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Full Length Article

Novel silicon nanoparticles with nitrogen-doped carbon shell dispersed in nitrogen-doped graphene and CNTs hybrid electrode for lithium ion battery

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ABSTRACT

A Si-rGO/NCT composite, in which Si nanoparticles (SiNPs) are enwrapped with N-doped carbon and combine with N-doped graphene and CNTs as conductive matrices synthesized by simple solution-mixing and carbonization process with pyrolyzing melamine formaldehyde resin (MFR) is developed as a promising candidate anode material for lithium ion batteries (LIBs). The N-doped carbon outside SiNPs can not only improve the electrical conductivity of the composite, but also buffer the stress causing by huge volume change of SiNPs during the lithiation/delithiation process. The Si-rGO/NCT composite exhibits high specific capacity and good cycling stability (892.3 mAh g^{-1} at 100 mA g^{-1} up to 100 cycles), as well as improved rate capability. This approach provides a very facile route to obtain silicon-based anode materials.

1. Introduction

Driven by an ever emerging demand for high energy density and long cycle life batteries for various technological and consumer applications, including electric vehicles, portable electronics, and renewable energy storage, extensive researches have be conducted on high-performance electrode materials for lithium ion batteries (LIBs) [1–6]. Silicon (Si), with up to 3579 mAh g^{-1} ($Li_{15}Si_4$) theoretical specific capacity and relatively low working potential, is believed to be a promising candidate anode material for future LIBs [7–11]. Nevertheless, the practical application of silicon as anode material has been hindered by pulverization of electrode structure and poor cycle stability resulting from severe volume changes during the process of Li-ion insertion and extraction [12–17]. Therefore, it has been an urgent problem to obtain silicon-based anode materials to realize high capacity and long cycle stability of rechargeable LIBs. Hence, tremendous work have been devoted to overcome those issues caused by the huge volume change of Si during the lithiation-delithiation process. Numerous nanostructures, including porous Si nanowires [8,18], Si nanotubes [19,20], Si nanosheets [21], porous SiNPs [22,23], and Si-based composites, have been employed to improve structural integrity and cycle performance via suppressing the volume expansion of Si. Besides, silicon also suffers from poor electrical conductivity. To overcome the deficiency, it is used in combing Si with good conductive matrices, such as graphene, carbon nanotubes [24], and other carbon materials [25,26]. Among the carbon materials, graphene has been more and more frequently utilized to make composites with silicon based materials and other anode materials [27–29] because of its unique structure and superior performance, such as excellent electronic conductivity, good chemical stability, superior mechanical-flexibility, and high theoretical surface area [30–35]. A Furthermore, doping foreign atoms into carbon materials is another device of improving capacity storage of anode materials [36]. Among various chemical doping, doping nitrogen is regard as the most promising, since that incorporating nitrogen into the materials will alter the construction of neighboring carbon atoms and afford a great deal of defect sites in the plane, thus improving the chemically active of carbon-based electrodes [37]. Also, nitrogen-doped carbon not only own intrinsically superior electrical conductivity, but also possess excellent interfacial stability for that notable electrons move from the internal electro-active materials to the carbon layer [38]. It is hoped that when SiNPs embedded in N-doped carbon combine with N-doped graphene and CNTs as conductive matrices will improve rate capability and

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cycle performance of Si-based anode materials. To the best of our knowledge, few works, if any, have been reported about preparing composite of SiNPs enwrapped with N-doped carbon combining with N-doping graphene and CNTs as conductive matrices.

In this present work, a novel silicon-based composite composed of silicon nanoparticles coated with N-doped carbon and conductive matrices of N-doped graphene and CNTs (Si-rGO/NCT) were fabricated by a facile method in which melamine formaldehyde resin is used as the N-containing carbon precursor. The obtained silicon-based composite not only presents high reversible capacity but also delivers good rate capability. The improved electrochemical properties are attributed to the synergistic effect between SiNPs with N-doped carbon, N-doped graphene and CNTs. This facile method provides an easily unscaled approach for the silicon-based LIBs anode materials.

2. Experimental

2.1. Materials

Reagents were obtained as follows: SiNPs were received from J&K Scientific Ltd. (30–50 nm in size, 97% purity) without further purification. Formaldehyde and melamine were obtained from Aladdin. CNTs were purchased from Shenzhen SUSN Sinotech New Materials Co., Ltd. without further purification. Graphene oxide (GO) was prepared from nature graphite power using a modified Hummers' method [39,40].

