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RAPID COMMUNICATION

Bicontinuous nanotubular graphene-polypyrrole hybrid for high performance flexible supercapacitors

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Abstract
Conductive polymers, particularly polypyrrole (PPy), are emerging as promising electrode materials for flexible supercapacitors because of their high pseudocapacitance, low density, high mechanical flexibility and low material costs. However, the practical implementations of PPy based supercapacitors have been prevented by the poor charge/discharge rate capability and low cycle stability. In this study we report a novel three dimensional interconnected nanotubular graphene-PPy (nt-GPPy) hybrid by incorporating PPy into highly conductive and stable nanoporous graphene. The bicontinuous nanotubular hybrid material with a large specific surface area and high conductivity demonstrates significant enhancement in supercapacitance performance of PPy in terms of high specific capacitance, excellent cycling stability and high rate capability.
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Introduction

Among electrochemical energy storage devices, electrochemical supercapacitors offer several merits including high energy density, high power density and long cycle stability, which are expected to bridge a gap between secondary batteries with a low power density and conventional capacitor with a low energy density [1-5]. Based on the

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materials of the electrodes, the mechanisms of energy storage in electrochemical supercapactitors predominately include two ways: the electric double-layer capacitance (EDLC) and pseudocapacitance. Commonly, pseudocapacitance by a surface faradic process can be realized by fast and reversible redox reactions of transition metal oxides, such as $Ni(OH)_2$, Co_3O_4, RuO_2, MnO_2 and NiO, and conductive polymers, including polypyrrole (PPy), polyaniline and poly(3,4-ethylenedioxythiophene), while porous carbon and its derivative materials with a large specific surface area are mainly used as the electrodes of EDLC supercapacitors [5-16]. The demands of light weight and flexible energy storage devices for portable electronics have stimulated tremendous interests to develop new electrode materials. Conductive polymers, particularly PPy, are emerging as promising candidates because of the low mass density, mechanical flexibility, high pseudocapacitance and low material costs [15,16]. However, the practical implementations of PPy based supercapacitors have been prevented by the poor charge/discharge rate capability and low cycle stability [17-21]. To overcome these challenges, many PPy based composites have recently been developed by using macro/nanoporous carbon materials and porous metals as the reinforcements, aiming at the improvement in cycle stability and rate capability [21-26]. In those composites, porous supports offer a three-dimensional conductive pathway, facilitating charge transport effectively, and micro- and nano-size pore channels serve as reservoirs of electrolytes for short ion diffusion distance and low resistance. Additionally, nanoporous architectures supply a large effective surface area, benefiting high specific capacitance. Although high rate capability and stability of the nanoporous PPy composites have been the recent topic of intense studies, the overall specific or volumetric capacitances based on the total mass or volume of the composite electrodes are usually very low because of the large volumetric and/or mass fraction of the porous reinforcements and inefficient utilization of the active material limited by low effective specific surface area, which produce insuperable problems for practical applications.

Graphene, a monoatomic layer of sp^2 bonded carbon, poses the desired properties of ultra-large specific surface area, excellent electrical conductivity [27] and remarkable mechanical flexibility [28,29] for electrochemical supercapacitors. Electrochemical performance of conductive polymers, in term of capacitance values and cycle stability, is particularly enhanced by utilizing graphene and reduced graphene oxide (RGO) as conductive supports [24,30,31]. However, most research efforts in this area deal with discrete 2D graphene sheets composited with PPy [22,24,31], which cannot fully utilize the large surface area and high conductivity of graphene because of the ineffective stacking and disconnection of 2D graphene sheets. One of the most attractive and easily implementable processes to efficiently realize electrochemical properties of graphene and loaded active materials is to develop a 3D interconnected graphene network. Improvement in supercapacitor performance has been achieved in $Ni(OH)_2$/3D interconnected graphite network composites [32] and 3D graphene/PPy foams [33]. In this study we report the synthesis and supercapacitor performance of a novel 3D bicontinuous nanotubular graphene-polypyrrole (nt-GPPy) hybrid material with the significant improvement in energy storage of PPy. The nt-GPPy based supercapacitor shows high rate capability and specific capacitance while maintaining structure stability and geometrical integrity of the tubular nano architecture after long-time cycling.

Experimental procedure

Fabrication of nanotubular graphene

Nanotubular graphene was prepared by a nanoporous nickel based CVD approach, which has been detailed elsewhere [34]. Briefly, nanoporous nickel (np-Ni) with a pore size of ~10 nm, fabricated by dealloying 150 μm thick $Ni_{30}Mn_{70}$ alloy sheets, was used as the templates for CVD synthesis of graphene at 800 °C. Graphene continuously grew on ligament surface of np-Ni during the CVD process until the entire surface of ligaments covered by graphene and finally formed a Ni-graphene core-shell structure (graphene@np-Ni) with narrow pore size distribution and average ligament size of 380 nm. Nanotubular graphene@np-Ni hybrid was used as the template to deposit polypyrrole (PPy) on the outer side of the nanotubular graphene.

Fabrication of nanotubular graphene-PPy composite

The synthesis procedure of nanotubular graphene-PPy composite (nt-GPPy) is summarized in Figure 1. Nanoporous Ni-graphene-PPy (np-NiG/PPy) composite was constructed by electrochemically depositing polypyrrole into the graphene@np-Ni using a three-electrode system (Iviumstat electrochemical analyzer, Ivium Technology) with graphene@np-Ni as working electrode and platinum foil and Ag/AgCl as counter and reference electrodes, respectively.

Electrochemical deposition was performed using a cyclic voltametry method at a potential window of −0.5 to 0.9 V and a constant scan rate of 20 mV s^{-1} in an aqueous electrolyte containing 0.1 M pyrrole monomer and 0.2 M sodium-potassium hydrant tartrate [35]. The graphene@np-Ni template was uniformly coated with nanometer thick PPy and the loading amount of PPy in the hybrid structure was tuned by number of cyclic voltametry electrodepositing. The relationship of the deposition cycle with the mass and thickness of PPy and PPy/graphene ratios are listed in Table S1. The large curvature gradient of graphene results in a high density of topological lattice defects, which obviously enhance the wetting ability for easy deposition of PPy coatings [34,36]. Furthermore, since the pyrrole monomer is a hydrophobic solute in aqueous solutions, weakly hydrated pyrrole monomer solutes in hydrophilic aqueous solution are segregated from the solution and concentrated on hydrophobic surface [37] and hence a PPy layer can be formed as a continuous uniform coating on the graphene surface.

After deposition, the resulting composite was washed with deionized water to remove impurity and excessive pyrrole monomer residue inside pore channels. Finally, 3D interconnected hollow nanotubular microstructure of nt-GPPy composite was achieved by the dissolution of Ni in 3 M

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