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Interfacial engineering of Si/multi-walled carbon nanotube nanocomposites towards enhanced lithium storage performance

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A R T I C L E I N F O

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ABSTRACT

Investigation of interfacial reactions between Si and multi-walled carbon nanotubes (MWCNTs) and their effect on lithium storage properties has not yet been reported. Herein, deposition of amorphous Si nanoparticles on MWCNTs is reported by a low pressure chemical vapor deposition. The structural and interfacial evolutions upon high-temperature annealing are systematically investigated, and the results show that Si nanoparticles gradually react with MWCNTs from interfacial regions by forming Si–C bonds with increasing annealling temperature, and Si nanoparticles completely convert into SiC by reacting with the interfacial carbon atoms at 1200 °C. When examined as anode materials for lithium ion batteries, the Si/MWCNTs with partial interfacial SiC demonstrate the best lithium storage properties, owing to the robust connections between Si and MWCNTs via a chemical bonding of Si–C, which buffers the volume changes during the Li–Si alloying-dealloying.

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1. Introduction

Since observation of the intense photoluminescence from nanostructured Si because of poor optical properties of bulk Si two decades ago [1,2], intensive research efforts have been devoted to the fabrication of Si nanostructures by developing various synthetic approaches including gas phase decomposition of silane [3] and solution methods [4], which paved ways for new application areas such as drug delivery [5] and Li-ion battery (LIB) anode [6], which are still receiving growing attentions. To date, nanostructurization of Si has been proved to be the most effective mean to overcome the major obstacle for commercialization of Si-based LIBs [7,8], which are suffering from quick capacity fading resulting from structural pulverization due to the large volume changes up to 400% during Li–Si alloying-dealloying [9–12]. A number of Si nanostructures have been employed to solve this problem, including Si nanoparticles [13,14], Si nanowires [15], Si nanotubes [16], Si thin films

[17,18], and nanoporous Si [19,20]. Furthermore, these Si nanostructures have been often dispersed on a carbon support [21,22] or embedded in a carbon matrix. Various carbon materials have been used, including amorphous carbon [23], multi-walled carbon nanotubes (MWCNTs) [24], and graphene [25]. As a support, MWCNTs are mostly attractive, because of their superior mechanical strength, high electrical conductivity and network formation capability [26–32].

Although Si anode relies on carbon materials for Si dispersion and conductivity [23–32], there were few reports which investigated interaction of Si nanoparticles with the surface of MWCNTs as well as its effect on Si anode performance. Interfacial instability is a fundamental issue in maintaining structure integrality and functionality in heterogeneous materials. Even if nanoparticles do not crack, they could easily detach from the conducting phases, resulting in undesirable capacity loss [33,34]. Given that the surface areas of MWCNTs are dominated by basal plane sp2 carbons, which inherently have a weak interaction with Si [35,36], interfacial delamination remains a significant challenge. And Si nanoparticles are susceptible to easy stripping, migrating and agglomerating unless a chemical bonding is formed.

In this work, we deposited Si nanoparticles on MWCNTs by a low-pressure chemical vapor deposition (LPCVD) method, and systematically investigated the structural and interfacial evolutions





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upon high-temperature annealing using Raman, X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) analyses. Moreover, the effect of the structural and interfacial evolutions on the lithium storage properties has been studied, finding that formation of Si–C chemical bonding between Si nanoparticles and MWCNTs can effectively enhance the capacity retention, which buffers the volume changes during the Li–Si alloying-dealloying and alleviates the severe pulverization problems of Si–based anode materials for LIBs.

2. Experimental

2.1. Materials synthesis

2.1.1. Synthesis and functionalization of MWCNTs

Multi-walled carbon nanotubes were produced by chemical vapor deposition using Co/Fe–Al₂O₃ as catalysts, ethylene as carbon source, which was delivered in a mixture with Ar and H₂. The pristine MWCNTs were stirred in a mixture of sulfuric acid and ammonium peroxydisulfate solution at room temperature for 48 h to remove amorphous carbon and attach functional groups to the outermost walls. Finally, the functionalized MWCNTs were obtained after thoroughly washing with distilled water, followed by freeze drying under vacuum.

2.1.2. Preparation of Si/MWCNT nanocomposites and post annealing

Si nanoparticles were deposited on the surface of MWCNTs by low pressure chemical vapor deposition using silane as silicon source. The functionalized MWCNTs were loaded into a tube furnace, which was pumped to vacuum and then purged with argon at a flow rate of 200 sccm. When increasing the temperature to 500 °C, a mixture gas containing 4% silane in argon at the flow rate of 70 sccm was introduced to deposit Si nanoparticles onto the outermost walls of MWCNTs. The pressure inside the furnace was maintained at 20 Torr during CVD process. The loading amount of Si on MWCNTs was controlled at around 40 wt%, which was determined from the weight changes of the samples before and after Si nanoparticles deposition, and further confirmed by TGA analysis (Fig. S1 in supporting information). The Si/MWCNT nanocomposites were further annealing at temperatures ranging from 800 °C to 1300 °C for 30 min under Ar atmosphere, in order to investigate the structural and interfacial evolutions and their effect on lithium storage properties.

