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Nickel hexacyanoferrate flower-like nanosheets coated three dimensional porous nickel films as binder-free electrodes for neutral electrolyte supercapacitors

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ABSTRACT

Nickel hexacyanoferrate (NiHCF) flower-like nanosheets coated three dimensional (3D) hierarchical porous Ni composite films are successfully prepared by the combination of hydrogen-bubble template electro-deposition and electrochemical polymerization methods. The novel 3D porous NiHCF/Ni composite films demonstrate excellent electrochemical performance as binder-free integrated electrodes for supercapacitors in KNO_3 neutral electrolyte. Comparing to the NiHCF coated on smooth Ni film, the 3D hierarchical porous NiHCF/Ni film electrodes exhibit about 10 times larger specific capacitance in KNO_3 neutral electrolyte. The 3D porous NiHCF/Ni film electrodes also illustrate good long-term stability for about 18,000 charge-discharge cycles. The improvement of electrochemical performance might be ascribed to the large specific area, highly conductive pathway and fast ion diffusion for the flower-like NiHCF nanosheets directly growth on the 3D hierarchical porous interconnected conductive scaffold current collectors.

1. Introduction

Supercapacitors (electrochemical capacitors) have been attracted intensive attention as energy storage devices since they possess much higher power density and cyclic stability than traditional batteries as well as higher energy density than conventional dielectric capacitors [1–6]. Nickel hexacyanoferrate (NiHCF) is considered to be one of the most promising electrode materials for electrochemical capacitors, which could switch between reduced and oxidized states in neutral electrolyte containing alkali metal cations such as potassium, lithium, and sodium [7–10]. Comparing to the acid or base electrolyte popularly used for transition metal oxide electrodes, the neutral electrolyte does not easily corrode other components. In addition, the neutral aqueous electrolyte is much cheaper than the organic electrolyte. However, the low electrical conductivity of NiHCF like to the transition metal oxide electrode materials would make against the electrochemical performance. Moreover, the traditional electrode fabrication method would easily result in “dead area” of active materials by mixing the electroactive materials with non-conductive polymer binder then deposited on the metallic foil or foam current collectors [2,11].

Recently, three dimensional (3D) porous micro/nanostructured interconnected metal matrix composite electrodes without binder have attracted great attention for electrochemical energy storage and conversion, in which the active materials are directly grown on the metal substrate and interconnected with the 3D conductive metal nanostructure scaffold [12–16]. The highly open porous structure would enlarge specific surface area and utilization of electroactive materials. In addition, the 3D porous conductive network supported active materials would not only provide a highly conductive pathway for electrons and facilitate the ion transport but also reduce the contact resistance between active materials and current collectors. A lot of methods have been developed to fabricate 3D porous metals such as de-alloy, H_2 gas bubble dynamic template, carbon template, SiO_2 template, polymer template, etc [16–20]. Among them, H_2 gas bubble dynamic template is a facile and cost-effective method since there

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is no necessary to remove other materials to form porous structure and the fabrication of highly open porous metal is only one electrodeposition process.

Herein, flower-like NiHCF nanosheets are directly fabricated on the 3D porous Ni interconnected current collectors as integrated film electrodes for supercapacitors with neutral electrolyte. The structure and performance of the 3D porous NiHCF/Ni films are also investigated.

2. Experimental

2.1. Preparation of 3D porous NiHCF/Ni films

Porous Ni film was prepared through a hydrogen bubble template electrochemical deposition [20]. Nickel foil was used as the cathode and substrate for porous Ni electrochemical deposition after cleaning five minutes with 1 M HCl, ethanol and deionized water. And a large area of nickel foil was processed as the anode. The distance between cathode and anode was kept at 2 cm. Porous Ni was deposited on the surface of the Ni substrate under a constant current density of 5 A/cm^2 for 60 s by using DC power PSW80-13.5 with electrolyte consisting of 0.2 M $NiCl_2$ and 2 M NH_4Cl at room temperature. After the electro-deposition, the porous Ni was thoroughly rinsed with secondary deionized water in order to remove the electrolyte solution from inside the pores for five times, dried first with an airflow and then in a vacuum oven at 50 °C for 5 h.

NiHCF films were prepared using electrochemical polymerization method [10,21]. The as-prepared porous Ni or smooth Ni foil substrate as the working electrode, a large area platinum foil as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Potentials were reported with respect to the SCE reference electrode. The electrochemical polymerization deposition experiments were performed in a freshly prepared solution of 0.5 mM $NiSO_4$, 0.5 mM $K_3Fe(CN)_6$ and 0.1 M K_2SO_4 under quiescent conditions. Electro-polymerization of NiHCF film was carried out potention dynamically by subjecting the working electrode to potential cycling in the potential range of 0–0.85 V at a scan rate of 100 mV s^{-1} for 100 cycles. After deposition, the NiHCF films were rinsed with secondary deionized water in order to remove the electrolyte solution for five times and then dried with airflow.

