Interfacial Engineering of Si/Multi-Walled Carbon Nanotube Nanocomposites Towards Enhanced Lithium Storage Performance

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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 annealing 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

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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.

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 sp^2 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 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- Al_2O_3 as catalysts, ethylene as carbon source, which was delivered in a mixture with Ar and H_2 . 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 (Figure S1 in supporting information). The Si/MWCNT nanocomposites were further annealing at temperatures ranging from 800 °C to 1300 °C for 30 minutes 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 ($\lambda=1.5418\text{\AA}$) operated at a voltage of 30 kV and a current of 10 mA. Raman spectra were measured on a Renishaw Raman RE01 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 Ar-filled 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 Figure 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 (Figure 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 (Figure 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 (Figure

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 (Figure 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 (Figure. 1d), which are further confirmed by Raman and XRD analyses (Figure 2-3).

Figure 1. (a) SEM and (b) TEM images of the functionalized MWCNTs. (c) SEM and (d) TEM images of their Si/MWCNT counterparts after deposition of Si nanoparticles.

Figure 2 compares the Raman spectra of the functionalized MWCNTs and the as-prepared Si/MWCNTs hybrid and its structural evolutions upon high-temperature annealing. Figure 2a shows two typical Raman peaks at 1345 cm^{-1} and 1580 cm^{-1} (Figure 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 $800\text{ }^{\circ}\text{C}$, 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 $1000\text{ }^{\circ}\text{C}$ (Figure 2c-e). However, this typical Raman peak for Si nanoparticles becomes weak and finally disappears when increasing annealing temperature from 1100 to $1300\text{ }^{\circ}\text{C}$ (Figure 2g-h), suggesting the gradual conversion from Si to SiC, which is further confirmed by the XRD results (Figure 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 $\sim 480\text{ cm}^{-1}$ 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 $\sim 912\text{ cm}^{-1}$ appears in the samples after annealed at 800 and $900\text{ }^{\circ}\text{C}$, which is from second order scattering of 2TO mode.

Figure 2. Raman spectra of (a) MWCNTs, (b) as-prepared Si/MWCNTs and annealed Si/MWCNTs at different temperatures ranging from 800 to 1300 °C (c-h).

The reaction between Si and MWCNTs was further confirmed by the relative evolution of D-band and G-band of MWCNTs at 1344 and 1580 cm^{-1} , respectively. As the intensity of D-band is proportional to the disorder degree of MWCNTs [41], intensity ratio of D-band to G-band (I_D/I_G) has been used to determine the crystallization degree of carbon-based materials [41], which is more sensitive than XRD. Table 1 summarizes the I_D/I_G ratios and peak positions of D-band and G-band determined from Raman spectra, as showed in Figure 2 (See Table S1 in supporting information for standard deviations). It is observed that the high temperature annealing does not result in significant peak position shifts for both D-band and G-band. However, the I_D/I_G ratio shows an abrupt increase for the sample annealed at 900 °C (Figure 2d and Table 1), suggesting

that interfacial reaction happened. The ratio further increases for the sample annealed at 1000 °C (Figure 2e and Table 1), suggesting the lasting interfacial reaction between Si nanoparticles and MWCNTs which results in increased disorder of MWCNTs. With further increasing the annealing temperature from 1000 to 1300 °C, the interfacial reaction continues as revealed by the decreased and finally disappeared Si Raman peak (Figure 2f-h), while the I_D/I_G ratio remains unchanged after fully converting Si into SiC. This can be explained by countering effect of carbon crystallization induced at higher temperature.

Table 1. Effect of annealing temperatures on the intensity ratios of D-band to G-band (I_D/I_G).

Sample	$I_D/I_G^{a)}$	Wavenumber	
		[cm ⁻¹]	
		D-band	G-band
a	1.5	1345	1580
b	1.4	1350	1589
c	1.4	1344	1575
d	1.8	1344	1573
e	2.0	1346	1580
f	2.0	1348	1580
g	2.0	1346	1587
h	2.0	1350	1589

^{a)}Integrated area ratio of D-band to G-band.

Figure 3 compares the XRD patterns of the MWCNTs and the as-prepared Si/MWCNTs hybrid and its structural evolutions upon high-temperature annealing. As shown in Figure 3a,

