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Short communication

Nanoporous gold on three-dimensional nickel foam: An efficient hybrid electrode for hydrogen peroxide electroreduction in acid media

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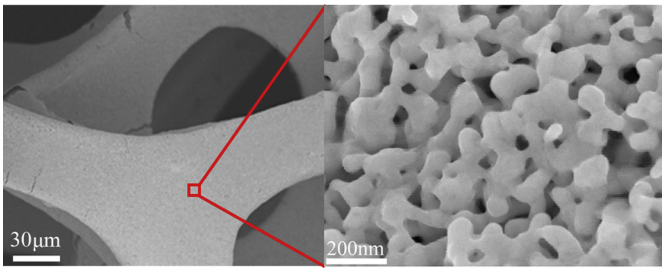
HIGHLIGHTS

- A novel method to fabricate nanoporous gold (NPG) by chemical dealloying of electrodeposited Au–Sn alloy.
- NPG was produced on three dimensional (3D) Ni foam surface.
- The good electrochemical performance is achieved on the 3D NPG/Ni foam hybrid electrode.
- The 3D NPG/Ni foam hybrid electrode exhibits superior activity and excellent durability toward H_2O_2 electroreduction.

GRAPHICAL ABSTRACT



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ABSTRACT

A hybrid structure of nanoporous gold (NPG) on three-dimensional (3D) macroporous Ni foam has been synthesized by electrodeposition of Au–Sn alloy film followed by a facile chemical dealloying process under free corrosion conditions. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are used to characterize the morphology and structure of the NPG/Ni foam hybrids. It is shown that the Ni foam skeletons are uniformly wrapped by the NPG film which is composed of bicontinuous nanostructures consisting of interconnected ligaments and nanopores. Electroreduction of H_2O_2 on the NPG/Ni foam hybrid electrode in acid media is investigated by linear scan voltammetry, chronoamperometry and electrochemical impedance spectroscopy. It is found that such hierarchical porous electrode displays superior activity, durability and mass transport property for H_2O_2 electroreduction. These results demonstrate the potential of the NPG/Ni foam hybrid electrodes for the applications in fuel cell technology.

1. Introduction

Hydrogen peroxide (H_2O_2) has been extensively investigated as the oxidizer to replace oxygen for some types of fuel cells, such as direct borohydride-hydrogen peroxide fuel cells [1–3] and direct hydrazine-hydrogen peroxide fuel cells [4,5]. These particular chemistries are best suited for air-independent applications under extreme conditions such as outer space and underwater environments. Compared to oxygen, H_2O_2 as the oxidizer allows much improved reaction kinetics on the cathode together with higher power densities and theoretical open circuit voltages [2,6].

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Designing cathode catalysts with improved H_2O_2 reduction kinetics can furthermore improve the performance of these fuel cell technologies [7,8], and a variety of different catalyst materials have been investigated including noble metals [9,10] and transition metal oxides [11,12]. Among these, nanostructured gold-based catalysts, such as nanoparticles [13,14], clusters [15] and nanodendrites [16] have drawn great attention due to their high chemical stability and excellent electrocatalytic performance toward H_2O_2 reduction. However, the current gold nanostructure-based electrodes suffer from several disadvantages including non-uniform dispersion, structural discontinuity and severe agglomeration during operation. Therefore, there remains great demand to pursue alternative nanostructure control strategies to design electrodes with improved utilization and efficiency toward H_2O_2 electroreduction.

Recently, nanoporous gold (NPG) materials have stimulated great research interest due to their intriguing properties [17–21] that arise from their unique bicontinuous structure consisting of both solid ligaments and void channels. The excellent structural integrity, mechanical stability, chemical stability and electrical conductivity of NPG has been demonstrated beneficial for a variety of different applications including heterogeneous catalysis [22–24], surface enhanced Raman scattering (SERS) [25,26], supercapacitors [27,28], electrochemical actuators [29] and biosensors [30]. NPG electrodes have also been successfully developed for the electrochemical reduction of H_2O_2 [31], accomplished using thin, two-dimensional (2D) planar electrode structures. In order to improve the efficiency of these electrodes, it is however important to increase the catalyst surface area that is available to facilitate the H_2O_2 electroreduction. In this context, the development of interconnected, three-dimensional (3D) NPG electrode structures would therefore provide significant improvements.

