



Electrochemical characteristics of nano-graphene on a macroporous electrically conductive network prepared by hydrothermal carbonization



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ABSTRACT

Nano-graphene is fabricated on a macroporous electrical conductive network by hydrothermal carburization and subsequent annealing in Ar and the electrochemical characteristics are studied systematically in an alkaline electrolyte. The nano-graphene on the nickel particles improve the electrochemical properties of the three-dimensional (3D) electrode, especially the solution resistance, ion adsorption/desorption processes due to the large surface area and large surface defect concentration, as well as stability in the electrolyte. The novel 3D electrode has excellent electrochemical properties and large potential in energy storage and photoelectrochemical devices.

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1. Introduction

The merits of three dimensional (3D) structures with short transport lengths and high surface-to-volume ratios are more obvious as on-board power sources become increasingly smaller. The 3D architectures enable better utilization of space in energy storage devices enabling a smaller footprint while retaining large power and energy densities [1–6]. In 3D energy devices, the three-dimensional electrode is the basic and important component which affects the performance of the energy device. In this respect, the combination of rechargeable devices such as batteries and supercapacitors fabricated in a 3D architecture by microelectromechanical (MEMS) techniques is a good direction. Different kinds of 3D architectures such as interdigital structures, nanometer- or micrometer-sized wire arrays, and microchannel plates (MCP) can be fabricated on silicon by standard MEMS techniques [7–18].

In addition to the electrode architecture, the choice of the electrode materials is crucial. Carbon materials such as active carbon, fullerene, carbon nanotubes, and graphene have been extensively studied because of their potential applications in energy storage, solar cells, sensors, and catalysts [19–21]. Carbon-based electroactive materials with small size and abundant surface area provide large electroactive regions and short diffusion paths for efficient access by the electrolyte to the electrode. In particular, graphene, a single layer of carbon atoms arranged in a honeycomb lattice, has the desirable 2D structure boasting high electrical and thermal conductivity, mechanical strength, and large specific surface area [22]. Recently, 3D graphene structures have attracted increasing attention due to the high porosity and large specific area [23–25], and the 3D architecture based on graphene can be as a network to produce the pass channel for fast electron and ion transport. It is suitable for future applications in energy, catalysis, sensing, and biomedical engineering and science for 3D graphene structure due to its excellent electrochemical properties [26–28]. There are several approaches to convert 2D graphene into a 3D architecture, for example, by using a template, layer stacking, and chemical vapor deposition (CVD) [29,30]. For example, a 3D graphene foam can be synthesized by CVD using nickel foam as the porous template on which graphene is deposited by CVD followed by removal of the template to form the 3D graphene foam.

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However, fabrication of 3D graphene foam is hindered by spontaneous agglomeration and restacking of the graphene nanosheets due to the large Van der Waals attraction between adjacent sheets [31]. Aggregation of graphene degrades the properties such as the specific surface area and ion transport.

3D Si architectures, such as Si microchannel plates (SiMCP), can be formed by standard MEMS techniques [32–34]. The SiMCP is a perforated through-hole substrate which can be formed by photo-assisted electro-chemical etching followed by electrochemical peeling from the Si substrate to form the free-standing stable layered structure. The SiMCP has a big area ratio (>70%) and aspect ratio (length/diameter of hole >40 or more) and the surface area gain can be larger than 100. After electroless plating of nickel, the 3D macroporous electrically conductive network (MECN) is formed and it has good stability in alkaline media and can even be annealed at a high temperature in subsequent processing steps. Hence, the MECN has been employed to fabricate 3D nano-graphene by hydrothermal carbonization [35] and the structure delivers better performance pertaining to field emission and supercapacitance [36,37]. Such as, after the active material Co (OH)₂ deposited on the nano-graphene coated MECN, the 3D electrodes exhibit a fast electron and ion transport properties and demonstrate the excellent stability and durability. However, it is necessary to understand the electrochemical properties of the 3D graphene structure on MECN in order to provide insights into the fabrication of future high-performance 3D energy devices. In this work, the electrochemical properties of 3D nano-graphene prepared on MECN are studied systemically by electrochemical methods.

2. Experimental details

All the chemical reagents were analytical grade (AR) and used as received without further purification. Nickel chloride hexahydrate (NiCl₂·6H₂O) and ammonium chloride (NH₄Cl) were purchased from Aladdin Reagent and triethylene glycol (C₆H₁₄O₄), sodium hypophosphite monohydrate (NaH₂PO₂·H₂O), ethanol, and other reagents were bought from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the experiments.

A p-type (100) silicon wafer with a thickness of 525 μm was used and the standard microelectronics fabrication steps were implemented to produce the SiMCP. The steps included thermal oxidation to produce a masking layer and 3 μm × 3 μm squares were patterned by lithography and wet etching. The patterned wafer was pre-etched in a tetramethyl ammonium hydroxide (TMAH) solution (25% at 85 °C) and anodized on a computer-controlled photo-assisted electrochemical system. More details about the process can be found in Refs. 33 and 34. The SiMCP was cut into 1 cm × 1 cm square pieces for further processing.