2.2. Preparation of Si-rGO/NCT composite material

In a typical synthesis of Si-rGO/NCT composite, 20 mg graphite oxide was dispersed in 20 ml of deionized water by stirring for 0.5 h and then strong sonicating for 0.5 h to obtain a homogeneous GO dispersion. Then 100 mg Si and 20 mg CNTs were added successively under stirring for 0.5 h, following by another strong sonication for 0.5 h. After that, 2 ml of formaldehyde was added dropwise into the above mixture under stirring for 0.5 h. Then 400 mg of melamine was added in the solution. After vigorous stirring for another 3 h, the resulting products were dried at 80 °C overnight. Finally, the obtained products were transferred into a tube furnace and calcined at 800 °C for 6 h with a heating rate of 2 °C min^{-1}, under an argon atmosphere. The prepared sample is denoted as Si-rGO/NCT composite. For comparison, the counterpart Si-rGO/T composite and Si-rGO/NC composite were prepared as the same process procedure of Si-rGO/NCT composite expect without adding formaldehyde-melamine and CNTs respectively. In some cases, the Si-rGO/NCT composite was further immersed into 5 wt% HF under room temperature for 3 h, washed, and then dried, thus obtaining rGO/NCT assemblies.

2.3. Characterization

X-ray diffraction (XRD) patterns were acquired by a DX-2700 Diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) images were performed on a JSM-6390 field emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analyses were carried out with a JEM-2100 (JEOL) microscopy at an operating voltage of 200 kV. Raman spectras were measured using an Invia Raman microscopy (Renishaw, England) with a 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurement was carried out with an ESCALAB-250Xi (USA) spectrometer using Al Kα radiation as X-ray source. Thermogravimetric analysis (TGA) was carried out on a DTG-60H thermal analyzer under air flow from room temperature to 800 °C at a heating rate of 5 °C min^{-1}. The specific surface area and pore diameter were tested by Brunauer-Emmett-Teller (BET) measurement on a 3H-2000PS1 specific surface and pore size analysis instrument.

2.4. Electrochemical measurements

Electrochemical properties were evaluated using coin-type half-cells (CR 2025) employing the prepared anode materials as the working electrode, lithium foil as the counter/reference electrode and polypropylene microporous film (Celgard 2300) as the separator. To prepare working electrodes, the active materials were grinding with mortar and pestle firstly, then the active materials, acetylene black and sodium alginate binder with a mass ratio 60: 20: 20 were mixed into a homogeneous slurry with deionized water as the solvent. The slurry was pasted onto copper foil uniformly and dried at 110 °C for 24 h in a vacuum oven. Test cells were assembled in an argon-filled glove box with moisture and oxygen level below 1 ppm. The electrolyte was 1.0 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volumetric ration of 1:1, while 5 w% fluoroethylene carbonate was added for stabilizing cycling. The cycling performance and galvanostatic charge-discharge test of the cells were carried out using a LANDCT 2001A battery testing system (Wuhan, China) within a 0.01–2 V voltage limit at room temperature. The specific capacity is calculated according to the total mass. Cyclic voltammogram (CV) measurements were conducted using a CHI760E electrochemical workstation in the voltage range of 0.01–1.2 V at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI760E electrochemical workstation with an AC voltage of 5 mV perturbation and the frequency ranges from 100 Hz to 0.01 kHz.

3. Results and discussion

The schematic fabrication of Si-rGO/NCT composite is illustrated in Fig. 1. Firstly, SiNPs and CNTs are dispersed into GO solution by stirring and sonication. Subsequently, formaldehyde and melamine are added to the mixture. After some time, formaldehyde polymerizes with melamine into melamine formaldehyde resin (MFR). MFR not only wraps outside the surface of SiNPs but also serves as the bonding material to crosslink GO sheets and CNTs. After carbonization, the melamine formaldehyde resin outside SiNPs and GO are converted into N-doped carbon and N-doped graphene, respectively. The MFR plays a very important role in the synthesis of Si-rGO/NCT composite, it not only acts as the source of nitrogen element, but also plays a part in preventing the agglomeration of SiNPs.

Fig. 2a shows the XRD patterns of the SiNPs, Si-rGO/NC, Si-rGO/T, and Si-rGO/NCT composites. The major identified peaks at 28.5°, 47.2°, 56.2°, 69.2°, 76.3° and 88.2° are indexed as the (111), (220), (311), (400), (331) and (411) planes of the cubic diamond phase of silicon (JCPDS 27-1402) respectively [41], indicating the structural preservation of crystal silicon nanoparticles in both cases after experiencing our designed processing [42]. The absence of the diffraction peaks derived from graphene, carbon nanotubes and carbon in the XRD patterns of Si-rGO/NC and Si-rGO/NCT composites can be attributed to that (1) graphene and carbon nanotubes are evenly distributed in the composites, (2) the content of graphene and carbon nanotubes in the composites are rather low, (3) the carbon (from pyrolyzed melamine formaldehyde resin) is amorphous [43]. A broad diffraction peak at $2\theta = 16°–24°$ in the Si-rGO/T composite is derived from the carbon nanotubes [5].

The further verification for the formation of the Si-based composites is given from the Raman patterns. The Raman spectras of all Si-based composites are compared in Fig. 2b. In all four spectras, the bands at 515 cm^{-1} correspond to the typical Raman mode