Fabrication of Sandwich-structured Si Nanoparticles- Graphene Nanocomposites for High-performance Lithium-ion Batteries

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Abstract

A novel method was developed to synthesize ordered sandwich-structured magnesiothermo-reduced Si nanoparticles (MR-Si NPs)-thermally reduced graphene oxide (TRGO) nanocomposites that combines magnesiothermic reduction, freeze-drying, and thermal reduction. The MR-Si NPs were dispersed into ordered graphene oxide (GO) layers with the aid of sonication. This MR-Si@TRGO composite structure was retained by freeze-drying and followed by thermal reduction. The key features of the nanocomposites, including nanoparticle crystal phase, size, and dispersity on the TRGO matrix, could be controlled by tuning reaction conditions such as reduction temperature and duration. The influence of the weight ratio of active materials: conductive agent: binder, the types of binder, and the content of electrolytes on the electrochemical performance as an anode in lithium-ion batteries was systematically investigated. The electrode fabricated using the MR-Si@TRGO nanocomposites under optimized conditions (80:10:10 for the weight ratio of MR-Si@TRGO: acetylene black: CMC; the electrolyte containing 5 v% vinylene carbonate) exhibited a reversible capacity of 746 mAh g⁻¹ after 160 cycles at 1000 mA g⁻¹, which is substantially higher than 701 mAh g⁻¹ after 120 cycles for the MR-Si@TRGO in the absence of vinylene carbonate, 330 mAh g⁻¹ for commercial graphite reported, and 10 mAh g⁻¹ for pure MR-Si NPs tested at 200 mA g⁻¹ with a weight ratio of 50:30:20 optimized for active materials: acetylene black: PVDF.

Keywords: Nanocomposites, Silicon nanoparticles, Graphene, Magnesiothermic reduction, Lithium ion battery.

1. Introduction

Along with the rapid depletion of fossil resources, human beings are facing serious global energy crisis, environmental pollution, and climate abnormality. As one of the most efficient environmentally friendly energy storage systems, rechargeable lithium ion batteries (LIBs) have attracted tremendous attention owing to their high energy density, high voltage, and eco-friendliness. Since the first commercial LIB introduced in 1991, LIBs have been widely used in portable electronic devices [1-3]. However, graphite, the most commercially successful anode material in LIBs, has an intrinsic low Li storage capacity (372 mAh g^{-1} theoretical capacity) that does not meet the growing demands of power tools, electric vehicles, and stationary storage systems [4]. Therefore, silicon, which is the second most abundant element on Earth and has a high theoretical charge capacity (4200 mAh g^{-1}) [5-7], has been considered one of the most promising anode materials for next-generation LIBs. However, Si undergoes large volume changes (up to about 400%) during lithium ion insertion/extraction which can result in seriously irreversible capacity loss, poor cycling stability, and electrode pulverization [8,9]. In order to minimize structural (either disintegration or degradation) and thus enhance capacity retention and electrochemical stability, extensive efforts have been spent in modifying the microstructure of the Si particles, particularly by nano-miniaturization [10,11] and introduction of porosity [12].

Recently, there is much attention on composites of Si and carbon materials with high electrical conductivity and small volume changes on lithiation, such as dispersion of Si NPs in carbon nanotubes and graphene sheets [13-16], and very encouraging capacity of $\sim 3200 \text{ mAh g}^{-1}$ was obtained [17,18]. Graphene, a two-dimensional (2D) monolayer of carbon atoms with a honeycomb crystal lattice, appears to be an attractive matrix to disperse Si NPs. Owing to its high electronic conductivity, mechanical strength, and flexibility, graphene sheets play key roles in serving both as an electrically conductive network and an elastic buffer for the Si NPs [19-21]. Under carefully controlled conditions, Si NPs and graphene sheets can form ordered, layer-by-layer nanocomposites of significantly improved cycling performance. Recently, Wong and his co-workers synthesized silicon nanoparticles through magnesiothermic reduction of rice husks and further prepared a binder-free composite system comprising Si nanoparticles and graphene as an anode. This Si/graphene composite exhibited a reversible capacity of 1000 mAh g^{-1} at 1000 mA g^{-1}

¹[22]. Chang and his co-workers prepared a Si nanoparticles/reduced graphene oxide hybrid, which exhibited 80% capacity retention after 100 cycles at 2.4 A g⁻¹ and excellent rate capability of 700 mAh g⁻¹ at 24 A g⁻¹[23].

