



Pomegranate-Like Silicon/Nitrogen-doped Graphene Microspheres as Superior-Capacity Anode for Lithium-Ion Batteries



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ABSTRACT

Herein, pomegranate-like Silicon/Nitrogen-doped graphene microspheres (PSNGM) constructed by individual Si nanoparticle core wrapped by flexible nitrogen-doped reduced graphene oxide nanosheets (NG) have been synthesized through a facile and industrially large-scale spray drying approach. The PSNGM anode delivers excellent electrochemical performance: the reversible specific capacity at 100 mA g^{-1} remains as large as $1141.6 \text{ mAh g}^{-1}$ after 150 cycles, with a high capacity retention of 96.1% from 2nd to 150th cycle; the capacity at 100 mA g^{-1} can recover back to $\sim 1340 \text{ mAh g}^{-1}$ even after suffering a high current density of 5000 mA g^{-1} . The excellent performance is attributed to the unique pomegranate-like structure, nanoparticulation of Si and nitrogen doping of graphene: the pomegranate-like skeleton forms a highly conductive network, in which each Si nanoparticle is homogeneously wrapped by flexible and conductive N-doped graphene nanosheets; flexible porous pomegranate-like structure can effectively accommodate the large volume variation during cycling; the N-doped graphene matrix guarantees its high conductivity for better electron and ion kinetics. The presented spray drying strategy is facile, low-cost and effective for large-scale industrial production of Si/graphene composite anode, and it can also be extended to fabricating other high-capacity electrode materials with low conductivities and large volume expansion.

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1. Introduction

Lithium-ion batteries (LIBs) with high energy and power density have attracted extensive attention owing to their potential application in energy storage devices such as electric vehicles (EVs) and hybrid electric vehicles (HEVs), making them one of the most promising energy devices [1,2]. To meet the demands of high energy and power density, silicon-based LIBs were investigated to be a possible candidate for the high theoretical capacity of 4200 mAh g^{-1} , which is almost ~ 10 times than that of graphite anode (about 372 mAh g^{-1}) [3,4]. However, large-scale application of silicon-based LIBs has been hindered by the remarkable volume expansion ($\sim 300\%$) accompanied with the formation of $\text{Li}_{15}\text{Si}_4$ during lithium insertion/extraction [3,5,6]. To address the problem, various strategies were employed to fabricate special structures, including nanoparticle structures (solid and hollow core-shell structures and yolk-shell structures [7–11], porous

structures [12–14], nanowires [15–21], nanotubes and nanofiber structures [22,23], and silicon-based composites [12,23–26], which are able to accommodate the volume variations. For instance, Cui Yi group prepared Si/C composite anode material with a structure of pomegranate which delivered excellent cyclic performance [27]. These efforts of fabricating special structures lead to significant improvement of the electrochemical performance of silicon-based anodes [28].

Since the discovery in 2004, graphene has been a rising star in the field of material science for its superior properties (including outstanding conductivity, excellent stability in both thermal and chemical, high flexibility and huge specific surface area) due to the unique atomically 2-dimensional (2D) structure, which makes it a desirable candidate as mixture for electrochemical materials [29,30]. When applied in LIBs, graphene has significantly elevated the performance of the electrode materials based on silicon [31–35], sulfur group [36–41], and transitional metal sulfides [1,42–44]. Moreover, nitrogen doping in the graphene could enhance the conductivity and the intercalation of Li ions [45].

In the past years, significant efforts have been made to prepare Si/graphene composites to enhance the electrochemical

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performance of Si-based anodes. For example, multilayered Si/reduced graphene oxide composite has been synthesized exhibiting excellent cyclic performance [26], free-standing Si/graphene membrane has been fabricated, which displayed long operating life [46]. In those composites, graphene with superior conductivity, excellent flexibility and huge specific surface area exhibited significant improvement of the Si-based anode.

However, so far, there are still many challenges for large-scale synthesis silicon/graphene composite with excellent electrochemical performance. Firstly, the graphene tends to form irreversible agglomerates and restack owing to van der Waals interactions, which will decrease the effective wrapping role of the graphene. Secondly, the design and optimization of the graphene matrix structure that make individual silicon nanoparticle homogeneously wrapped by graphene nanosheets are still under investigation. Finally, the large-scale and low-cost industrial production of graphene-based silicon anodes with excellent electrochemical performance is still in very early stage.

Herein, to address the issues mentioned above, pomegranate-like Si/N-doped graphene microspheres (PSNGM) constructed by Si nanoparticles wrapped by nitrogen-doped reduced graphene oxide (NG) nanosheets have been synthesized through a facile spray drying approach. The PSNGM anode delivers excellent electrochemical performance, which is attributed to the unique pomegranate-like structure, nanoparticlization for Si and nitrogen doping for graphene.

