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Synthesis of graphene-siloxene nanosheet based layered composite materials by tuning its interface chemistry: An efficient anode with overwhelming electrochemical performances for lithium-ion batteries

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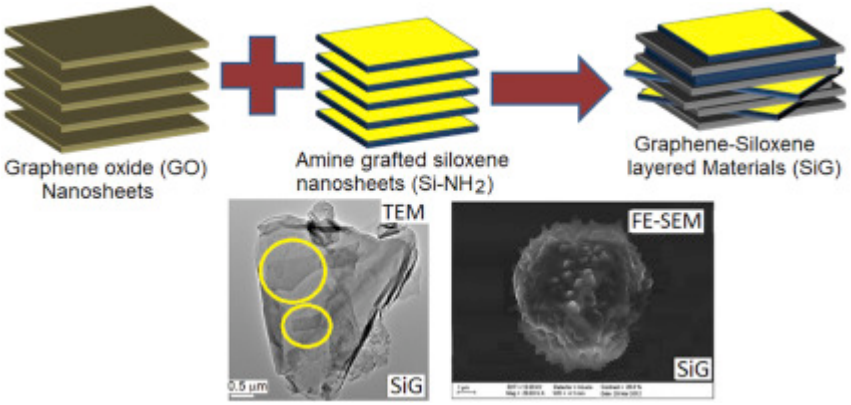
Highlights

- A method of preparing 3D structured graphene-siloxene (SiG) composites is reported.
- Intercalation of siloxene in the graphene layers is revealed using FE-SEM and TEM.
- Prepared SiG render first charge capacity of 3016 $mAhg^{-1}$ at 205 mAg^{-1} current rate.
- At 4.1 Ag^{-1}, SiG anode delivers reversible capacity of 1040 $mAhg^{-1}$ for 1000 cycles.

Abstract

Owing to its high theoretical storage capacity, two dimensional (2D) silicon nanosheets is the one among the most exciting anode material for the next generation lithium ion (Li-ion) batteries. However, deprived electrochemical properties due to the huge volume expansion resulting in rapid capacity decay, thereby hindering its commercial application aspect of silicon nanosheet based materials. The present work proposes a novel concept of synthesizing graphene-siloxene (SiG) based multi-layered structures by tuning the interface chemistries of graphene oxide and siloxene sheets derived from topochemical transformation of calcium silicide ($CaSi_2$). Morphological characterization using Field emission scanning electron microscopic and transmission electron microscopy reveal the successful formation of few- to multi-layered SiG composite materials with intercalated/surface grafted siloxene nanosheets on the graphene layers. Owing to its hierarchical composite structure, SiG as anode delivers the first discharge and charge capacity values as high as 3880 $mAhg^{-1}$ and 3016 $mAhg^{-1}$ respectively measured at the current rate of 205 mAg^{-1}. Even at high current rate (4.1 Ag^{-1}), SiG composite materials delivers first charge capacity of 1480 $mAhg^{-1}$ with good cycling performance (1040 $mAhg^{-1}$) after 1000 cycles. Due to its enhanced lithium storage, cycling stability and rate capability, synthesized SiG composites could be a potential anode candidate for Li-ion batteries.

Graphical abstract



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Introduction

Innovative energy storage technologies are essentially important for the operation of

electric vehicles and for the exploration on practical usage of many types of renewable energy sources [[1], [2], [3], [4]]. Though the commercially available lithium battery technologies are favourable energy storage devices for portable electronics, they cannot meet requirements of advanced energy storage applications due to their confined energy storage capacity restricting its stable operation. Therefore, it is essentially important to develop alternative anode materials meeting the demands for energy storage requirements [5,6].

In recent eras, nanostructured silicon materials have received wide attention, not only for the many technological applications presently in use and envisioned for the future, but also from the research perspective on fundamental principles [6,7]. Owing to its overwhelming theoretical storage capacity ($4200\,mAhg^{-1}$) in comparison to conventional carbonaceous materials ($372\,mAhg^{-1}$) and reasonably low working potential (~0.5 V versus Li/Li^{+}), silicon is expected to be outstanding anode material for next generation lithium batteries for advanced energy storage applications [[8], [9], [10], [11], [12], [13], [14]]. Also, the elongated voltage plateau upon discharging enables a stable voltage during electrochemical cycling [15]. Extensive research work has been carried out on the synthesis and application aspects of several various nanostructured silicon based materials, such as nanoparticles [8,9], nanowires [10,11], nanotubes [1,12] and thin films [13,14]. However, the silicon anode undergoes a huge volume change (upto 400%) during galvanostatic charge–discharge cycle, leading to the pulverization of the silicon particles, which in turn results in drastic capacity fade [16,17]. One of the plausible solutions to circumvent this problem is to prepare a carbon coated silicon composite materials that minimizes dimensional changes and thereby overcoming the pulverization issues of Li alloy electrodes during cycling [[18], [19], [20], [21]].

