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In situ growth of self-supported and defect-engineered carbon nanotube networks on 316L stainless steel as binder-free supercapacitors

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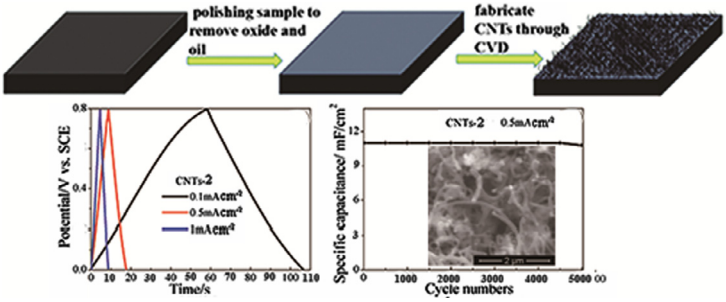
GRAPHICAL ABSTRACT



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ABSTRACT

Self-supported and defect-engineered carbon nanotube networks directly grown on 316L stainless steel are used for binder-free supercapacitors. In situ growth of the carbon nanotube networks on 316L stainless steel is obtained through the chemical vaporization deposition and thermal treatment to generate various defects. The relationship between the microstructures of carbon nanotube networks and electrochemical characteristics is investigated. The as-prepared carbon nanotube networks are characterized by scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and Raman analysis. Cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy tests are also carried out to evaluate their capacitive properties, suggesting that the electrochemical characteristics are significantly affected by annealing time. The carbon nanotube networks annealed at 500 ^{0}C for 2 h display high capacitance of 11 mF cm^{-2} and excellent cycling lifetime with capacitance retention ration 97% at the scan rate of 0.5 mA cm^{-2} for 5000 periods, which is attributed to the defect engineering increasing the defects of carbon nanotube networks, enhancing hydrophilic property and facilitating the transportation of electrolyte ions.

1. Introduction

Supercapacitor (SC) has attracted attentions due to high power density, high discharge currents, good stability, long life cycle and so on [1–3]. However, the energy density of SC is lower than traditional energy storage devices, such as rechargeable batteries, which makes it very difficult for SC to be applied in large capacity applications [4,5]. Hence, it is significative to develop novel electrodes in SC with high energy density and high power density.

Carbon nanotube (CNT) with unique architecture, excellent conductivity, and high surface area, is a prospective electrode material that mainly works through electric double-layer process without phase transformation [6–8]. Surface area with regular pore size,

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defects and particle size have strong effects on the performance of CNT [9]. Traditionally, carbon materials are usually supported by a conducting current collector (such as nickel foam, aluminium foil, silver and copper) [10–12]. During preparing electrodes, the addition of binders may block the nanotubes of CNT, decrease the electrolyte-accessible surface area and reduce the conductivity of electrodes, which can deteriorate the capacitance performance of CNT [13,14]. In addition, bad adhesion can increase the internal resistance between the CNT and the current collector, which can weaken the rate performance of CNT [15,16]. Thus, great efforts have been made to design self-supported and binder-free electrode materials to enhance the capacitance performance of CNT. The self-supported CNT materials can be directly used as electrodes without adding additional binders and conductive agents. Furthermore, in comparison with binder-needed counterparts, the rate performance and power density can be greatly enhanced by utilizing binder-free electrodes [17,18]. Recently, various approaches have been developed to improve the performance of CNT *via* structural functionalization, such as porous carbon, activated carbon and defective CNTs [19–21]. Some conventional chemical techniques, such as acid treatment, refluxing and sonication, can generate defects and functional groups, which may provide pseudocapacitance [22,23]. However, these synthetic methods are accompanied with complicate processes and require harsh reaction conditions. In contrast with these techniques, thermal treatment can form the active sites and remove the surface O-functionalities, which can improve the electrochemical properties of CNT [24].

CNT is usually fabricated by the chemical vaporization deposition (CVD) technique [25–27]. However, the method often requires additional catalysts, such as metal catalyst and organic catalyst, which are difficult to purge and have some influence on electrochemical performance of CNT [28,29]. Therefore, the defective carbon nanotube networks (CNTs) were in-situ grown on the surface of 316L stainless steel (SS) by CVD and heat treatment without additional catalysts. The self-supported and defect-engineered CNTs were directly used as binder-free supercapacitors. The defects in CNTs were controlled by annealing at different times. The relationship between different degree of defects in CNTs and electrochemical characteristics was investigated. Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used to extensively analyze the capacitive performance of CNTs, indicating that the electrochemical characteristics were significantly affected by annealing time.