However, to convert Si-graphene composites with attractive properties to practical lithium ion battery anode material demands a low-cost and high-yield fabrication method. In the present study, we developed a strategy for facile synthesis and assembly of ordered sandwich-structured magnesiothermo-reduced Si nanoparticles (MR-Si NPs)-thermally reduced graphene oxide (MR-Si@TRGO) nanocomposites for high-performance lithium ion batteries. Fig. 1 illustrates schematically this facile method. Among the many methods to prepare Si NPs [24-29], in order to avoid demanding synthetic conditions, complicated procedure, or micro-scale yield, we chose magnesiothermic reduction of SiO₂ because of its potential for low-cost large-scale production [30]. For graphene, thermal reduction of graphene oxide was chosen for a similar reason. Under optimal conditions, MR-Si NPs could be uniformly deposited on layer-by-layer assembled graphene sheets, forming ordered sandwich-structured MR-Si@TRGO nanocomposites. Although the composite was assembled in solution, its microstructure was retained by freeze-drying that removed the solvent through evacuation without collapsing the microstructure [31-33]. The key features of the nanocomposites, including nanoparticle crystal phase, size, and dispersity on the TRGO matrix, were successfully controlled via magnesiothermic reduction conditions such as reduction temperature and duration. Their electrochemical performance at different weight ratios of active materials: conductive agent: binder, types of binders, and electrolyte contents for lithium ion batteries was systematically investigated. Under optimized conditions, as well as 80:10:10 for the weight ratio of MR-Si@TRGO: acetylene black: CMC and 5 v% vinylene carbonate for the electrolyte, the fabricated electrode exhibited substantially improved performance at high current density (1000 mA g⁻¹) as compared to the electrodes fabricated using MR-Si@TRGO without adding vinylene carbonate, commercial graphite, and pure MR-Si NPs at low current density (200 mA g⁻¹) at the 50:30:20 weight ratio of active materials: acetylene black: PVDF. Thus, the method reported here provides a low-cost alternative to prepare Si-based anodes.

2. Experimental Section

2.1. Materials

All chemicals, including silica nanopowders (15 ± 5 nm, 99.5%, Sigma-Aldrich Ltd.), magnesium powders (analytical reagent, 325 mesh, Linfeng Chemical Reagent Ltd.), graphene oxide (A&W MaTech Ltd.), polyvinylidene fluoride (PVDF, 99.5%, Hefei Kejing MaTech Ltd.), sodium carboxymethyl cellulose (CMC, 94%, Hefei Kejing MaTech Ltd.), and vinylene carbonate (VC, 98%, Guangdong Wengjiang Chemical Reagent Co., Ltd.) were used as-received without further purification.

2.2. Synthesis of MR-Si NPs

A uniform mixture of SiO_2 and Mg (SiO_2 :Mg molar ratio of 1:2.5) was prepared by mixing the powders together at 500 rpm for 1 h under N_2 atmosphere using a planetary ball mill (Nanjing University Instrument Plant, China). The mixture was transferred into a graphite crucible and heated to 700-850 $^\circ\text{C}$ in a tube furnace, with a heating rate of 5 $^\circ\text{C}/\text{min}$ and an Ar flow rate of 100 ml/min for different duration (2-5 h) to effect magnesiothermic reduction. After reaction, the system was cooled to room temperature, and the yellow powder product was stirred in 2 M HCl for 3 h to dissolve unreacted Mg and the by-products MgO and Mg_2Si . Finally, the MR-Si NPs were washed by ethanol three times and vacuum-dried at 70 $^\circ\text{C}$ for 12 h.

2.3. Assembly of MR-Si@TRGO nanocomposites

50 mg of the as-synthesized MR-Si NPs was dispersed in 50 mL water by sonication for 10 min. 25 mL of graphene oxide (GO) aqueous dispersion (1 mg/mL) was then added and the mixture was sonicated for another 2 h. The resulting suspension was freeze-dried, and the dried sample was placed in a tube furnace and heated at 10 $^\circ\text{C}/\text{min}$ to 900 $^\circ\text{C}$ for 2 h in an Ar atmosphere. The as-synthesized MR-Si@TRGO nanocomposites were stored in an Ar glove box.