Though extensive research has been reported on the synthesis and application aspects of various nanostructured silicon's, very little work has been done on the two dimensional (2D) silicon nanomaterial with sheet morphologies having nanometer level thickness and submicro- to micrometer level lateral dimensions [[22], [23], [24], [25]]. These nanomaterials have been receiving undue attention in recent years, since they show unusual physical properties, which are the results of a quantum size effect associated to their ultrathin structure [22,23]. Theoretical modelling studies on monolayer silicon nanosheet with (111) honeycomb arrangement, revealed that these sheets preferably exists in a low-buckled morphology [26,27]. Several experimental studies have also revealed that chemical functionalization of the single-layered Si nanosheet yields stable structures with unique properties [[23], [24], [25]]. Owing to the large volume expansion and thereby rapid capacity decay, the use of silicon nanosheets in next generation Li-ion batteries still remains a challenging task, though,

it showed better lithium storage properties, when compared to silicon nanoparticles [28,29]. One of the remedial measures to overcome this issue is to encapsulate silicon sheets between the graphene sheets.

Ever since its discovery, two dimensional graphene nanosheets has been broadly explored in various application areas such as electronics, catalysis, sensing and energy storage [[30], [31], [32], [33], [34], [35], [36], [37]] Alternatively, these nanosheets have become promising nanoscale building blocks for the development of new composite materials, thanks to its unique nanostructure with excellent properties [38,39]. Due to good electronic and mechanical properties with tunable surface chemistry, these nanomaterials can be used as an ideal template in controlling the properties of the nanocomposite materials. Significant research has been done in recent years on the development of graphene based nanostructured electrode materials for lithium-ion batteries [[40], [41], [42]]. Recently, Kim et al. [43], reported the bulk synthesis of silicon nanosheets by magnesiothermic reduction of sand and its graphene based composites with significantly improved lithium storage properties.

Alternatively, in the present research, we introduced a novel concept where the siloxene nanosheets prepared via. Topochemical reaction from calcium silicide ($CaSi_2$) is effectively intercalated between the graphene sheets by tuning its surface chemistry leading to few- to multi-layered graphene-siloxene composites (SiG). Synthesized graphene-siloxene nanostructures have been extensively characterized using various tools and examined for its electrochemical characteristics by fabricating lithium-ion half-cell using lithium metal as counter and reference electrode.

Section snippets

Synthesis of siloxene nanosheets

Synthesis of layered siloxene ($Si_6H_6O_3$) was done by following the method described by Yamanaka et al. [44], 10g of $CaSi_2$ (Sigma Aldrich Inc., South Korea) was added to 37% HCl (Sigma Aldrich Inc., South Korea) at −10°C in the ice-cold bath and stirring

was continued for 5 days. The obtained product was filtered and washed with 10% hydrofluoric acid (HF; Sigma Aldrich Inc., South Korea) followed by acetone and then dried under vacuum at 110°C yielding approximately 7g of yellow coloured…

Results and discussion

Fig. 1 (a) illustrates the synthesis scheme of the graphene-siloxene (SiG) few- to multi-layered composites using calcium silicide. Initially, amine functionalized siloxene nanosheet is synthesized in two steps. In the first step, H terminated siloxene with Si (111) layers have been synthesized using calcium silicide by the synthetic route suggested by Yamanaka et al., [44]. These Si (111) layers consists of two dimensional (2D) silicon nanosheets stacked in the form a graphite like crystal…

Conclusions

In summary, graphene-siloxene (SiG) nanosheet based few- to multi-layered composite materials have been successfully synthesized by tuning the interface chemistry of graphene oxide and siloxene nanosheets followed by calcination at 800°C. Successful formation of layered SiG materials is revealed using FE-SEM results. Effective encapsulation of crystalline siloxene nanosheets within graphene sheets is corroborated using TEM. Crystalline characteristics of encapsulated siloxene nanosheets are…

Author contributions

A.M.S generated the research idea, proposed the research plan, interpreted the data and wrote the manuscript. K.T, M.J.K.R and G.S carried out material characterizations as per the research plan proposed by A.M.S. K.T & M.J.K.R fabricated the Li-ion batteries, compiled the experimental results and helped in data interpretation and manuscript preparation. S.R, R.K and S.R provided research support for this project, helped in data analysis and manuscript preparation.…

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> ...Moreover, functionalized PEO-based SPE enables to reduce crystallization and improve electrochemical properties (e.g., ionic conductivity and Li ion transference number). A small molecular FSA with a functional group of –NH2 and FSO2− has an intimate compatibility with emerging used anode materials, such as metallic Li [31], graphite [32], graphene-siloexne [33], compared with the character of an unstable interphase and poor ionic conductivity derived from LiTFSI-based electrolyte [30,34,35]. To the best of our knowledge, this is the first study that introduces FSA for a chemical reaction with an epoxy group for obtaining a network of CSPEs....

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> ...As for Si-NH2, there are two peaks located at 2990–2860 cm−1, corresponding to the stretching vibrations of νNH2/CH2 in the APTEs molecules [27,28]. A strong peak is observed at 3440 cm−1, indicating the stretching vibrations of the NH bond [29–31]. In addition, a characteristic peak around 1000–1250 cm−1 can be illustrated to Si-O-Si stretching vibration modes [32]....

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