Electrochemical reduction approach-based 3D graphene/Ni(OH)$_2$ electrode for high-performance supercapacitors

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ABSTRACT

Using a simple electrochemical reduction approach, we have produced three-dimensional (3D) graphene foam having high conductivity and well-defined macroporous structure. Through a hydrothermal process, Ni(OH)$_2$ sheets are grown in-situ onto the graphene surface. This monolithic 3D graphene/Ni(OH)$_2$ composite is used as the free-standing electrode for supercapacitor application; it shows a high specific capacitance of 183.1 F g^{-1} (based on the total mass of the electrode), along with excellent rate capability and cycle performance. The asymmetric supercapacitor based on the 3D graphene/Ni(OH)$_2$ as a positive electrode and active carbon (AC) as a negative electrode is also assembled and it exhibits a specific capacitance of 148.3 F g^{-1} at 0.56 A g^{-1} and a high energy density of 52.7 W h kg^{-1} at a power density of 444.4 W kg^{-1}. Moreover, 3D graphene/Ni(OH)$_2$//AC has a good cycle stability (87.9% capacitance retention after 1000 cycles), making it promising as one of the most attractive candidates for electrochemical energy storage. This excellent electrochemical performance results from the multiplexed 3D graphene network facilitating electron transport; the interlaced Ni(OH)$_2$ sheets shorten ion diffusion paths and facilitate the rapid migration of electrolyte ions.

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1. Introduction

The energy and power densities of energy storage devices need to be improved to meet the growing power demand in many fields, such as cordless electric tools, various micro devices, power backup, and industrial energy management [1–3]. In this context, supercapacitors (SCs) are considered as promising candidates for energy storage due to their high power performance, long life cycle, and low maintenance cost [4–7]. However, SCs are still not capable of delivering high energy densities comparable to those of lithium ion batteries, and this drawback restricts the use of supercapacitors mainly to high-power applications, such as emergency power supplies, hybrid vehicles, and portable electronics for military devices [8–12]. The low output energy density from SCs, due to poor stability, low conductivity and large volume change of the electrodes, is the major hindrance to practical application of SCs [13]. Hence, development of novel electrode materials, which possess high conductivity, large specific surface area, and short electron and ion diffusion pathways, is important for improving power production of SCs.

In particular, the structure of the electrode directly affects its electrochemical properties. Generally, the electrochemical electrode is planar. Such flat (two-dimensional) electrodes suffer from inadequate contact with electrode active materials and from low surface-area-utilization efficiency. Numerous efforts have been made to design three-dimensional (3D) electrodes, such as Ni foam; however, due to their high weight and large space volume, the gravimetric capacitance with respect to the total mass of the electrode is very low. So, a high-strength, light-weight and binder-free electrode material is more desirable for electronic applications.

Graphene, an ideal electrical material [14–18], can not only be used as a graphene-based composite electrode, involving graphene/NiO [19], graphene/Co$_3$O$_4$ [20], graphene/SnO$_2$ [21], graphene/Co(OH)$_2$ [22], MnO$_2$/graphene/carbon nanotubes [23], and graphene/Fe$_2$O$_3$ [24], but also work as a conductive matrix for anchoring nanoparticles, such as graphene composite film [25], graphene papers [26–28] and 3D graphene materials [29,30]. 3D graphene, which facilitates ion transport by providing a smaller resistance and shorter diffusion pathways, is strongly recommended for the fabrication of advanced electrochemical capacitors

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[31]. Therefore, construction of 3D graphene networks is attracting considerable attention. However, the conductivity of graphene is largely compromised by the chemical groups and defects introduced during the synthesis process [32,33]. Furthermore, the aggregation and restacking of graphene nanosheets during processing leads to significantly reduced surface areas, making it difficult for ions to gain access to the electrode surfaces. The recently reported electrochemical reduction-grown graphene foam promises to mitigate the above problems that inhibit the performance of graphene composites. Being different from chemical vapor deposition (CVD) and chemical reduction, the electrochemical method has no need for hazardous chemicals as reductants or rapid heat-treatment at high temperature; it proceeds under mild conditions. Therefore, 3D graphene foam synthesized by the electrochemically controlled reduction of graphene oxide (GO) greatly decreases defects and intersheet junctions due to their highly continuous and conductive properties.