2.2. Characterization of 3D porous NiHCF/Ni films

The crystalline phase of the films were characterized by X-ray powder diffraction (XRD; Rigaku X-ray Diffractometer with Cu-Ka (1.5418 Å) from 10 to 90° at a scanning speed of 5° min^{-1} operating at 30 kV and 20 mA. The morphology observation was carried using Field Emission Scanning Electron Microscopy (FESEM, Nova NanoSEM 450). The Fourier transform infrared spectrum (FTIR) was recorded using a VERTEX 70 spectrometer. The spectra were collected from 4000 to 400 cm^{-1} with 4 cm^{-1} resolution over 40 scans. All spectra were collected against the background spectrum of KBr.

2.3. Electrochemical test of 3D porous NiHCF/Ni films

Before electrochemical measurements were performed, the samples were immersed in 1 M KNO_3 solution for 5 h. Electrochemical measurements were carried out with a Zahner Zennium electrochemical workstation using a conventional three-electrode electrochemical cell in 1 M KNO_3 solution as electrolyte. The as-prepared NiHCF film electrode was used as the working electrode, the potential was referred to a saturated calomel electrode (SCE) and a platinum foil was set as the counter electrode. Cyclic voltammetry was conducted on each sample at various scan rates over a range of 0.01–0.1 V s^{-1}. Galvanostatic charge–discharge experiments were carried out at different current densities.

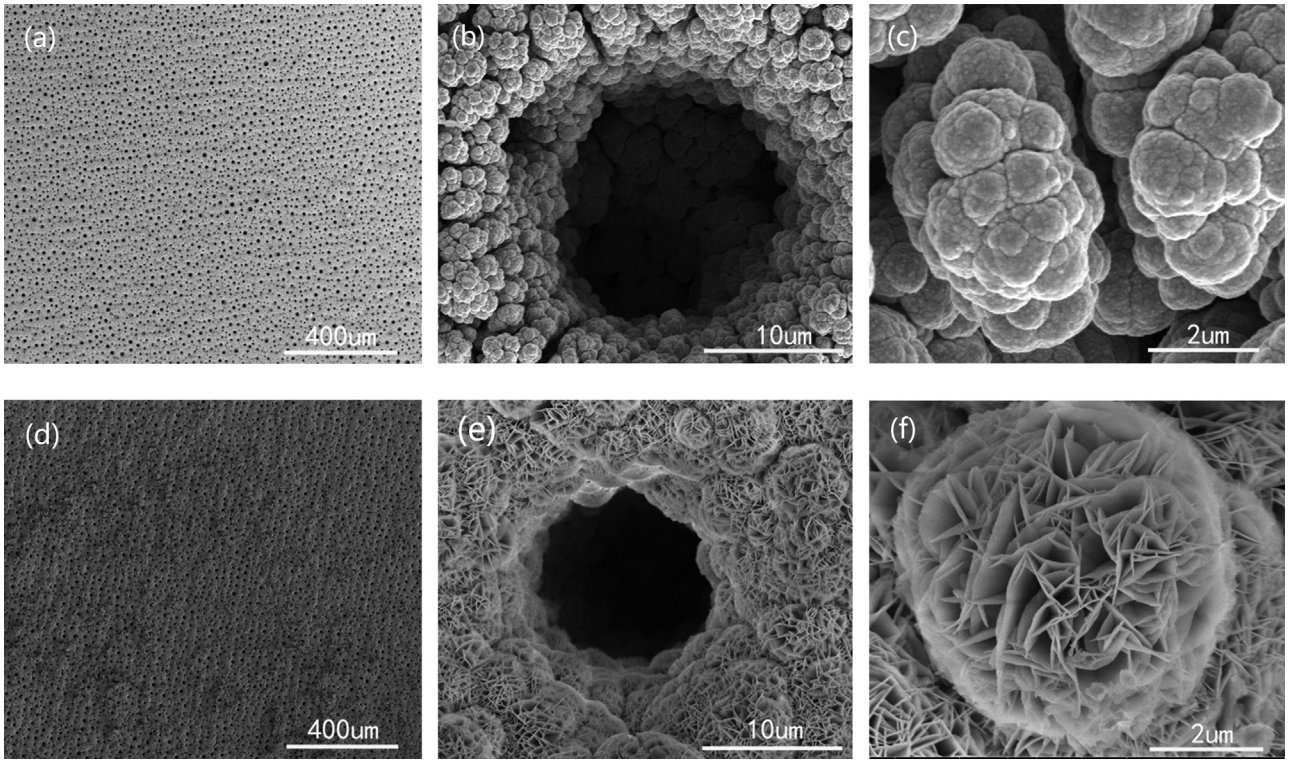

Fig. 1. SEM images of porous Ni films (a–c) before and (d–f) after coating NiHCF.