2.4. Characterizations

Raman spectra were collected with a J-YT640000, John Yvon Raman laser spectrometer using 514.5 nm laser excitation. The crystalline phases of powder samples were characterized by X-ray diffraction (XRD) using a D8-Advance, Bruker AXS diffractometer ($\text{Cu-K}\alpha$ radiation, $\lambda=1.5418$ Å, 40 kV, 100 mA, from $2\theta=5^\circ\sim 80^\circ$, scan-speed 0.8 sec/step, and increment of 0.02 deg/s). The morphology and microstructure were characterized by field emission scanning electron microscopy

(FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100). Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C thermogravimetric analyzer. The samples (12 mg) were heated in air from room temperature to 800 °C at 10 °C/min. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI-5000 VersaProbe X-ray photoelectron spectrometer. The specific surface areas were analyzed with the Brunauer-Emmett-Teller (BET) method using a BELSORP-MINI nitrogen adsorption apparatus, and the pore size distribution by the Barrett-Joyner-Halenda (BJH) method.

2.5. Electrochemical measurements

To form the working electrodes, a slurry consisted of the powder samples (MR-Si or MR-Si@TRGO), acetylene black (as a conductive agent), and polyvinylidene fluoride (as a binder) with a weight ratio of 50:30:20 in N-methyl-2-pyrrolidone was uniformly plastered onto a copper foil current collector via doctor blade processing, followed by drying under vacuum at 100 °C for 12 h. A two-electrode 2016 type coin cell with a lithium metal counter electrode and a polypropylene separator (Celgard2400) were used to assess the electrochemical performance. The electrolyte was 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v).

For comparison, a new working electrode consisting of the MR-Si@TRGO nanocomposite, acetylene black (as a conductive agent), and CMC (as a binder) with a weight ratio of 80:10:10 in deionized water was uniformly plastered onto a copper foil current collector via doctor blade processing. 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (1:1 by volume) plus 5 v% vinylene carbonate was used as the electrolyte. Other experimental conditions and procedures were the same as described in the above fabrication of electrodes.

The electrochemical test cells were assembled in an argon-filled glove box (Etelux, Lab2000) in which H₂O and O₂ concentration were kept below 0.1 ppm. The galvanostatic charge–discharge measurements were carried out on Neware, BTS-3000 in the voltage range of 2.0 to 0.01 V (vs. Li/Li⁺) at room temperature (25±1 °C). The cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) were measured on an electrochemical workstation (CHI660D) at a scanning rate of 1 mV/s. EIS were recorded by applying an AC voltage of 10 mV amplitude over the frequency range from 100 kHz to 0.01 Hz.

3. Results and Discussion

3.1. Synthesis and characterization of MR-Si NPs

Fig. 2 shows the XRD patterns of the MR-Si NPs synthesized at different magnesiothermic reduction temperatures (700-850 °C) and duration (2-5 h) with other conditions identical. Patterns A and B show that the samples formed at 700 and 750 °C for 2 h contained both cubic phase Si and small amounts of residual amorphous SiO₂ as indicated by a broad peak at 20-26°. Increasing the reduction temperature to 800 and 850 °C resulted in the disappearance of this broad peak at 20-26°, but a new peak corresponding to SiC appeared at 36°, as shown by patterns C and D. The by-product SiC was formed by reaction: $\text{Si} + \text{C} = \text{SiC}$ [34]. The carbon source is the graphite crucible which used as a reactor for SiO₂ and Mg.

As expected, the amorphous SiO₂ was removed by prolonged reduction at 700 °C. As shown by patterns E and F, pure cubic Si phase was obtained by 3 and 5 h reduction. The longer reduction was also carried out at 750 and 800 °C (Figure S1). Pure cubic phase Si was obtained at 750 °C for 3 and 5 h also, but Si and SiC coexisted in all samples obtained at 800 °C.