2.2. Characterization

The phase of the Si/MWCNT nanocomposites were recorded on a Bruker D2 PHASER X-ray diffractometer (XRD) using Cu K α radiation ($\lambda = 1.5418$ Å) operated at a voltage of 30 kV and a current of 10 mA. Raman spectra were measured on a Renishaw Raman REO1 scope with a 514 nm excitation Argon laser. Scanning electron microscopy (SEM) was performed in a FEI Quanta 250F SEM. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out by JEOL JEM 2100F TEM operated at 200 kV. The thermogravimetric analysis (TGA) was performed with METTLER TOLEDO thermal analysis TGA/DSC system.

2.3. Electrochemical measurements

The electrochemical properties of Si/MWCNT nanocomposites as anodes for Li-ion batteries were investigated using a half cell configuration. The CR2025 coin-type cells were assembled in an Arfilled glove-box with both water and oxygen less than 0.1 ppm. The working electrodes were prepared by casting a slurry containing the active materials (60 wt%), carbon black (20 wt%) and sodium alginate (20 wt%) on Cu foils, followed by drying at 80 °C for 24 h under vacuum. Lithium foil was used as the counter electrode and a Cellgard 2400 microporous membrane as the separator. An electrolyte containing 1.0 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) (1:1, v/v) was used. The galvanostatic charge and discharge experiments were performed on a NEWARE battery test system in the voltage range of 0.01–2.0 V vs. Li/Li⁺ at 25 °C. Specific capacities were reported based on the composite mass of as-prepared Si/MWCNTs and annealed counterparts at different temperatures.

3. Results and discussion

As shown in Fig. 1a, the functionalized MWCNTs have lengths of hundreds of nanometers and diameters of around 15 nm, displaying well-defined tubular structure consisted of around ten rolled layers of graphene with both wall thickness and tube diameter of ~5 nm (Fig. 1b). Si nanoparticles were deposited on the MWCNTs via LPCVD method using SiH₄ as Si source, and the distribution, size and shape of Si nanoparticles are strongly dependent on the surface characteristics of MWCNTs. When pristine MWCNTs were used without functionalization, only limited Si nanoparticles with typically spherical shape are randomly distributed on the surfaces of MWCNTs with wide particle size distribution (Fig. S2 in supporting information). However, the functionalized MWCNTs obtained after treated with ammonium persulfate display high loading of Si nanoparticles with greatly improved size and distribution uniformity (Fig. 1c). Moreover, the Si nanoparticles with sizes of 5–15 nm show semi-spherical morphology with large contact area when coupling on the surfaces of MWCNTs (Fig. 1d). The improvement can be explained by the introduction of functional groups on the MWCNTs surface including -OH and -COOH groups, which have higher affinity to Si and provide low energy sites for Si nucleation and growth [37–40]. Notably, the TEM image also reveals that the as-deposited Si nanoparticles are amorphous (Fig. 1d), which are further confirmed by Raman and XRD analyses (Figs. 2-3).

Fig. 2 compares the Raman spectra of the functionalized MWCNTs and the as-prepared Si/MWCNTs hybrid and its structural evolutions upon high-temperature annealing. Fig. 2a shows two typical Raman peaks at 1345 cm⁻¹ and 1580 cm⁻¹ (Fig. 2a), which can be indexed to D-band and G-band of MWCNTs [41]. After deposition of Si nanoparticles, a broad peak centered at 474 cm⁻¹ at low wavelength region emerges, which is typical for the amorphous or poorly crystallized Si nanostructures [42]. After annealing at 800 °C, the Raman peak at 474 cm^{-1} for amorphous Si nanoparticles shifts to 504 cm⁻¹ and remains the same shape even with increasing the annealing temperature from 800 to 900 and 1000 °C (Fig. 2c–e). However, this typical Raman peak for Si nanoparticles becomes weak and finally disappears when increasing annealing temperature from 1100 to 1300 °C (Fig. 2g-h), suggesting the gradual conversion from Si to SiC, which is further confirmed by the XRD results (Fig. 3). It's well acceptable that the Raman peak position of Si is both crystallinity- and size-dependent, and the typical Raman peak for bulk crystalline Si is at 522 cm⁻¹ coming from the first order transverse optical (TO) phonon scattering. With decreasing Si particle size, the position of this peak would red-shift to low energy due to the quantum phonon confinement and reach a minimum of \sim 480 cm⁻¹ typical for amorphous Si. Therefore, the Raman shifts in our samples, firstly from 474 to 504 cm⁻¹ and then from 504 to 511 cm⁻¹ are most likely induced by increased crystallinity of Si nanoparticles rather than particle size increasing. And the disappearance of Raman peak is caused by reaction of Si nanoparticles with MWCNTs. In addition to the peak at 504 cm⁻¹, a new peak at ~912 cm^{-1} appears in the samples after annealed at Download English Version:

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