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Ammonia strengthened graphene/CNT-wrapped polyaniline-nanofiber composites loaded with palladium nanoparticles for coin cell supercapacitors

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ABSTRACT

Supercapacitors with high specific capacitance, energy and power densities as well as high cycle stability are demonstrated in this work. A newly developed palladium nanoparticle loaded reduced graphene oxide/CNT hydrogel (rGO/CNT@Pd) was synthesized and combined with polyaniline nanofibers (rGO/CNT@Pd + PANI Nf). The prepared materials were synthesized by a hydrothermal route, simultaneously reducing graphene oxide and $PdCl_2$. Including pre-synthesized PANI nanofibers in the process led to formation of a 3D rGO/CNT matrix incorporating PANI and effectively preventing swelling/shrinkage damage during electrochemical testing. Subsequent ammonia treatment led to strengthening of the 3D matrix which further improved supercapacitor cycling stability. Material characterizations using scanning and transmission electron microscopy as well as X-ray diffraction and Raman spectroscopy were performed and Pd nanoparticle formation and uniform distribution in the rGO/CNT hydrogel was observed. The materials were used to construct CR2032 coin cell supercapacitors and tested by 2-electrode cyclic voltammetry and galvanostatic charge-discharge with 2 M H_2SO_4 electrolyte. Ammonia strengthened rGO/CNT@Pd + PANI Nf exhibited excellent electrochemical performance with a specific capacitance of 611.8 F g^{-1} and energy and power densities of 85 Wh kg^{-1} and 10.2 kW kg^{-1} at a current of 1.5 A g^{-1}. Ammonia treatment effectively increased the cycle life of the composite and 84.3% of capacitance was retained after 10000 charge-discharge cycles.

1. Introduction

In anticipation of a coming energy and ecologic crisis interest in the development of high performance, low cost and environmentally friendly energy storage has been growing steadily. One type of energy storage devices, so-called supercapacitors (SC), have attracted an enormous increase in research activity due to their potential application in modern technology. SCs are electrochemical energy storage devices that take an intermediary position between batteries and conventional dielectric capacitors. They typically possess high power densities (10 times that of generic batteries), high energy density (several orders higher than dielectric capacitors), fast charging (within seconds), excellent cycle stability, small size, and light weight [1–4]. Thus, SCs are an ideal solution for a large range of modern electronic applications such as portable systems, hybrid electric vehicles, memory protection in CMOS logic circuits, home-electronics, PCs, UPS in security alarm systems, remote sensing, smoke detectors et cetera [5–7].

Basic SCs are composed of two electrodes, an electrolyte and a separator between the electrodes. Performance of SCs is mainly determined by working voltage, specific capacitance, specific energy (energy density), specific power (power density) and cycle life. The primary factor that affects the performance of SCs is the choice of electrode materials. SCs store energy by two distinct physicochemical principles: Electrochemical double layer capacitance (EDLC) and pseudocapacitance. Thus, electrode materials used for SCs are typically divided into carbon based materials such as carbon nanotubes, graphene, and active carbons on the one hand as well as materials such as transition-metal oxides, hydroxides and conducting polymers on the other [8–11].

Carbon based SCs primarily rely on EDLC, storing and releasing energy by ion adsorption and desorption at the interface between

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electrode and electrolyte. Specific capacitance of this type of SC is determined by the ratio between the pore size of the active electrode material and the size of ions in the electrolyte, i.e. the electrochemically effective surface area. Carbon based electrochemical double layer SCs possess high power densities and long life cycles. But by relying exclusively on EDLC their area of application is limited. Pseudocapacitive SCs based on transition metal oxides, hydroxides or conducting polymers exhibit fast redox kinetics with relatively higher capacitance while their generally lower mechanical stability and cycle life are major limitations. However, electrodes based on composites of active carbon materials and pseudocapacitive materials combine the advantages of EDLCs and pseudocapacitors and were shown to be able overcome these shortcomings [12–17].

One hugely promising active carbon material is graphene, an atomically thin two-dimensional sheet of sp^2-hybridized carbon atoms arranged in a honeycomb crystal lattice. As the carbon component in electrode material composites, it offers high carrier mobility, large electrical conductivity and high specific surface area. It has been demonstrated that this high surface area leads to a large theoretic double layer capacitance of up to 21 $mFcm^{-2}$ [18–20]. Graphene has been prepared by various methods such as exfoliating graphite [21], thermal decomposition of SiC [22] or oxidation of graphite [23]. Conversion of graphite into graphene oxide (GO) and subsequent thermal or chemical reduction into reduced graphene oxide (rGO) is a facile and scalable way to produce large quantities of graphene [24–28]. However, due to van der Waals forces graphene sheets are prone to restacking, dramatically decreasing specific surface area which reduces achievable capacitance of the SC.

