annealing treatment to prepare a novel composite architecture based on Co$_3$O$_4$ nanosheet arrays supported on 3D hierarchical porous NPG/Ni foam. The hybrid electrode material was found highly effective toward the electrocatalytic reduction of peroxide in alkaline medium. The Co$_3$O$_4$@NPG/Ni foam electrode exhibited the best performance in comparison with the NPG/Ni foam and Co$_3$O$_4$/Ni foam electrodes, as well as an excellent stability and durability for peroxide electroreduction. The present study shows that Co$_3$O$_4$ nanosheet arrays supported on NPG/Ni foam represent a promising electrode material for fuel cells and electrochemical sensors.

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