two prominent peaks at $2\theta=26.7^\circ$ and 42.3° appear in MWCNTs (Figure 3a), which can be indexed to the (002) and (100) reflections of graphite [43, 44]. After deposition of Si, no new XRD peaks can be observed except for the significantly broadened (002) peak for MWCNTs (Figure 3b). This is consistent with Raman spectra that the as-deposited Si nanoparticles are amorphous. The crystallization of amorphous Si is revealed from the XRD patterns of the samples annealed at 800 and 900 °C, respectively (Figure c-d). Three new peaks at $2\theta = 28.4^\circ$, 47.3° and 56.1° are observed, which can be assigned to the (111), (220), and (311) reflections of silicon (JCPDS card No. 65-1060). An additional new peak at $2\theta = 35.6^\circ$ belonging to β -SiC (111) reflection (JCPDS card No. 65-0360) emerges in the sample annealed at 1000 °C (Figure 3e), suggesting the chemical reaction between Si nanoparticles and MWCNTs. With increasing the annealing temperature, the intensity of SiC (111) peak increases along with emergence of two new peaks at $2\theta = 59.9^\circ$ and 71.7° , which can be assigned to (220) and (311) reflections of β -SiC. The peaks from Si are still observable in the sample annealed at 1100 °C (Figure 3f). However, all Si peaks disappear in the samples annealed at 1200 and 1300 °C (Figure 3g-h), suggesting a complete conversion of Si nanoparticles to SiC and formation of SiC/MWCNT hybrid, which is consistent with the Raman results.

Figure 3. XRD patterns of (a) MWCNTs, (b) as-prepared Si/MWCNTs and the counterparts after annealing at different temperatures ranging from 800 to 1300 °C (c-h).

Figure 4a shows TEM image of SiC/MWCNTs hybrid recorded from the sample annealed at 1300 °C. Apparently, numerous SiC nanoparticles with irregular shapes are uniformly distributed on the MWCNTs, and enlarged TEM image shown inset of Figure 4a reveals that the SiC nanoparticles are half-embedded into cavities of the carbon tubes, owing to the consuming of the carbon atoms of MWCNTs in order to react with Si and form SiC. To further study the conversion of Si nanoparticles to β -SiC, selected area electron diffraction (SAED) was carried out. Figure 4b-c compare the SAED patterns recorded from the two samples annealed at 1100 °C and 1300 °C, respectively, which greatly differ from each other relating to the different phase

structures. The SAED pattern recorded from the sample annealed at 1100 °C can be assigned to (111), (220), (331) and (311) planes of Si, and (111), (200), (220) and (311) planes of SiC (Figure 4b), respectively, suggesting partial conversion of Si to SiC. However, the SAED patterns recorded from the sample annealed at 1300 °C can be all indexed to (111), (200), (220) and (311) planes of SiC (Figure 4c), suggesting complete conversion of Si nanoparticles to SiC nanoparticles.

Figure 4. (a) TEM image of SiC/MWCNTs hybrid recorded from the sample annealed at 1300 °C with inset showing SiC nanoparticles imbedding into the cavities of MWCNTs. (b, c)

SAED patterns recorded from the two samples annealed at 1100 °C (b) and 1300 °C (c), respectively.

Figure 5 shows HRTEM images of samples obtained after annealing as-prepared Si/MWCNTs at different temperatures, clearly revealing the structural and interfacial reaction between Si nanoparticles and MWCNTs upon high-temperature annealing. The as-deposited amorphous Si nanoparticles become crystalline once upon annealing at 800 °C (Figure 1d vs. 5a), and the lattice fringes with spacing of 0.31 nm can be well indexed to the (111) plane of Si. Besides, the multiwall structure of carbon nanotubes is clearly observed with ordered alignment. With further increasing annealing temperature to 1000 °C, the crystallinity of Si nanoparticles further increases (Figure 5b), and at the same time the reaction between Si nanoparticles and the surface carbon atoms of MWCNTs happens forming interfacial β -SiC. However, it is apparent that the reaction is limited to consume disordered carbon atoms on the surface of the MWCNTs, and formation of Si-C bonds. The positional shift of carbon atoms is evident (arrow with label of ordered carbon in Figure 5b), but overall structure of the outmost layer of crystallized carbon remains intact. When the temperature increased to 1100 °C, substantial interface reaction takes place, resulting in the destruction of side walls of MWCNTs and the formation of β -SiC (Figure 5c and Figure 3f) in the interfacial region. As shown in Figure 5c, the lattice spacing measured in the interfacial region is 0.25 nm, corresponding to the (111) planes of β -SiC, while unreacted Si away from carbon nanotubes can be clearly observed with lattice spacing of 0.31 nm relating to (111) plane of Si, indicating the partial reaction between Si and MWCNTs at 1100 °C. After annealed at 1200 and 1300 °C, all Si nanoparticles were converted to β -SiC. As shown in Figure 5d, the side walls of MWCNTs which closely contact with Si nanoparticles are completely

destructured. The lattice spacing of 0.25 nm measured within the particle can be indexed to (111) plane of β -SiC. The result is well consistent with the results observed from Raman, XRD and SAED characterizations.

Figure 5. HRTEM images of the hybrids obtained after annealing Si/MWCNTs at different temperatures of (a) 800 °C, (b) 1000 °C, (c) 1100 °C and (d) 1300 °C, respectively.

