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.

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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 ~3200 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

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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}[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 SiO$_2$ 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 thermally reduced graphene oxide 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 °C in a tube furnace, with a heating rate of 5 °C/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$_2$Si. Finally, the MR-Si NPs were washed by ethanol three times and vacuum-dried at 70 °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 °C/min to 900 °C for 2 h in an Ar atmosphere. The as-synthesized MR-Si@TRGO nanocomposites were stored in an Ar glove box.
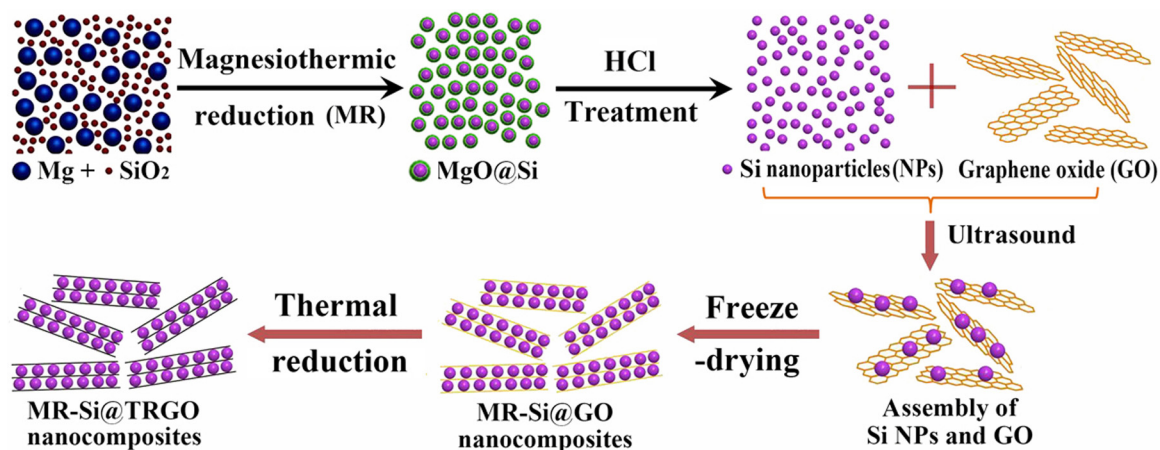

Fig. 1. A schematic illustration of the synthesis and assembly of sandwich-structured magnesiothermo-reduced Si nanoparticles- thermally reduced graphene oxide (MR-Si@TRGO) nanocomposites for high-performance lithium ion batteries.