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Facile synthesis of silicon nanoparticles inserted into graphene sheets as improved anode materials for lithium-ion batteries†

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Silicon nanoparticles have been successfully inserted into graphene sheets via a novel method combining freeze-drying and thermal reduction. The as-obtained Si/graphene nanocomposite exhibits remarkably enhanced cycling performance and rate performance compared with bare Si nanoparticles for lithium-ion batteries.

The development of high energy density and long cycle life lithium-ion batteries is of great technological importance for use in portable electronics, electric vehicles, and the storage of renewable energy.^{1–6} To meet these requirements, the electrode materials of lithium-ion batteries must have high specific storage capacities and satisfactory cycle life. Recently, silicon has been intensively investigated for use as high-capacity anode material owing to its highest known capacity (4200 mA h g⁻¹), which is ten times higher than that of graphite (372 mA h g⁻¹).^{7–11} Unfortunately, the practical application of silicon as an anode material is seriously hindered by the huge volume changes (>300%) and low intrinsic electrical conductivity during lithium uptake and release from silicon, leading to dramatic pulverization of silicon nanoparticles and rapid capacity fading.^{12,13} To overcome these issues and improve the overall electrochemical performance of silicon anodes, one effective strategy is to use carbon coatings, which can not only restrict the large volume change of silicon to keep the electrode integrity, but also enhance the electrical conductivity. For example, Liu and co-workers reported carbon-coated silicon nanocomposites with high capacities prepared by a spray-pyrolysis technique.¹⁴ Hu *et al.* synthesized Si@SiO_x/C nanocomposites with good electrochemical performance by a hydrothermal carbonization method.¹² Another effective strategy is to fabricate silicon nanostructures, such as nanowires, nanotubes, and nanospheres, in which the stress caused by the volume change can be accommodated more easily than that in bulk silicon.¹³ Recently, Yushin *et al.* have reported nanosized Si-in-C tubes which were fabricated using chemical vapor deposition (CVD) and exhibited high capacity and stable performance.¹⁵ Cui and Yao *et al.* have prepared interconnected silicon hollow nanospheres by CVD

and a template etching method and achieved a high initial discharge capacity of 2725 mA h g⁻¹ with excellent cycling performance.¹⁶ More recently, our group have reported Cu@Si@Al₂O₃ nanocable arrays and silicon/carbon nanoporous microspheres with favorable cycling and rate performance.^{17,18} So far, advanced carbon coatings for silicon-based nanomaterials and their facile fabrication methods are still highly desired toward cost-effective anode materials.

Graphene, a two-dimensional carbon nanomaterial, has attracted enormous attention owing to its unique properties and potential applications in the areas of electronics as well as energy conversion and storage devices.^{19–23} Recently, it has been demonstrated that graphene is very useful in the design of superior anode materials for lithium-ion batteries due to its high electronic conductivity, mechanical strength, and flexibility.²⁴ However, in the cases of silicon-based anode materials, there are still many difficulties in the utilization of graphene. For example, silicon nanoparticles are difficult to be homogeneously dispersed within graphene layers by simply mechanical blending.²⁵ High temperature commonly used during the synthesis of graphene/nanosized silicon composites often leads to the conglomeration of silicon nanoparticles.²⁶ In addition, the electrode films obtained from the assembly of silicon nanoparticles and graphene by filtration might be too thick to guarantee quick lithium ion diffusion into the structure.^{27,28} An advanced technique for inserting Si nanoparticles into graphene sheets remains a great challenge. Herein, we report a facile method for preparing such structures. Silicon nanoparticles inserted uniformly into graphene are realized by combining freeze-drying and thermal reduction. The as-prepared silicon nanoparticles intercalated in graphene sheets form a typical hierarchical micro–nano structure, in which graphene plays the roles of both an electronically conductive network and an elastic buffer for the silicon nanoparticles. As a result the cycling performance and rate capability of the silicon nanoparticles inserted into graphene are significantly improved when being used as anode materials in lithium-ion batteries.

Freeze-drying is defined as direct sublimation of solvents under vacuum to dry samples and maintain their microstructures. It is a well-established approach to create aligned porous structures,²⁹ three-dimensional nanocomposites,³⁰ and organic nanoparticles.³¹ Graphite oxide (GO) obtained from the modified Hummer method was used as the precursor of graphene sheets and silicon nanoparticles (<300 nm) were used as starting materials

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Fig. 4 (a) Cyclic voltammetry profiles of the Si/TRG composites and (b) galvanostatic discharge-charge curves for different cycles. (c) Cycling performance of the Si/TRG composites and Si nanoparticles. (d) Rate capability of the Si/TRG composites.

the total mass of the Si/TRG composites in the context. After the first cycle, the Coulombic efficiency could increase and stabilize at 98%–100% in subsequent cycles. For comparison, pristine Si nanoparticles were also tested for lithium-ion batteries. Apparently, the Si/TRG composites show much better cycling performance than the Si nanoparticles (Fig. 4c). After 100 cycles, the reversible capacity of Si/TRG composites is still as high as 1153 mA h g^{-1} , which is more than 3 times higher than that of the theoretical specific capacity of currently used graphite (LiC_6 , 372 mA h g^{-1}), while that of Si nanoparticles is only 13 mA h g^{-1} . Another much improved property of the Si/TRG composites is their excellent rate capability (Fig. 4d). The Si/TRG composites exhibit stable and reversible capacities of 1304, 1014, and 803 mA h g^{-1} when the current densities increase from 1000 mA g^{-1} , to 2000 mA g^{-1} , and 4000 mA g^{-1} . The superior cycling and rate performances of Si/TRG composites could be attributed to the following reasons. On the one hand, the graphene sheets could provide sufficient electrons for the Si nanoparticles, withstand the deformation pressure from Li-Si alloying and dealloying processes, and maintain an integrated structure. On the other hand, the existence of nanospace between graphene sheets and Si nanoparticles could enhance Li^+ diffusion to the encapsulated Si nanoparticles, as well as accommodate the alloyed Si nanoparticles. Electrochemical impedance spectroscopy (EIS) measurements of the samples before and after being used clearly indicate the enhanced electronic conductivity and less SEI formation for the Si/TRG composites compared to pristine Si nanoparticles (Fig. S9 in ESI†). The robust structure of the Si/TRG composites is confirmed by the TEM images of the sample after being used in lithium-ion batteries for 100 cycles (see Fig. S10 in ESI†).

In summary, we have developed a novel method for the preparation of Si nanoparticles intercalated in graphene sheets *via* combining freeze-drying and thermal reduction. The as-achieved Si/TRG composites exhibit remarkably improved cycling performance (*ca.* 1153 mA h g^{-1} after 100 cycles) and rate performance in comparison with bare Si nanoparticles, which could be attributed to the unique structure of the nanocomposite. In addition, the obtained nanocomposites are micrometre-sized aggregates which

promise ease of process. Taking the facile synthesis and excellent performance of Si/TRG composites into account, it would be of significant interest to extend to other high capacity electrode materials with large volume change and low electronic conductivity.

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