The morphology of the MR-Si NPs prepared at different temperatures and duration was studied by SEM (Fig. S2). Fig. 3A-C show the SEM images of the MR-Si NPs formed at 700, 750, and 800 °C for 3 h. Relatively, the (700 °C-3 h) sample was better dispersed. Increasing the reduction temperature caused the particles to sinter. The average particle sizes of the MR-Si NPs were calculated by Scherrer equation using the X-ray diffraction peak and summarized in Fig. 3D. Consistent to the SEM images, the samples formed at 700 °C showed the smallest average particle size among the three temperatures. The variation of particle size with different reduction time was similar for the three temperatures, and the 3 h samples showed the smallest size. This could be due that the reduction of SiO₂ started from the surface and proceeded inward. As the SiO₂ core shrank, smaller Si particles were formed, reducing the average Si NPs size. With prolonged heating to 5 h, the Si NPs began to sinter into larger particles.

3.2. Assembly and characterization of MR-Si@TRGO nanocomposites

The MR-Si NPs formed at 700 °C for 3 h was chosen to demonstrate the assembly and properties of the MR-Si@TRGO nanocomposites. As shown in Fig. 4A,

the MR-Si@TRGO nanocomposites assembled in a manner that the thermally reduced graphene oxide sheets dispersed the Si NPs very effectively, while forming locally ordered stacking pattern of periodical sandwich structures. Such composite structure can suppress agglomeration of nanoparticles, thereby promoting the electrochemical performance and stability of the composites [18]. Several pores with different sizes were observed from the top-view of the composites (Fig. 4B). N₂ adsorption-desorption analysis indicated the mesoporous structure of the composites with the majority pore size around 4 nm (Fig. S3). The BET specific surface area was about 67 m²/g. The high density of porous channels inside the MR-Si@TRGO nanocomposites serve to provide efficient ionic transport pathways, thus enhancing the electrochemical performance. Fig. 4C and 4D clearly show that the MR-Si NPs are uniformly dispersed between the thermally reduced graphene oxide sheets, resulting in the formation of sandwich structured composites. In this MR-Si@TRGO nanocomposites, the Si content was calculated to be 74%, based on TGA measurements (Fig. S4).

The composition and crystal phase of the MR-Si@TRGO nanocomposites were characterized by XRD. As shown in Fig. 5, the diffraction patterns of both MR-Si NPs and TRGO were detected for the nanocomposites. The broad hump in the range of 24-28° was attributed to graphene sheet stacks [17].

Fig. 6 shows the XPS spectra of the MR-Si@TRGO nanocomposites and GO as the negative sample. As shown in Fig. 6A and 6B, the XPS spectra of GO clearly indicates a considerable degree of oxidation with five different peaks at 284.0, 285.2, 286.4, 288, and 289.2 eV, corresponding to C=C/C-C in aromatic rings, C-O (epoxy and alkoxy), C-OH, C=O, and COOH groups, respectively [35]. Elements of Si, O, and C were detected in the XPS spectrum of the MR-Si@TRGO nanocomposites (Fig. 6C) [36]. The relative intensity of Si was very weak because the MR-Si NPs were embedded between the thermally reduced graphene sheets and thus limited areal coverage (Fig. 4C) [37]. The intensities of peaks due to carbon bonded to oxygen were decreased substantially in MR-Si@TRGO nanocomposites (Fig. 6D), indicating that most of the oxygen-containing functional groups were removed after thermal reduction.

Fig. 7 shows the Raman spectra of MR-Si@TRGO nanocomposites, MR-Si NPs, TRGO, and GO. In the Raman spectra of TRGO and GO (Fig. 7C and 7D), only D and G bands were observed at around 1350 and 1595 cm⁻¹, respectively. The G-band

is characteristic of graphitic sheets, corresponding to a well-defined sp^2 carbon-type structure; whereas the D-band can be attributed to the presence of defects within the hexagonal graphitic structure [39]. Thus, a smaller I_D/I_G ratio indicates lower defects and disorders of the graphitized structures [36]. The Raman spectrum of the MR-Si@TRGO nanocomposites (Fig. 7A) was composed of D band, G band, and three absorptions around 263, 516, and 950 cm^{-1} corresponding to pure MR-Si NPs [39] (Fig. 7B). The I_D/I_G ratio increased from 1.38 for GO to 1.56 for the MR-Si@TRGO nanocomposites, which indicated a decrease in the average size and an increase in the number of the sp^2 graphite domains. A similar increase in the I_D/I_G ratio after reduction has been observed in other systems [35].