The effect of structural and interfacial evolutions between Si and MWCNTs on the electrochemical properties was investigated as anode materials for Li-ion batteries (LIBs). Figure 6a shows the cycle performance of the as-prepared Si/MWCNTs hybrid and the counterparts

after annealing at different temperatures at a current density of 200 mA g^{-1} . The Si content in the as-prepared Si/MWCNTs is $\sim 43.7 \text{ wt.}\%$ as revealed by TGA analysis (Figure S1). The as-prepared Si/MWCNTs with Si nanoparticles in amorphous state deliver a discharge capacity of $1625.4 \text{ mA h g}^{-1}$ and a charge capacity of $1017.4 \text{ mA h g}^{-1}$ in the first cycle with an initial Coulombic efficiency of 62.6%. And the discharge capacity remains $484.6 \text{ mA h g}^{-1}$ after 100 cycles with a capacity retention of 46%. For the sample annealed at 800°C , the amorphous Si nanoparticles became crystalline and no interfacial reaction was observed, and the first discharge capacity increased to $1898.5 \text{ mA h g}^{-1}$, which decreased to 432 mA h g^{-1} at 100 cycle with a lower capacity retention of 30.8%. For the sample annealed at 1000°C , it was observed that Si nanoparticles reacted with MWCNTs at defective sites by forming Si-C chemical bonding. As an interesting consequence, an initial discharge capacity of $2014.6 \text{ mA h g}^{-1}$ is obtained, which still remains $937.8 \text{ mA h g}^{-1}$ after 100 cycles with a much improved capacity retention of 68%, which is much higher than that for the samples annealed at 800°C . The initial Coulombic efficiencies were 68.6% and 64.7% for the samples annealed at 800 and 1000°C , respectively, slightly higher than that of the as-prepared Si/MWCNTs. As a comparison, the sample annealed at 1100°C exhibits a much decreased Li storage capacity, as a large percentage of Si nanoparticles have been converted into SiC which was suggested to be inactive for Li storage [45, 46]. The first discharge capacity is only $742.9 \text{ mA h g}^{-1}$ with an initial Coulombic efficiency of 50.0%, while the reversible discharge capacity is only $312.4 \text{ mA h g}^{-1}$ after 100 cycles, indicating the deteriorated lithium storage properties due to the excessive formation of SiC. On the basis of the above results, we propose that the chemical bonding between Si and MWCNTs via Si-C bonds may contribute to the improved lithium storage capacity and cycle performance, as revealed by the capacity retention behaviors (Figure S3 in supporting information). The formation of

interfacial Si-C bond firmly bands Si nanoparticles on the surface of MWCNTs, avoiding their dislocation and thus resultant pulverization problems of the electrodes upon repeated Li-Si alloying-dealloying. Figure 6b shows the rate performance of the sample annealed at 1000 °C with Si-C chemical bonding, which delivers higher reversible specific capacities of 1211.3, 1097.3, 973.0, 856.3, and 629.6 mA h g⁻¹ each after 10 cycles at current densities from 200 to 500, 1000, 2000 and 5000 mA g⁻¹, respectively. When recovering the current density to 200 mA g⁻¹, the reversible specific capacity of the electrode still keeps a high discharge capacity of 986 mA h g⁻¹ after another 10 cycles, indicating the good rate capability.

Figure 6. (a) Cycle performance of the Si/MWCNTs and the counterparts obtained after high-temperature annealing at different temperatures. (b) Rate performance of the annealed Si/MWCNTs at 1000 °C with a SiC interfacial layer between Si and MWCNTs.

4. Conclusions

In summary, Si nanoparticles were deposited on the surfaces of MWCNTs by a LPCVD method at 500 °C, and the structural and interfacial evolutions of Si/MWCNTs upon high temperature annealing were thoroughly investigated together with their effect on lithium storage properties. The evolution of amorphous Si to crystalline Si and SiC, and the interfacial reaction between Si and MWCNTs can be readily controlled by adjusting the annealing temperatures ranging from 500 to 1300 °C. Crystallization of Si nanoparticles has been observed after annealing the as-prepared Si/MWCNTs at 800 °C. Up to 1000 °C, Si-C bonds formed preferentially in the interfacial region from the defective sites and outmost layer of MWCNTs. Once increasing temperature to 1100 °C, Si nanoparticles partially converted to β -SiC which resulted in the sidewall destructions of MWCNTs. Si nanoparticles completely transformed into SiC nanoparticles after annealed at 1200 °C, which half-embedded into the sidewalls of MWCNTs. The interfacial reactions between Si and C atoms preferentially happened within the interface regions, which was an *in situ* transformation through mutual interfacial diffusion of Si and C atoms. Thus the chemical bonding between Si and MWCNTs can be engineered via controlled annealing strategy. When examined as anode materials for LIBs, the Si/MWCNTs with limited interfacial SiC formed demonstrated the best capacity retention behaviors, owing to the robust attachment of Si nanoparticles on MWCNTs via a chemical bonding of Si-C, which would greatly buffer the severe volume changes during the Li-Si alloying-dealloying processes.

More importantly, our work demonstrated that interfacial engineering could be important for designing advanced nanostructured hybrid materials with enhanced electrochemical performance.

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