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Short communication

Decoration of graphene with silicon nanoparticles by covalent immobilization for use as anodes in high stability lithium ion batteries

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HIGHLIGHTS

- Si nanoparticle–graphene hybrids were fabricated by covalent immobilization.
- High dispersion of Si nanoparticles and graphenes were obtained.
- The Si–graphenes exhibited good cycle stability for lithium ion battery anodes.

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ABSTRACT

Si nanoparticle–graphene hybrids are fabricated by covalent immobilization and subsequent heating in a H_2 + Ar atmosphere. The absence of a graphite (002) peak in X-ray diffraction shows that the hybrid synthesized by this approach prevents graphene nanosheets re-agglomerating. Transmission electron microscopy shows a homogeneous distribution of Si nanoparticles on the graphene. Galvanostatic charge/discharge tests demonstrate that the Si nanoparticle–graphene hybrid has much better charge capacity retention than pristine Si nanoparticles and a Si nanoparticle/graphene mixture. The relationship of the capacity to the weight ratio of Si nanoparticles and graphene in the hybrid has been investigated. The results reveal that the hybrid of with a weight ratio 15:1 (Si:G) exhibits the most stable cycle performance, which retains 92.7% capacity of the 1st cycle after 50 charge/discharge cycles. The 1st Li^+ insertion capacity is 1297 mAh g^{-1}, and the 50th Li^+ insertion capacity is 1203 mAh g^{-1}.

1. Introduction

The possibility of applying rechargeable lithium ion batteries in mobile and stationary power storage has generated numerous studies to improve their energy density, power density and cycle life. One active research area is to replace graphite as the energy storage component in the anode with materials of higher storage capacity. Si has attracted much attention as anode material for its high theoretical capacity (4200 mAh g^{-1}). However, the poor cycle performances resulting from the low intrinsic electronic conductivity and the large volume change in Li^+ insertion/extraction process hampers its practical implementation [1]. Various forms of Si electrode materials have been explored to overcome these disadvantages [2–10], such as Si nanotubes [2–4] and nanowires [5,6] by chemical vapour deposition, Si nanofilms [10] by electrodeposition. According to these previous literatures, constructing sufficient inner-space for Si grains to accommodate the volume expansion during Li^+ insertion is a universal strategy. However, these studies are still not satisfactory, either because of high cost manufacturing, and/or low output for practical implementation. Therefore, there is a critical need to design a Si-based electrode with high Si grains' dispersion using a more accessible method.

Graphene having high conductivity, high mechanical strength, and super-high specific surface area [11–21], is a good candidate as fillers to construct inner-space for Si materials [22,23]. In addition, the low cost starting material and the readily scalable preparation process also bring graphenes a promising commercial prospect for their practical application. However, the homogeneous dispersion of Si grains and graphenes in the material is the prerequisite of generating sufficient inner-space. In this study, monolayer Si nanoparticles (SNs) were firmly anchored on graphene oxides (GOs) by covalent immobilization. Then, the as-synthesized Si–GO

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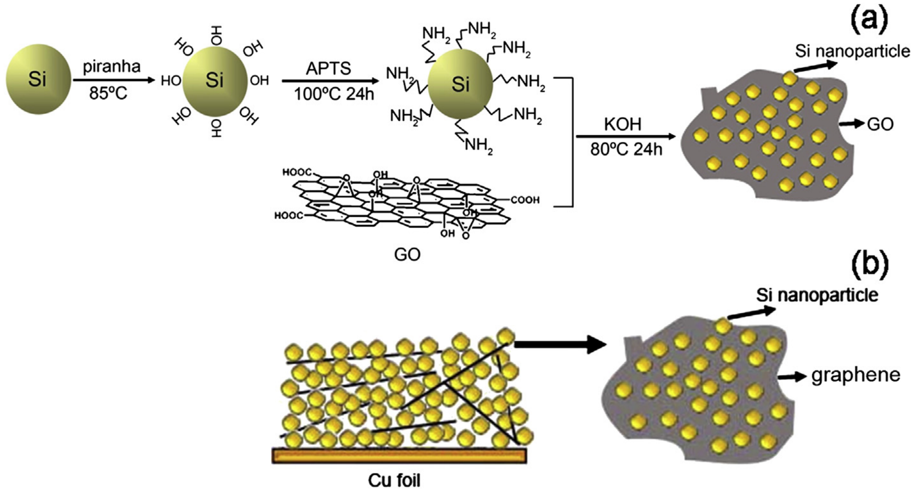

Fig. 1. (a) Scheme of fabricating Si–GO hybrid and (b) Si–graphene anode.

hybrid was reduced to Si–graphenes in H_2 5% + Ar 95% atmosphere. This process caused a uniform dispersion of SNs on graphene surface, prevented SNs aggregating and the irreversible agglomerates of the graphenes in the following battery assembling.