$Ni(OH)_2$ is a competitive electrode material because of its high theoretical specific capacitance ($2082 \, F \, g^{-1}$) [34], excellent redox activity [35], and good stability in alkaline electrolyte [36]. $Ni(OH)_2$-based nanocomposites are extensively employed in SCs [37], electrochemical sensing [38], lithium-ion batteries [39] and fuel cells [40]. Herein, we demonstrate a facile and controlled electrochemical reduction method to synthesize 3D graphene foam. This novel 3D macroporous electrode is a free-standing, flexible, conductive and monolithic graphene foam coated with active $Ni(OH)_2$, which takes full advantage of the synergistic effects between graphene sheets and $Ni(OH)_2$. 3D graphene/$Ni(OH)_2$ composites show remarkably superior electrochemical performance than the standard planar carbon electrode owing to their ability to three-dimensionally interface with electrolyte, facilitate electron transfer, and provide multiplexed and highly conductive pathways.

2. Experiment section

2.1. Material synthesis

Synthesis of 3D graphene foam. GO was prepared from graphite powder by a modified Hummers method as described previously [41,42]. 50 mg GO was mixed with 50 mL distilled water and ultrasonicated for 1 h. The nickel foam after pretreatment was dipped into this solution repeatedly, and then GO was homogeneously coated onto the surface of Ni foam. After that, 3D graphene was obtained by a direct electrochemical reduction process. The electrochemical reduction of GO was carried out with a reduction potential of $-1.0 \, V$ in potassium biphthalate (KHP) solution (pH 4.003) in a standard three-electrode cell with saturated calomel electrode (SCE) and Pt foil as the reference and counter electrode, respectively. Subsequently, the Ni foam was removed from the HCl solution to leave an interconnected 3D graphene foam [43].

Preparation of graphene/$Ni(OH)_2$ sheets composite. 0.3 g of $NiCl_2$ and 0.4 g of hexamethylenetetramine (HMT) were dispersed

in 15 mL of deionized water to form a clear solution. The solution was put into a 50 mL capacity Teflon-lined autoclave, and the 3D graphene foam immersed into this solution, followed by heating in an oven at 140 °C for 12 h. Finally, the 3D graphene foam with light-green deposits was washed with deionized water and dried at 60 °C.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max Ultima III X-ray diffractometer with a Cu Kα radiation source ($\lambda = 0.15418 \, nm$) operated at 40 kV and 150 mA at a scanning step of $0.02°$ in the 2θ range of 15–85°. Transmission electron microscopy (TEM) observation was performed on a Philips CM-200 FEG with an accelerating voltage of 200 kV. Scanning electron microscopic (SEM) observation was performed on a Hitachi S-4800 scanning electron microscope with an Energy dispersive spectrometer (EDS). Raman measurements were performed with a Jobin Yvon HR800 micro-Raman spectrometer at 457.9 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5700 ESCA spectrometer with monochromated Al KR radiation (hv = 1486.6 eV). All XPS spectra were corrected by the C1s line at 284.5 eV.

2.3. Electrode preparation and electrochemical characterization

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and amperometry measurements were performed using a CHI660D electrochemical workstation. The 3D graphene/β-$Ni(OH)_2$ composite serves as the working electrode ($1 \, cm^2$), while a platinum foil electrode ($1 \, cm^2$) and a SCE were used as the counter and reference electrodes, respectively. $2.0 \, mol \, L^{-1}$ KOH solution was used as the electrolyte. EIS measurements were conducted in the frequency range from 0.01 Hz to 100 kHz at open circuit potential with an ac perturbation of 10 mV.

The asymmetric supercapacitor was measured with a two-electrode system, where 3D graphene/$Ni(OH)_2$ composite was the positive electrode, and AC mixed with 5%PTFE to disperse in 1-methyl-2-pyrrolidinone (NMP) and then coated onto a nickel foam substrate was the negative electrode. The two electrodes and a separator (cellulose acetate membrane) was measured in a $2.0 \, mol \, L^{-1}$ KOH aqueous solution.

3. Results and discussion

3.1. Formation process of 3D graphene/$Ni(OH)_2$ composites

Fig. 1 illustrates the preparation process of 3D graphene/$Ni(OH)_2$ nanoarchitectures. After dipping into GO solution several times, Ni foam is covered with GO homogeneously. Then the electrochemical reduction of GO is carried out in a standard three-electrode cell, and only GO in direct contact with a conducting Ni foam electrode is electrochemically reduced, provided the electrolyte (ions) has access to it. During the reduction process, more and more insulating GO transforms to

Fig. 1. Scheme for the synthesis of 3D graphene/$Ni(OH)_2$ composites. (a) The porous Ni foam substrate. (b) GO is homogeneously coated onto the surface of Ni foam after dipping repeatedly. (c) A few layers of graphene are formed on the porous nickel by electrochemical reduction. (d) 3D graphene network is synthesized after removing Ni foam. (e) $Ni(OH)_2$ sheets are directly grown onto 3D graphene.