2. Experimental

2.1. Synthesis of PSNGM

Graphene oxide (GO) used in this study was prepared from expanded graphite powder as reported before [47]. The Si nanoparticles (80–100 nm) were homogeneously dispersed in the mixture of deionized (DI) water and ethanol (V/V=1:1) assisted by ultrasonic treatment for 2 h to form solution A with concentration of 1 g L^{-1} , and the as prepared GO was ultrasonically immersed in DI water to obtain solution B with a GO hydrosol of 3 g L^{-1} . Subsequently, the solution B was added into solution A under ultrasonic treatment for 2 h, and the volume ratio of solution A and B was 12:1. The mixed solution was dried by a spray dryer with inlet air temperature of 180°C to obtain the pomegranate-like Si/graphene oxide microspheres (PSGOM) precursor powder. Finally, the PSNGM were prepared by the reduction of PSGOM precursor with the attendance of hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) vapor at 130°C for 3 h, which successfully realized the reduction of GO and the N-doping of graphene nanosheets by the reaction of GO and hydrazine hydrate [48]. The preparation of NG is similar to PSNGM without the presence of Si. To prepare the un-doped pomegranate-like Si/graphene microspheres (PSGM), the PSGOM was annealed at 500°C for 2 h under Ar_2 atmosphere. Thus there was no introduction of N element during the preparation of PSGM.

2.2. Material characterization

The prepared samples were characterized by X-ray diffraction (XRD Rigaku D/MAX-rA diffractometer) using $\text{Cu K}\alpha$ radiation scanning from 10° to 80° . Raman spectra were carried out at room temperature with excitation laser lines of 532 nm (Horiba). The electronic binding energy of the composite was tested by X-ray photoelectron spectroscopy (XPS, Kratos XSAM800, Al K α radiation). The morphology and structure of the composite were examined by field emission scanning electron microscopy (FESEM, JSM-7000F, JEOL) and transmission electron microscopy (TEM, Tecnai F20 at 200 kV). The content of each component was

characterized by thermal gravimetric analysis (TGA, TG-DSC HT/1600) under air.

2.3. Electrochemical measurements

The working anode was prepared by mixing active material, carbon black (super P Timcal) and poly (vinylidene) fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP) solvent with a weight ratio of 7:2:1 to form homogeneous slurry. Subsequently, the slurry was spread on Cu foil followed by heating treatment in a vacuum oven at 120°C for 12 h. The coin cells (CR2025) were assembled in a glovebox with an inert atmosphere of argon, where H_2O and O_2 were below 0.5 ppm. The charge/discharge measurements of the cells were investigated by a cell testing system (Neware) between 0.01 and 1.00 V at various current densities. The cyclic voltammetry (CV) at a scan rate of 0.1 mV s^{-1} between 0 and 1 V and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (CHI660D).

3. Results and Discussion

The preparation process is schematically illustrated in Fig. 1. Firstly, to address the problem of the poor dispersivity of silicon nanoparticles in DI water, they were dispersed in a mixture of DI water and alcohol. Subsequently, the mixing solution was sprayed into vaporized droplet with huge surface area and dried in only a moment, which resulted in the precursor's forming a pomegranate-like structure of sphere with an average size of several micrometers. Finally, in order to keep the sphere shape of the precursor, the reduction reaction was performed with the vapor of hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$). The hydrazine hydrate acts as not only the reduction agent, but also the nitrogen dopant, which is similar to many other previous reports [48]. The possible formation mechanism is as follows. Firstly, during the mixing and ultrasonic process, the individual Si nanoparticle was homogeneously wrapped by GO nanosheet in the mixed solution, and GO wrapped Si (Si@GO) particles were obtained; Then, during the spraying process, a secondary wrapping happened, i.e., many individual Si@GO particles were wrapped by GO nanosheets again, and larger pomegranate-like microspheres were formed.

The as prepared PSNGM composite was characterized by X-ray diffraction using copper $\text{K}\alpha$ radiation. As comparison, the bare Si and NG were also tested. Fig. 2(a) shows the XRD patterns of the tested samples. The peaks centered at 28.4° , 47.3° , 56.1° , 69.1° and 76.3° correspond to (111), (220), (311), (400) and (331) planes of Si lattice (PDF No. 27-1402), respectively. The typical peaks of Si emerging in the curve of PSNGM indicate that the Si crystalline did not change during the synthesis process. There is a gentle peak at approximately 26.2° in the curve of PSNGM composite, implying the presence of NG in the composite. The fading of the characteristic peak is probably contributed to the perfect dispersion and cladding of the NG [49].

To further prove the existence of NG, Raman spectra was acquired. As observed in Fig. 2(b), the Raman spectroscopy suggests that the bare Si nanoparticles have a sharp characteristic peak centered at 520 cm^{-1} and two weak peaks at 295 cm^{-1} and 950 cm^{-1} , indicating the crystalline of Si. The identified D band of NG at 1350 cm^{-1} which represents the defects and disordered carbon is a little stronger than the G band at 1590 cm^{-1} corresponding to sp^2 ordered carbon, implying that much disordered carbon with defects was formed during the synthesis process (the formation and reduction of GO) [26,46]. More importantly, those defects can offer abundant Li ions diffusion channels, and facilitate the penetrating of the electrolytes into the NG to react with Si nanoparticles [50].

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