One approach, that has received intense research interest, is to produce 3D graphene structures. These structures consist of groups of 2D graphene formed or connected into well-defined 3D architectures. Important examples of 3D graphene include graphene foams [29], graphene networks [30] and graphene aero- and hydrogels [31–34]. Macroporous graphene hydrogels, in particular, can be produced by a classical hydrothermal method. Heat and extreme pressure of the hydrothermal process lead to reduction of the GO sheets and cross-links them into 3D structures due to the effect of van der Waals' forces, π–π stacking as well as hydrogen bonds of the aqueous medium [35]. Furthermore, studies have shown that the graphene gel structure can be strengthened by including metal salts or certain organic molecules in the hydrothermal process [36–38]. Han et al. [39] proposed a simple method to improve the stability of graphene hydrogel by soaking the material in ammonia solution at elevated temperatures. This led to formation of additional covalent C–N bonds between rGO sheets by reaction of ammonia with carboxyl/epoxy groups. The process was shown to increase the mechanical strength of the hydrogel significantly.

To improve the capacitive behavior further, graphene can be loaded with functional molecular spacers which prevent restacking and provide additional electrochemically active sites for adsorption of composite materials and ions. Such materials include noble metal nanoparticles (NPs) that prevent restacking of graphene sheets and, additionally, their good conductivity and electrochemical stability make them interesting candidates for materials in SCs [40]. Furthermore, noble metal NPs can facilitate effective transport of electrons from the faradic reactions of pseudocapacitors to the current collectors. Noble metal NPs usually include the platinum group, silver and gold. Up to now, mostly Ru [41,42], Pd [1,2,43], Pt [44,45], Ag [46,47] and Au [48,49] NPs have been studied as electrode materials for supercapacitors. Noble metal NPs themselves, however, do not show pseudocapacitive behavior. Instead they enhance the electrical double layer capacitance by providing larger electrochemically active surface areas for the adsorption of ions. However, due to their high cost, noble metal integration with other sustainable and cheap materials is considered one of the most attractive ways to optimize material properties and consumption [40].

Additionally, introducing polyaniline (PANI) in SC electrode material can greatly increase the capacitance of the SC. PANI is a well-known conducting polymer exhibiting good environmental stability, interesting electrochemical activity and unusual doping/dedoping chemistry [18]. PANI occurs in three idealized oxidation states: (i) leucoemeraldine, (ii) emeraldine and (iii) (per)nigraniline. Conductivity of PANI increases from the undoped insulating base form to the fully doped, conducting acid form. The polyemeraldine-salt is the most electrically conductive form with its imine nitrogens protonated. PANI is another important candidate for SC applications due to its relatively high electrical conductivity and high faradic reactivity. PANI based materials have been demonstrated to exhibit high pseudocapacitance. In particular, PANI-graphene composites prepared by various methods have recently been reported to yield high specific capacitance ranging from 200 to 900 $F\,g^{-1}$ [10,29,50–52].

In this work we report a novel and environmentally friendly approach to synthesize 3D graphene/CNT-wrapped polyaniline nanofiber composites decorated with palladium nanoparticles. This was achieved by a simple hydrothermal reduction route in which GO/CNT, mixed with pre-prepared PANI Nf, and $PdCl_2$ were simultaneously reduced. This method allows to wrap PANI Nf in an interconnected 3D graphene matrix that combines high conductivity with mechanical stability. Moreover, ammonia strengthening was used to further increase the mechanical stability of the 3D rGO/CNT matrix. This improves electrochemical cycle life of the electrode material by effectively hindering swelling/shrinking of PANI during (dis-)charging. CR2032 coin cell SCs using this new ammonia strengthened rGO/CNT@Pd PANI Nf composite as active material exhibit excellent electrochemical performances.

2. Experimental

2.1. Chemicals and materials

Graphite powder (K9) was purchased from Thai Carbon & Graphite Co., Ltd. Chemical vapor deposition derived CNT was obtained from Chiangmai University, Thailand. Sodium nitrate ($NaNO_3$, ≥99%), potassium permanganate ($KMnO_4$, ≥99%), aniline (≥99.5%), ammonium persulfate (APS, ≥ 98%) and palladium (II) chloride ($PdCl_2$, 99%) were purchased from Sigma Aldrich. Sulfuric acid (H_2SO_4, AR grade, 98%) and hydrochloric acid (HCl, AR grade, 37%) were supplied by RCL Labscan. Hydrogen peroxide (H_2O_2, AR grade, 30% w/w) was obtained from Chem-Supply.

2.2. Materials preparation

2.2.1. Graphene oxide/CNT

To prepare GO/CNT by a modified Hummers' method, 60 ml of concentrated sulfuric acid was added to 2 g graphite powder, 0.5 g CNT and 1.25 g $NaNO_3$. The mixture was transferred into an ice bath. After 25 min under mild agitation $KMnO_4$ (7.5 g) was added slowly and the mixture was kept in the ice bath for an additional 25 min. Following this, the mixture was heated and kept at 35 °C for 45 min until it formed a thick paste. Then, 70 ml of deionized water was added and the mixture was kept at 98 °C for another 45 min. Finally, the mixture was diluted with 350 ml DI water and 15 ml H_2O_2 (30% w/w) was added. The product was filtered and washed with DI water until the pH of the filtrate became neutral. (pH 7, measured with a Sartorius PP-20.). A rotary evaporator (IKA RV10) was used to