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The effect of graphene coated nickel foam on the microstructures of NiO and their supercapacitor performance

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ABSTRACT

Cotton-like NiO is formed on the surface of bare Ni foam after hydrothermal process and calcination process, while ultrathin NiO nanoflakes occur on Ni foam coated with graphene. The high specific capacitance of 1782 F g^{-1} at 1 A g^{-1} and 90.2% capacity retention at 1 A g^{-1} after 5000 cycles charge-discharge test are found. The graphene induces the high electrical conductivity and excellent interfacial contact, in addition, the graphene facilitates the forming of ultrathin NiO nanoflakes which result in huge pseudocapacitance due to large surface area and abundant mesoporous. The unique microstructure characteristic promotes interfacial electron transport in the electrode material and improves ion diffusion during the electrochemical reaction process.

1. Introduction

Recently, more and more researchers have paid close attention to develop efficient energy storage and transform devices due to the requirements of environment-friendly and renewable energy [1]. Supercapacitors are considered as the most attractive energy storage devices due to their fast recharge capability, high power density and long cycle life in the application [2]. Generally, the supercapacitors could be divided into electric double-layer capacitors and pseudo-capacitors based on two kinds of charge-storage mechanisms. Energy storage of the former comes from reversible ion adsorption at the electrode/electrolyte interface, while the capacitance in pseudo-capacitors is achieved by reversible faradaic redox reaction on the surface of electroactive materials. The synergy of the two mechanisms also will induce a high specific capacitance. For example, the synthetic Co_3O_4 nanosheets on Ni foam electrode showed an ultrahigh specific capacitance of 6469 F g^{-1} at a current density of 5 mA cm^{-2} due to the Faradic capacitance from the redox reaction and electrical double-layer capacitance [3]. NiO was regarded as the high performance electrode material for supercapacitors due to its high theoretical capacitance and low cost [4,5]. NiO was easily obtained by facile synthesis process for electrode material and exhibited the high specific capacitance in alkaline electrolyte systems due to its relatively higher electrical conductivity than other metal oxides or hydroxides [6,7]. The hierarchical mesoporous rose-like NiO nanosheets [8], porous NiO nanowall arrays [9], mesoporous NiO microspherical structures [10], NiO nanowires [11], NiO nanoflakes [12] and porous hollow spheres of NiO nanosheets [13] showed the excellent electrochemical performance and stable cycle lifetime. It was worth noting that three-dimensional (3D) NiO nanotube with a highly porous structure arrays on Ni foam exhibited a high capacitance of 675 F g^{-1} at the 2 A g^{-1} as well as good cycling stability [14]. This superior electrochemical performance of NiO nanotubes electrode could be ascribed to the synergetic effect of its open tubular architectures and the short diffusion length which facilitated reaction of electrode material as supercapacitor [15]. Moreover, the specific capacitance of the NiO electrode depends strongly on the proper pore structures for high power density during charging/discharging operation. Mesoporous NiO electrode with a bimodal pore size distribution was regarded as a promising application for supercapacitors [16]. However, the low electrical conductivity of the NiO electrode would also induce high internal resistance and decreased performance for the electrochemical reaction [17]. The carbon nanotubes (CNTs) and graphene materials show good conductivity and high chemical stability. The excellent combination of vertically-aligned CNTs forests and reduced graphene oxide (RGO) sheets on Ni foam by combination of electrophoretic deposition (EPD) and floating catalyst chemical vapor deposition (FCCVD) enhanced significantly electron transfer during the charge/discharge process and improved supercapacitor performance of obtained electrode [18]. 3D RGO-CNT-polyaniline hybrid fabricated by combining EPD and FCCVD also displayed very high specific capacitance [19]. The RGO-CNT grown on carbon fiber (CF) fabricated by a combination of EPD and CVD displayed 4 times higher specific