Electroless nickel plating was performed. The SiMCP was dipped in diluted HF for 30 s to remove the native oxide and soaked in a buffer solution (0.1% Triton X-100 solution) for 30 s to decrease the inner stress and enhance wetting prior to immersion in a plating bath for 20 min at 90 °C. The plating medium was prepared by dissolving 6 g of NiCl₂·6H₂O, 10 g of NH₄Cl, and 2 g of NaH₂PO₂·H₂O in 200 ml of deionized water to form a green mixture. An appropriate amount of NH₄OH was added to adjust the pH 8–10 and it was stirred for 30 min. The nickel-coated SiMCP (MECN) was taken out and rinsed with water again.

Sodium acetate trihydrate was dissolved in triethylene glycol [CH₃COONa·3H₂O: C₆H₁₄O₄ = 1:10] and stirred magnetically for 30 minutes. The MECNs were introduced into the solution and sonicated for 5 minutes to fill the microchannels in the MECNs with the solution. The solution and MECNs were then transferred to a Teflon-sealed stainless steel autoclave, sealed tightly, inserted

in a vacuum oven heated to 250 °C, and kept at that temperature for 1–8 hours to produce different samples of the carbon-nickel alloy (NiC)/Ni/SiMCPs (designated as NiC-MCP). The samples were cooled in the autoclave to room temperature, taken out, rinsed with deionized water for 10 minutes, and vacuum dried at 80 °C. Afterwards, the NiC-MCPs were placed in a tube furnace at 650 °C and annealed in argon for 1 hour to cover the inner channels and surface of the MECNs with a nano-graphene layer (labeled as NG-MCP).

The morphology and microstructure of the samples were examined by scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan) and high-resolution transmission electron microscopy (HRTEM; Philips Tecnanai G2 F30) and the crystal structure was determined by X-ray diffraction (XRD, Rigaku, RINT2000, Japan). The electromechanical tests were performed on a CHI660D electrochemical workstation (Shanghai Chenhua CHI660D) in the three-electrode mode in which the sample, platinum electrode, and saturated calomel electrode (SCE) served as the working electrode, counter electrode, and reference electrode respectively. The samples were exposed to 1 mol L⁻¹ KOH electrolyte at room temperature (25 °C). Cyclic voltammograms (CV) were acquired in the potential range between -1.2 and 0.6 V vs. SCE at different scanning rates from 10 to 150 mV s⁻¹. The Tafel plots were obtained from the potentiodynamic polarization tests conducted at sweeping rates of 1 mV s⁻¹ in the anodic direction. The data in the Tafel plots in the range of ±200 mV from the open circuit potential were selected to evaluate the corrosion behavior. Electrochemical impedance spectra (EIS) was performed in the frequency range from 1 to 10,000 Hz at the open circuit potential (OCP). In the Mott-Schottky analysis, the impedance-potential curves were obtained by sweeping the potential in the positive direction at an excitation voltage of 5 mV and frequencies from 1 to 1000 Hz. The data were normalized by the foot print area.

3. Results and discussion

The top and cross-sectional views of the SiMCP are shown in the SEM images in Fig. 1(a) and (b). The microchannels have a depth of around 200 μm and size of 5 × 5 μm giving an aspect ratio of the microchannels of about 40. After electroless nickel plating, the surface and side-wall of the SiMCPs are coated uniformly with a thin disordered nickel layer with thickness about 0.5 μm (Fig. 1c and d) composed of porous nickel grains with a size of about 50 nm. Since the porous nickel balls are deposited on the outer and inner surfaces of the SiMCP and the porosity of the Ni electrode, the surface area of the 3D nickel layer increases by almost 100 times [22].

Fig. 1e–h depict the top-view images of the 3D NiC-MCPs prepared for different hydrothermal time from 1 to 8 hours. The Ni-C alloy layer becomes thicker with time. When carbon is introduced to the Ni layer during hydrothermal carbonization, the thickness of the Ni-C layer increases from about 1 μm (1 h, Fig. 1e) to about 1.5 μm (3 h, Fig. 1f). The wall thickness of the Ni-C layer reaches about 2 and 2.5 μm after 6 and 8 h, respectively. Local preferential growth is observed because the thick silicon layer is retained in these regions during photo-assisted electrochemical etching to form the SiMCP (Fig. 1a), for example, at the cross points and middle of the wall. A large amount of Ni is deposited on the projection of silicon structure during electroless Ni plating (Fig. 1c). The thicker Ni layer can be inserted with more carbon during hydrothermal carbonization and the Ni-C layer can expand perpendicular to the channel direction or along the channel direction at the cross points and middle of the wall (Fig. 1e–h). After hydrothermal carbonization for 8 h, the cubic holes in the SiMCP with a length of 5 μm change to irregular channel and the side length decreases to about 2.5 μm due to expansion of the Ni-C

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