2. Experimental

2.1. *Preparation of the Si–graphene hybrid*

All the reagents in the experiments were analytical pure. GOs were prepared by oxidizing graphite using the improved Hummers method [24–28] (The details are shown in supplementary material). Si crystalline powder (Alfa Aesar, APS 0.05–0.1 μm) was first cleaned for 0.5 h in a piranha solution (2:1 in volume, H_2SO_4/H_2O_2) at 85 °C, followed by rinsing with copious amounts of deionized water and ethanol. Then, the Si powder was dried in an oven overnight. The pretreated Si (0.2 g) and 0.2 mL (3–aminopropyl)triethoxysilane (APTES) were dispersed in ethanol by ultrasonic 0.5 h. The mixture was stirred for 24 h at 100 °C. After cooling to room temperature, GOs and 0.05 g KOH were added into the flask. The mixture was treated in ultrasonic for 0.5 h and then stirred at 80 °C continuously for 24 h, filtered, and washed with deionized water and ethanol. The resulting Si–GO hybrid powder was dried in the oven at 50 °C overnight. The process of fabricating

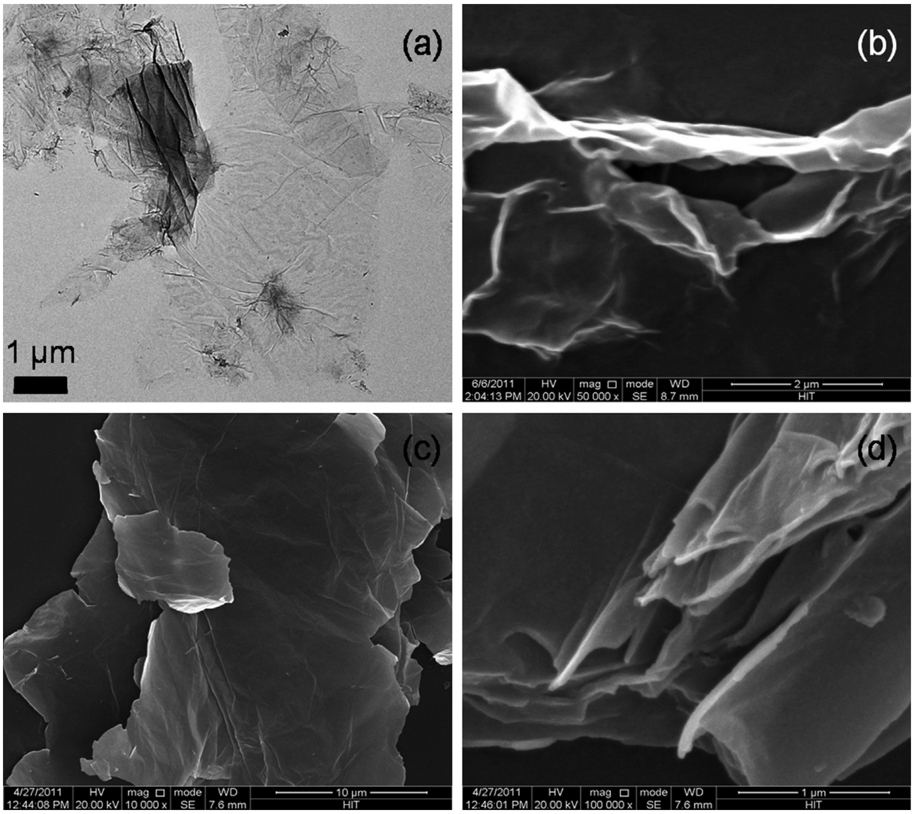

Fig. 2. (a) TEM and (b) SEM images of GOs, and (c, d) SEM of graphenes reduced from GOs directly in H_2 + Ar atmosphere.