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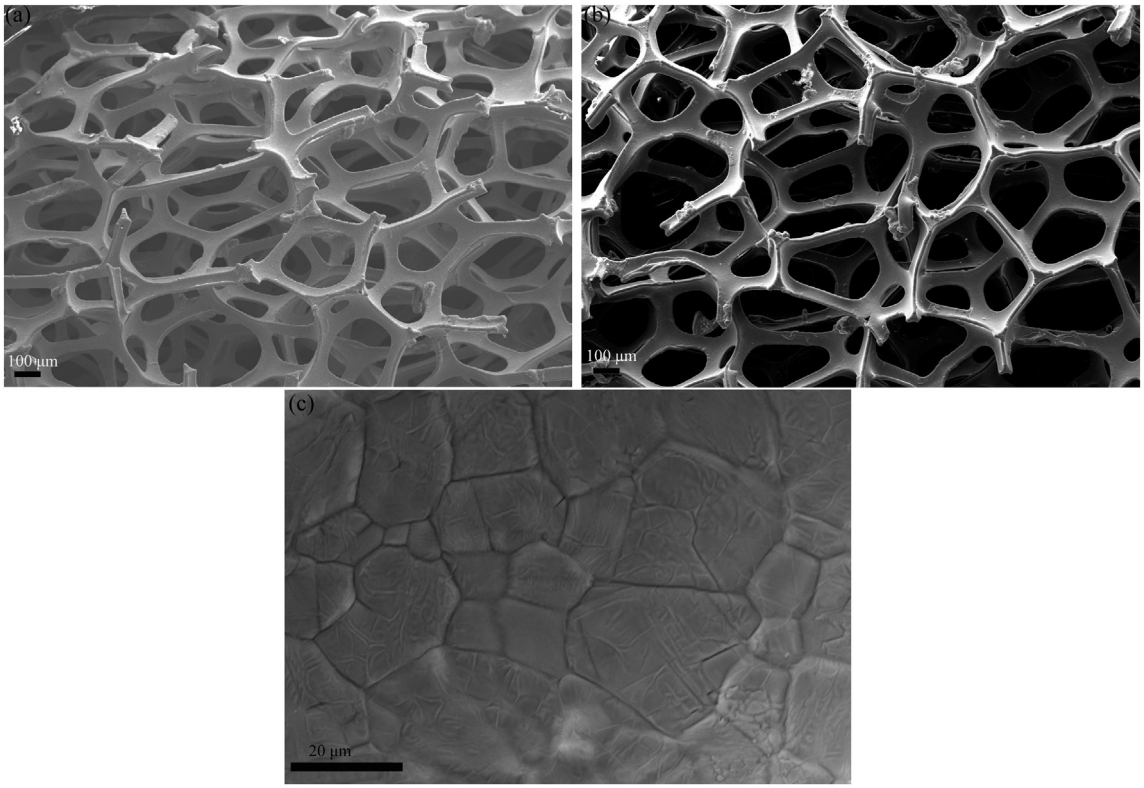

Fig. 1. SEM images of (a) bare Ni foam and (b, c) Ni foam coated with graphene.

capacitance than pure CF [20]. The graphene was studied extensively and could improve the electrical conductivity of metal oxides due to its high conductivity, electrochemical stability, high surface area and excellent mechanical property [21]. 3D MnO_2-graphene-CNT hybrid obtained by combining electrochemical deposition (ELD)-EPD and CVD showed higher specific capacitance than MnO_2-GO [22]. 3D MnO_2/graphene hybrid by electrodeposition and CVD exhibited a high specific capacitance of 326.33 F g^{-1} and good cycling stability [23]. Recent study showed that graphene nanosheets wrapped by porous NiO spheres also improved electrochemical performance as electrode material for supercapacitor due to the high surface area and the synergistic effects between the conductive graphene and porous NiO spheres [24]. NiO nanoparticle@RGO sheets composite electrode exhibited a high capacitance of 689 F g^{-1} at a current density of 0.8 A g^{-1} and high coulombic efficiency [25]. It was suggested that the pseudocapacitive behavior of NiO@graphene composites could be mainly attributed to reversible Faradaic transitions of Ni(II)/Ni(III) which greatly improved the capacitance of the electrodes [26].

The above investigations show that graphene catalysts might affect the microstructures of the oxides in the preparation process. In order to investigate the influence of the graphene coating on the microstructure of NiO during hydrothermal process and pseudocapacitance behavior, in the present study, Ni foam was coated with graphene by CVD. Then the microstructures of synthesized NiO on bare Ni foam and Ni foam coated with graphene on the supercapacitor performance were investigated.

2. Experimental methods

2.1. Materials preparation

Ni foam (4 cm × 2 cm × 1 mm) was carefully cleaned with 3 M HCl solution in the ultrasound bath for 20 min for removing the surface Ni oxide layer, and then washed with deionized water and absolute ethanol for several times. Graphene coating was formed on the surface of Ni foam according to Ref. [27].

Pre-cleaned Ni foam or obtained Ni foam coated with graphene was immersed in an ethanolic solution containing 20 mM (Ni $(OCOCH_3)\cdot 4H_2O$) at 60 °C for 30 min, respectively. Then they were air-dried and annealed at 280 °C for 30 min to obtain a NiO nanoseed layer. A piece of Ni foam or Ni foam coated with graphene with nanoseed layer was transferred into a Teflon-lined stainless steel autoclave containing 100 mL homogeneous pink solution mixed with 12 mM of nickel nitrate hexahydrate and 12 mM hexamethylenetetramine. The autoclave was capped and maintained at 120 °C for 18 h. The obtained samples were then taken out from the growth solution and rinsed with deionized water several times. Finally, the samples were further annealed at 400 °C for 1 h in argon environment during calcination process. The average loading density of NiO on bare Ni foam and Ni foam coated with graphene was about 1.32 and 1.55 mg cm^{-2}, respectively. When calculating the gravimetric specific capacitances of the electrodes, the mass of Ni foam was subtracted and only mass of NiO and graphene was used as the total mass of the active materials.

2.2. Material characterization

The crystallography structures of the products were determined by a Rigaku Ultima IV diffractometer using Cu K_α (0.154056 nm) and radiation at 40 kV and 40 mA. The microstructures of each synthetic sample were observed by field emission scanning electron microscopy (FE-SEM) of LEO-1530. The morphologies and structures were also observed with transmission electron microscopy (TEM and HRTEM JEM-2010 FEF; 200 kV). The N_2 adsorption–desorption values were determined by Brunauer–Emmett–Teller (BET) measurements using an ASAP-2010 surface area analyzer.

2.3. Electrochemical characterizations

The electrochemical measurements were performed by three-electrode cell system using a CHI 660E electrochemical workstation in 2 M