3.3. Electrochemical Performance

Fig. 8A shows the first three cyclic voltammetry (CV) curves of the MR-Si@TRGO nanocomposites (700 °C, 3 h) at a scan rate of 1 mV/s over the range 0.01-2.0 V. The broad cathodic peak at around 0.78 V appeared in the first cycle, but was not in subsequent cycles. No obvious oxidation peak corresponding to this reduction process was observed in the anodic branch, suggesting that it was due to the formation of solid electrolyte interphase (SEI) on the electrode surface [40]. The small peak at 1.3 V might be related to the reaction of the remaining oxygen functionalities in TRGO [37]. In the cathodic sweep of the second CV curve, there were two peaks at 0.051 and 0.20 V, corresponding to the formation of Li-Si alloy phases. Correspondingly, the two peaks at 0.31 and 0.55 V at the anodic sweep could be ascribed to the dealloying of Li-Si alloys. The results were well consistent with the data reported in the literature [41].

Fig. 8B displays the discharge-charge profiles of the electrode with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte cycled at a current density of 1000 mA g^{-1} between the voltage limits of 0.01-2.0 V vs. Li^+/Li . In the first lithiation cycle, a voltage drop slope from 1.0 to 0.2 V was observed due to the well-known SEI film formation and surface oxide layer decomposition. This was followed by a voltage plateau between 0.2-0.02 V due to lithiation of Si. The reaction occurred during the discharge can be expressed by: $Si + xLi^+ + xe^- \rightarrow Li_xSi$. In the first delithiation cycle, a potential plateau below 0.6 V was observed, corresponding to the reaction: $Li_xSi \rightarrow Si + xLi^+ + xe^-$ [42,43]. The initial lithiation and delithiation charge capacities were 1405 and 1119 mAh g^{-1} ,

respectively, with a Coulombic efficiency of 80% (the specific capacity was based on the total mass of MR-Si@TRGO nanocomposites). In subsequent lithiation/delithiation cycles, the voltage slope between 1.0-0.2 V was greatly shortened compared to the first cycle due to much less extensive SEI formation and thus less irreversible capacity losses [44]. The Coulombic efficiency quickly reached nearly 99% in the fifth cycle and remained relatively stable afterwards. These results were consistent with that observed from the cyclic voltammetry curves.

The extent of capacity fade with cycling is shown in Fig. 8C. The MR-Si NPs exhibited an initial discharge capacity of 3034 mAh g⁻¹ but the capacity dropped to only 10 mAh g⁻¹ after 40 cycles at 200 mA g⁻¹. On the other hand, the electrode with the 50:30:20 weight ratio of MR-Si@TRGO: acetylene black: PVDF showed good cycling performance. After 120 cycles, the reversible capacity of the MR-Si@TRGO nanocomposites can achieve a discharge capacity of 701 mAh g⁻¹ at 200 mA g⁻¹. With increasing the weight ratio of MR-Si@TRGO: acetylene black: binder to 80:10:10 while using CMC as binder and adding 5 v% vinylene carbonate into the electrolyte, the MR-Si@TRGO nanocomposites exhibited a significantly improved stable reversible higher capacity of 746 mAh g⁻¹ at 1000 mA g⁻¹ after 160 cycles, over twice that of the theoretical specific capacity of graphite (372 mAh g⁻¹). In MR-Si@TRGO nanocomposites, the highly conductive thermally reduced graphene oxide sheets effectively dispersed the MR-Si NPs, suppressed their agglomeration and buffered their volume changes during lithium ion insertion/extraction process, thereby achieving significantly improved cycling performance.

The above results demonstrate the enhanced cycling performance of the electrode with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte. This can be attributed to three reasons as follows. First, as compared with PVDF, CMC has better interaction ability with both active materials and the electrolyte, which can enhance the structural stability of the electrode during the charge/discharge process [45]. Second, the addition of vinylene carbonate into the electrolyte allows to form poly alkyl Li-carbonate species during the lithium ion insertion/extraction, which makes the SEI film exhibiting better flexibility and higher adhesion. This helps to suppress the volume changes of Si NPs and improve the cycling performance [46]. Third, the binder that is generally used to bond the electrode materials and current collector is an insulator. Increasing the weight ratio of active materials: conductive agent: binder from 50:30:20 to 80:10:10

decreases the loading concentration of the binder and thus results in a better electrical conductivity. These unique modifications allow to fabricate the electrodes with very stable microstructure and better conductivity so as to against the volume change of active materials and improve the cycling stability.