2. Experimental

2.1. Chemicals and materials

All chemical reagents purchased from China National Pharmaceutical Group Corporation were analytical grade and used without further purification. AISI 316L stainless steel foils (Good fellow, 0.015 wt% C, 16–18 wt% Cr, 10–14 wt% Ni, 0.3 wt% Mo, and Fe balance) were cut into $10 \times 10 \times 0.5$ mm^3 strips. All SS samples were mechanically polished by sequential grinding with SiC abrasive paper (1000 and 2000 grade), ultrasonically cleaned in acetone, ethanol and double distilled water (DDW) for 10 min, as well as dried in N_2 stream prior to anodization.

2.2. Preparation of the defective CNTs on 316L stainless steel

The SS samples were treated by anodization process according to our previous report [30]. The samples and graphite foils acted as the anode and counter electrode, respectively. The SS strips were connected to the negative and positive terminals of a DC power supply. The sample was placed in anhydrous ethylene glycol (EG, 99.8%) solution containing 5 vol% perchloric acid ($HClO_4$, 70%) at a constant voltage of 20 V for 20 min. After the anodization was completed, the power supply was turned off. The SS electrode was removed, washed several times with DDW and dried.

Then the above samples were synthesized in a horizontal CVD reactor using argon (Ar) as the carrier gas. The CVD process was as follows: firstly, the samples were placed into a quartz tube furnace. The tube was primarily purified with a mixed flow of Ar and H_2 (5% H_2, 95% Ar) at the flow rate of 120 sccm to reduce the surface oxide during the temperature up to 800 °C. In the growth step, the flow rates of Ar/H_2 and C_2H_2 were 500 and 20 sccm at 750 °C, respectively, which were controlled by digital mass flow meters. After keeping at 750 °C for 1 h, the furnace was cooled down to room temperature naturally under Ar/H_2 atmospheres. Afterwards the samples were annealed at 500 °C for 1 h, 2 h and 3 h in air, which were labeled as CNTs-1, CNTs-2 and CNTs-3. The samples without thermal treatment were named CNTs-0.

2.3. Material characterization

The morphologies of the as-prepared samples were investigated by the field-emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano, Eindhoven, Netherlands) at an accelerating voltage of 15 kV and a working distance of 5 mm. The samples for the TEM characterization were scratched from the SS and dispersed ultrasonically in ethanol for 30 min. Then, a suspension drop was dripped onto a carbon-coated copper grid and dried in air. Transmission electron microscopy and high-resolution transmission electron microscopy (HRTEM) were performed (TEM, JEM-2100UHR STEM/EDS, JEOL, Japan). The wettability was detected by OCA15PRO. Raman spectra were collected on a Renishaw confocal microscopy Raman spectrometer equipped with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.) at a 532 nm of laser excitation wavelength. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA) equipped with a monochromatic Mg Kα source was performed to reveal the chemical composition.

2.4. Supercapacitor characterisation

Electrochemical measurements were all carried out using a CHI 660E electrochemical workstation (Shanghai, Chenhua). Cyclic voltammetry (CV), galvanostatic charge–discharge cycle (GCD) and electrochemical impedance spectroscopy (EIS) measurements were conducted by a conventional three electrode with the as-synthesized samples as the working electrode, a platinum plate (10×10 mm^2) as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All electrochemical measurements were performed in 1 M Na_2SO_4 electrolyte. CV curves were conducted over the potential range of 0 to 0.8 V (vs. SCE) at different scan rates. The capacitance of the electrode was measured *via* the GCD betwwen 0 to 0.8 V (vs. SCE) at constant current of 0.1 mA cm^{-2} while voltage and time were recorded. EIS was conducted at the open circuit potential in the frequency range of 10^5–10^{-2} Hz with an AC perturbation of 5 mV.

3. Results and discussion

3.1. Structure and crystalline of the CNTs

The synthetic process of CNTs was shown in Fig. 1. Typically, in situ growth of CNTs on 316L SS can be obtained through the CVD technique using acetylene as a carbon source. Then annealing treatment in air is carried out to improve their hydrophilicity and