In the present work, NPG supported on 3D Ni foam are prepared as unique electrode structure for H_2O_2 electroreduction. The preparation process involves electrodeposition of an Au–Sn alloy film on the surface of the Ni foam, followed by a chemical dealloying process in which the tin component is etched away. The 3D Ni foam is a low cost metal substrate with high surface area and high conductivity, which has been applied as a template to host catalysts for effectively increasing the number of reaction sites [32–34]. There have been several reports that demonstrated successful synthesis of H_2O_2 electroreduction catalysts on the Ni foam skeleton [11,12,14]. However, in all of these studies, electrochemical reduction of H_2O_2 was conducted in alkaline media, probably because the Ni foam substrate is not suitable for use in electroreduction of H_2O_2 in acid solutions due to its instability. Nevertheless, the decomposition of H_2O_2 exhibits fast kinetics in alkaline media than that in acid media, which decreases the utilization efficiency of H_2O_2 [35]. In this context, it is considered to be a challenge to grow nanostructures on the Ni foam support as the electrocatalyst for H_2O_2 reduction in acid media. Herein, we demonstrate that the NPG film grown on Ni foams not only efficiently increases their stability in acid media, but also exhibits high catalytic activity toward H_2O_2 electroreduction in acid media. To the best of our knowledge, this is the first time that the Ni foam supported catalyst is developed for H_2O_2 electroreduction in acid media. It is believed that the NPG/Ni foam hybrid electrode with 3D hierarchical porous structures demonstrated in the present work will be a promising type of electrode material for the applications in a broad range of electrochemical processes.

2. Experimental

2.1. Electrode fabrication

The NPG/Ni foam hybrid electrode was prepared by a facile two-step procedure. First, the Au–Sn alloy film was grown on Ni foam by an electrodeposition process. In detail, Ni foam (20 mm × 60 mm × 0.1 mm, 100 pores per inch, 330 g m^{-2}, Changsha Lyrun Material Co., Ltd., China) was pretreated with 5 M HCl solution for 30 min to remove any potential nickel oxide species on the surface, and then rinsed with deionized water. An Au–Sn alloy film was deposited onto the pretreated Ni foam by a cathodic electrodeposition method using a constant current of 5 mA cm^{-2} for 5 min at 45 °C, operated by a KR-3001 30V/1A programmable DC sourcemeter (Kingrang Electronic Technology Co., Ltd., Shenzhen, China) and an Au–Sn alloy plating solution (Huizhou Leadao Electronic Material Co., Ltd., Huizhou, China. Website: www.leadao.cn). After deposition, the as-prepared Au–Sn alloy/Ni foam electrode was rinsed with deionized water and dried in air. In the second step, the Ni foam coated with an Au–Sn alloy film was immersed into 5 M NaOH and 1 M H_2O_2 solution at room temperature for 3 days. After free corrosion, the substrates were thoroughly rinsed with deionized water and dried in air.

2.2. Characterization

The morphology was examined using a field-emission scanning electron microscopy (SEM, JEOL, JSM-6700F, 15 keV). The crystal structure was analyzed by x-ray diffraction (XRD, Rigaku D/max-2200/PC) using Cu Kα radiation. Cyclic voltammetry (CV), linear scan voltammetry (LSV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) experiments (Gamry REF 600 Electrochemical Workstation) were performed in a conventional three-electrode electrochemical cell at room temperature using 0.5 M H_2SO_4 as the electrolyte. The Ni foam supported NPG (~4 cm^2 area) acted as the working electrode. A platinum plate and saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. EIS measurements were conducted by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 to 100 kHz.

3. Results and discussion

SEM images for the as-obtained Ni foam substrate at various magnifications are shown in Fig. 1A–C, displaying a 3D, highly porous and cross-linked structure. The average pore size of the Ni foam is about 100–200 μm, and the Ni grains of the skeleton can be seen at a higher magnifications (Fig. 1B and C). Fig. 1D–F displays the SEM images after the Au–Sn alloy film was deposited on the pretreated Ni foam using a cathodic electrodeposition method. It can be seen that the Ni foam surfaces are completely covered with small grains with an average size of 150 nm. After chemical dealloying of the Au–Sn alloy film, SEM images of the NPG film completely covering the surface of the Ni foam are shown in Fig. 1G–I. Comparing Fig. 1C with Fig. 1I, it is easily seen that the electrodeposition process followed by chemical dealloying of the Au–Sn alloy film results in a significant morphology change of the Ni foam surface, demonstrating the efficient formation of an NPG film. The high resolution SEM image (Fig. 1J) reveals that the film is composed of sponge-like bicontinuous nanostructures, which consist of interconnected ligaments and nanopores. The ligament size is about 50–100 nm and the pore size is 30–90 nm. The amount of Au on the Ni foam can be calculated from the mass difference between the bare Ni foam and the NPG-coated Ni foam. Therefore, the Au loading on the Ni foam is determined to be 150 μg cm^{-2}.

The crystal phase of the samples was examined by XRD, whereby the bare Ni foam shows three diffraction peaks at $2\theta = 44.3°$, 51.8° and 76.2° (Fig. 2, black line). These peaks can be indexed to the (111), (200) and (220) planes of the face centered