Synthesis of Graphene-wrapped Silicon Nanoparticles by Ultra-sonication

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Abstract. Composite electrodes composed of silicon nanoparticles (SiNPs) in accommodation with graphene oxide (GO) synthesized by the ultra-sonication method can be used as a Li-ion battery anode. SiNPs wrapped with graphene is found to be used as an advanced material for Li-ion anode battery because of the high charge storage capacity, low cost, large surface area, cyclic stability, and reliability in comparison to the conventional planner Si particle. The SiNPs coated with graphene can accommodate the volume expansion problem of Si during lithiation without any fracture. The graphene-wrapped SiNPs morphology and dimension were characterized by high-resolution transmission electron microscopy (HRTEM).

1. Introduction
Graphene is a two-dimensional (2D) sheet, consists of one layer carbon (C) atoms with honeycomb lattice arrangement, and graphene oxide (GO) is the oxidation of graphite. The graphene and graphene-based devices are advanced research material due to its large surface area, higher electric and thermal conductivity, and stability. In recent times, research on graphene composites with silicon, for application in energy storage, and conversion device is on the rise.

Doped Si materials enhance conductivity at a low mass density making it a good candidate for stable electrodes for electrochemical devices, e.g. electrochemical supercapacitors, and micro fuel cells. The graphene coating over porous Si (PS) passivates surface charge traps and improves electrode-electrolyte electrochemical interface [1] improving energy density up to 40 times compared to Si material. Su et al. demonstrated that the conductivity of the direct-graphene coated PS was ten times better than that of the direct-graphene coated flat Si [2, 3]. The enhanced conductivity is attributed to the presence of suitable quality graphene layer. The formation of which can further be improved by using gold (Au) catalysts. Graphene and graphene-based composites are used for high-performance Li-ion batteries (LIB) because of their excellent electronic and mechanical properties. The amorphous Si (a-Si) NPs and graphene composite prepared by Hummers method and thermal decomposition of silane gas (SiH₄) helps in reducing induced strain and stress occurring during volume expansion [4]. As reported, hierarchical nano graphene shell indicates elastic, sponge-like aspects, which minimizes the volume expansion of problem of Si during lithiation process. Additionally, graphene provides low diffusion barriers and stipulates enough free space to accommodate the fast migration of ions, which results in long-term cycling stability, and rate performance [5]. The composition of PS and reduced-graphene-oxide (rGO), fabricated by steam etching of SiNPs and rGO aerogel nano-sheets with nano-holes, establish a porous...
structure to condense SiNPs, that reduces the transfer distance of Li-Ions which further controls the aggregation and destruction of Si particles [6]. The composite electrode shows high specific capacity and excellent cycling stability (1004 mAh/g at 50 mA/g up to 100 cycles). The graphene-based materials adsorb hydrogen through physical absorption (or physisorption) compared to graphite, which is due to better electrical conductivity, larger surface area, and higher chemical tolerance. PS coated with Pd NPs followed by GO exhibits hydrogen storage capabilities up to 2.1 wt% hydrogen [7]. The use of composites of GO and PS is extended to hydrogen gas sensor [8].

Chemical inertness of pristine Si due to the weak reaction between Si and hydrocarbons imposes a significant restriction of direct graphene growth. Hence, application of surface engineering techniques for the growth of graphene becomes a critical process when Si is used as a substrate. The graphene-wrapped SiNPs composite, used as an anode for LIB, increase the capacity of the battery because of the large surface area. This paper reports the fabrication of graphene-wrapped SiNPs by the ultra-sonication method.

2. Materials and preparation method
Si (100) wafers (p-type, B-doped, 0.01–0.02 Ω-cm, 250 μm thick) were used to fabricate PS by electrochemical anodization technique using a solution consisting of 1:2 volume mixture of aqueous 48% hydrofluoric acid (HF) and acetic acid (CH₃COOH) [9]. An anodization current density of 30 mA/cm² for 5, 10, and 20 minutes helps in the production the PS samples. After the anodization, the PS film was lifted up from its parent wafer and crushed.

GO was prepared by the modified Hummers method. In a three-necked round bottom flask, two gram of fine graphite powder and 46 ml of concentrated H₂SO₄ were taken and stirred for 30 mins. The temperature of the reaction was kept below 10°C by keeping an ice bath below the flask. Six gram of KMnO₄, which serves as an oxidant, was then added and the mixture was again stirred for 30 minutes. The ice bath was then removed, and the mixture was vigorously stirred for one hour. The temperature rose to 30°C in this period. Controlled addition of water up to 92 ml was done to prevent the explosion of the reactants. The mixture was stirred for one hour with the temperature maintained at 98°C. Finally 50 ml of 30% H₂O₂ was added to oxidize the unreacted graphite. Ultrasonic treatment achieved the formation of GO from graphite oxide. The dissolved GO (in DI water with GO: DI:: 1:2 ratio) was mixed with freestanding PS film and was put in the ultra-sonication for nine hours to form graphene-wrapped SiNPs [10]. The colloidal was dried at 60°C in an oven to obtain The SiNPs-graphene composite in dry powder form.

3. Result and Discussion
The morphology of the composite, as shown in Figure 1 (a), indicates a curly flower structure of graphene composites wrapped with SiNPs, obtained from the ultra-sonication method. The FESEM image of the multilayered composite, as shown in Figure 1 (b), shows the layered structure of the composite, where well-separated GO films fully encapsulate Si particles. The TEM characterization techniques show the internal structure and crystal orientation of Si/graphene composite more precisely, as shown in Figure 2. The fringe spacing is 0.31 nm, corresponds to (111) plane of Si.

Figure 3 confirms the inter-atomic distance in graphene (0.207 nm) and Si (0.316 nm). Figure 4 shows the SEAD pattern of graphene composite SiNPs for different L values (i.e., L=205 mm and 150 mm, respectively). Energy dispersive spectroscopic (EDS) mapping verifies the composition of the sample, as shown in Figure 5, which, shows the presence of Si, graphene (i.e., C), and graphene composites through elemental mapping.
Figure 1. FESEM image of SiNPs-graphene composite (a) curly-flower structure (b) multi layered structure

Figure 2. Graphene-wrapped SiNPs TEM image at (a) high resolution (b) low resolution

Figure 3. Interatomic distance profiles for (a) graphene 0.207 nm, and (b) Si 0.316 nm
Figure 4. Diffraction pattern of SiNPs-graphene composite for (a) L=250 mm, and (b) L=150 mm

Figure 5. Elemental mapping of graphene-composite SiNPs
4. Conclusion
The PS, fabricated by electrochemical anodization, was coated with GO. The sample was characterized using FESEM, and HRTEM microscopy method. The characterization method confirms graphene and graphene composite SiNPs. The inter-atomic distance and crystal orientation of Si is 0.31 nm, (111) structure, respectively. The graphene-wrapped SiNPs can be used as the anode in LIB to overcome the lithiation problem.

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