To probe the electrochemical performance of the electrode fabricated with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte, different cycling rates within 200-8400 mA g⁻¹ have been used to investigate the rate capability of the samples (Fig. 8D). As expected, MR-Si@TRGO nanocomposites manifested an exceptionally high rate capability and could withstand high current density. For example, at a current density of 8400 mA g⁻¹ (equal to a current rate of 2 C), MR-Si@TRGO nanocomposites still delivered a favorable capacity of 401.8 mAh g⁻¹. When the current rate was returned to 500 mA g⁻¹, the stable high capacity of MR-Si@TRGO nanocomposites (1022 mAh g⁻¹, 97% of the initial reversible capacity) was resumed.

To confirm the improved electrochemical performance of the electrode fabricated with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte as compared to the pure MR-Si NPs anodes, the impedance of these two electrodes was examined using electrochemical impedance spectroscopy (EIS). Their Nyquist plots determined in the frequency range of 0.01 Hz to 100 kHz, carried out at the lithiated state (10 mV vs Li/Li⁺) at room temperature, are shown in Fig. 9. The typical impedance spectrum consisted of a semicircle at high-to-middle frequency range and a straight line at the low frequency range, which implied diffusion-controlled processes in the solid electrode. The semicircle in the medium frequency region is usually assigned to the charge-transfer resistance [37,40]. The diameter of the semicircle for the MR-Si@TRGO nanocomposites electrode in this region was much smaller than that of the pure MR-Si NPs electrode, which indicated lower contact and charge-transfer impedance for the MR-Si@TRGO nanocomposites.

The above results clearly demonstrated the superior cycling performance of the MR-Si@TRGO nanocomposites over to pure MR-Si NPs as an anode material for lithium storage. Galvanostatic discharge/charge cycling measurements were further applied to nine MR-Si NPs samples with the 50:30:20 weight ratio of MR-Si: acetylene black: PVDF (Fig. 3D and Fig. S2 B-J) in the absence of TRGO. Table 1 summarizes their electrochemical performance, in terms of initial discharge specific

capacities, first-cycle charge capacities, initial Coulombic efficiencies, and 10th-cycle charge capacities. Despite the promising first discharge and charge capacities, all the samples suffered from more serious irreversible capacity losses and poorer cycling stability after 10 cycles than the (700 °C-3 h) sample. These data indicated that severe volume change during lithium ion insertion/extraction still occurred in the simple MR-Si NPs as compared to the MR-Si@TRGO nanocomposites. The (700 °C-3 h) sample exhibited the highest first discharge and charge capacities of 3034 and 2242 mAh g⁻¹, respectively, and 74% Coulombic efficiency. It possessed the smallest particle size and high dispersity, as discussed above, which effectively increased Li-ion/Si contact area, decreased the absolute large volume change, and stabilized the structure during the lithium ion insertion/extraction process. However, the cycling performance of the (700 °C-3 h) sample still doesn't show good cycling performance. After we coupled the MR-Si NPs of the (700 °C-3 h) sample with the TRGO, the resulting MR-Si@TRGO nanocomposites have clearly demonstrated the superior electrochemical performance as shown in Fig. 8.

4. Conclusions

Ordered assembled MR-Si@TRGO nanocomposites were fabricated via a facile method combining freeze-drying and thermal reduction. The Si nanoparticles were synthesized by the magnesiothermic reduction of amorphous silica nanopowders. The Si nanoparticles formed by reduction at 700 °C for 3 h showed the highest purity, the smallest crystallite diameter, and the best dispersity on the thermally reduced graphene oxide matrix, and they formed a composite that exhibited the highest initial discharge and charge capacity as anode materials for lithium ion battery. The electrochemical performance of the Si nanoparticles was greatly enhanced by self-assembly between graphene sheets via combining freeze-drying and thermal reduction. The thermally reduced graphene oxide sheets provided good protection against agglomeration and volume change of the Si nanoparticles, and allowed favorable transport kinetics for both electrons and lithium ions. As a consequence, superior cycling performance (746 mAh g⁻¹, over 160 cycles) was achieved over the electrode fabricated with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte was used as anode material for lithium storage. Such a protocol to construct nanocomposites composed of layer-by-layer

assembled reduced graphene oxide sheets and electroactive nanoparticles can be extended to other metals or metal oxides with large volume change and low electronic conductivity for electrochemical energy storage and conversion applications.

Acknowledgments

This research was supported by the Natural Science Foundation of China (No. 51425202, No. 51202110), the Natural Science Foundation of Jiangsu Province (No. BK2012426, No. BK2012041), and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). H.H.K. is supported by the US DOE through the Center for Electrical Energy Storage (DE-AC-02-06CH11357). The authors thank Dr. L. Tong, Jiangnan Graphene Research Institute, for help with SEM characterization.

Supporting Information. Fig. S1-4, additional XRD patterns, SEM images, N₂ adsorption/desorption isotherms, and TGA curves. This material is available free of charge via the Internet at <http://www.elsevier.com>

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Table 1. Galvanostatic constant-current electrochemical results at 0.05 C cycling rate for MR-Si NP samples synthesized at different reduction temperatures and duration.

Samples (reduction temp. -duration)	Initial discharge specific capacity (mAh g ⁻¹)	1 st charge capacity (mAh g ⁻¹)	Initial Coulombic efficiency (%)	10 th charge capacity (mAh g ⁻¹)
700 °C-2 h	2532	1226	48	456
700 °C-3 h	3034	2242	74	614
700 °C-5 h	1020	451	44	124
750 °C-2 h	1184	605	51	135
750 °C-3 h	1743	909	52	150
750 °C-5 h	988	357	36	87
800 °C-2 h	1730	567	33	235
800 °C-3 h	1849	754	41	162
800 °C-5 h	820	321	39	176

Fig. 1. A schematic illustration of the synthesis and assembly of sandwich-structured magnesiothermo-reduced Si nanoparticles- thermally reduced graphene oxide (MR-Si@TRGO) nanocomposites for high-performance lithium ion batteries.

Fig. 2. XRD patterns of the MR-Si NPs prepared at (A) 700 °C for 2 h, (B) 750 °C for 2 h, (C) 800 °C for 2 h, (D) 850 °C for 2 h, (E) 700 °C for 3 h, and (F) 700 °C for 5 h. The standard XRD patterns of Si (JCPDS No. 27-1402) and SiC (JCPDS No. 29-1129) are provided.

Fig. 3. SEM images of the MR-Si NPs prepared at (A) 700, (B) 750, and (C) 800 °C for 3 h; (D) dependence of average sizes of MR-Si NPs on reduction temperature and duration.

Fig. 4. (A, B) Low- and (C, D) high-magnification SEM images of the assembled MR-Si@TRGO nanocomposites.

Fig. 5. XRD patterns of (A) MR-Si@TRGO nanocomposites, (B) MR-Si NPs, and (C) TRGO.

Fig. 6. XPS spectra of (A) GO, survey scan; (B) C1s of GO; (C) MR-Si@TRGO nanocomposites, survey scan; and (D) C1s of MR-Si@TRGO nanocomposite. The peaks marked with 1, 2, 3, 4, and 5 correspond to C=C/C-C in aromatic rings, C-OH, C-O (epoxy and alkoxy), C=O, and COOH groups, respectively.

Fig. 7. Raman spectra of (A) MR-Si@TRGO nanocomposites, (B) MR-Si NPs, (C) TRGO, and (D) GO.

Fig. 8. (A) Cyclic voltammetry profiles of the MR-Si@TRGO nanocomposites; (B) galvanostatic discharge–charge curves of the electrode with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte for cycles 1, 5, and 160 at a current density of 1000 mA g^{-1} ; (C) Cycling performance of (a) the electrode with the 50:30:20 weight ratio of MR-Si@TRGO: acetylene black: PVDF, (b) the electrode with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte, and (c) pure MR-Si NPs; (D) Cycling performance of the electrode with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte at various current densities.

Fig. 9. Nyquist plots of pure MR-Si NPs and the electrode with the 80:10:10 weight ratio of MR-Si@TRGO: acetylene black: CMC and the 5 v% vinylene carbonate electrolyte at a discharged potential of 0.1 V (vs. Li/Li⁺) from 100 kHz to 0.01 Hz.