Solvent Transfer of Graphene Oxide for Synthesis of Tin mono-sulfide Graphene Composite and application as Anode of Lithium-ion Battery

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ABSTRACT

Tin mono sulfide (SnS) graphene composite has been synthesized for anode of lithium-ion battery. For synthesis of composite, graphene oxide (GO)-water (H₂O) colloid has been destabilized and ensured the complete transfer of graphene oxide into another organic solvent *N,N*-dimethyl formamide (DMF). Mechanism for the destabilization of GO-H₂O colloid is established. Surface to surface attachment of SnS on graphene sheet is achieved by solvothermal solution phase assembly of graphene sheets and SnS nanoparticles in DMF solvent. Graphene plays role in nanoparticle formation in composite. Such confined composite has been cycled reversibly at current rate of 160 mA g⁻¹, in voltage region of 0.01 V - 2.5 V and exhibit a superior discharge capacity of 630 mAh g⁻¹ after 50th cycle. *Ex-situ* TEM analysis of used electrode reveal that the SnS nanoparticle-graphene composite with CMC binder perform better due to proper shape retention of electroactive materials during electrochemical cycling.

KEYWORDS

Colloid destabilization, Graphene oxide (GO), Graphene-tin(II) sulfide (SnS) composite, Lithium-ion battery, Solvothermal synthesis

1. INTRODUCTION

Electrochemical energy storage is one of the major option of storage system in several sectors of deployment. Among all electrochemical energy storage systems, lithium-ion battery is a major player, as it can be used from small consumer device to grid storage.¹⁻² As expected, future utilities depend upon its durability and capacity retention during numerous charge discharge cycles. Performance and stability of a lithium-ion battery electrode mainly depends on its electrode constituents *i.e.* electro-active material, their size, conducting material, binding agent and nature of current collector. Electro-active material in nano dimension plays a crucial role in its electrochemical stability as well as in improving electrode kinetics in terms of facilitating lithium-ion diffusion.³⁻⁴ To maintain proper contact between electro-active particles, conducting carbon source is being used such as, carbon black, carbon nanotube (CNT) and graphene.⁵⁻⁸ The carbonaceous materials play a major role in Li-cell electrochemistry *via*, 1) electronic conductivity among electro-active particles and current collector; and 2) **helping** in managing mechanical stress generated during cycling of electro-active material against lithium.⁹⁻¹² Thus, a composite of conducting material with the electro-active species is an attractive pathway to enhance the electrochemical performance of lithium-ion cell.^{7, 8, 11, 13, 14}

Graphene, a new allotrope of carbon, has shown better electrochemical charge storage activity with lithium as well as with sodium.¹⁵ Graphene is increasingly being identified as the next new lithium and sodium-ion battery material because it can contribute nearly double the specific capacity of graphite which has raised the prospect for the replacement of the graphite anode.^{6, 8, 16} The specific capacity can be further increased by preparing composite of graphene with semi-metals or metal oxides (*e.g.* Sn, Si, SnO₂) with high Li storage capacity. Many of these composites have shown higher specific capacities and rate capability as Li-ion battery anode.^{6, 17-}

¹⁹ Cyclic stability of these composites, however, is still not satisfactory and significant capacity loss is typical after initial cycles. The major reason behind the capacity fade can be the pulverization of electroactive material, morphological mismatch, distribution of electroactive materials on graphene sheet and nature of binder used for electrode preparation.^{17, 19-21}

As an excellent anode, tin-based alloying material has been reported in the literature which is theoretically superior in terms of volumetric and gravimetric energy density, in comparison to traditionally used graphite.²²⁻²⁵ Recently, our group has shown the versatility and excellence of SnO₂ and SnS -based anode in lithium as well as sodium-ion battery applications.^{17, 26-29} Theoretically, the SnS is a superior electro-active material in comparison to SnS₂ and SnO₂ because it results in minimum loss of Li during first discharge cycle, although, both (SnS and SnO₂) have same theoretical capacity.^{17, 27, 30, 31} In principle, SnS-graphene composite can improve anode material performance with respect to bare SnO₂, SnS and SnS₂ nanoparticles. However, in addition to interfacing SnS with graphene sheets, it is also important to obtain SnS particles well coated or confined by graphene sheets. Another electrode constituent, like carboxy methyl cellulose (CMC) or Na-alginate, as a binder can help to integrate better to the preferred hybrid structure as lithium-ion battery electrode.^{21, 27-33} Most of the researchers have synthesized the SnS₂ with graphene and major problem with their synthesis process is the conversion of Sn²⁺ of precursor salt to Sn⁴⁺ which finally result in a graphene composite with SnS₂.³⁴⁻³⁶ This change in oxidation state of tin is due to presence of oxygen containing functionalities on graphene oxide (GO) surface and water, in which GO is used to dispersed during composite formation. Water as solvent is more difficult to use than oxygen functionalities of GO surface because H₂O directly converts Sn²⁺ precursor to Sn⁴⁺ hydroxide and starts precipitation. This unwanted reaction further affects the distribution of nanoparticle on GO surface.

In the present work, an elegant and rational strategy has been discovered for synthesis of SnS nanoparticle on graphene surface in a single step. In this approach, a much lower degree of oxidative GO dispersion was used to form composite with tin (II) sulfide using solvothermal process. The solvent for solvothermal synthesis is selected, so that the precursor salts and GO can be easily dispersed in the solvent and at the same time, the solvent does not allow Sn^{2+} to convert in Sn^{4+} . Here, solvothermal reduction route has been adopted to achieve the reduction of GO to r-GO as well as the for formation of SnS-reduced graphene oxide (SnS/r-GO) composite. The source of reduced graphene oxide (r-GO) was GO which was synthesized by well-known Hummer's process³⁷ and dispersed in water. Further, GO-DMF colloid is prepared by destabilization of graphene oxide-water (GO- H_2O) colloid in first step, then GO was dispersed in DMF. It is already known that DMF is a good solvent for tin (II) halide^{17, 27} to SnS conversion and in present case DMF solvent was used as a common solvent. As a result, this resultant composite is used as lithium-ion battery anode because it has a very high reversible capacity as well as excellent cycling performance compare to SnS nanoparticles, exhibit a great potential as high rate lithium ion battery anode. The role of binder on electrochemical performance of composite is also studied.

2. EXPERIMENTAL

2.1 Tin sulfide nanoparticle synthesis

The tin nanoparticles were synthesised by the reaction of hydrated tin (II) chloride (Qualigen Excella R grade, India) with sodium sulfide flakes (Fischer Schientific, India) in presence of thiourea (SCDL chemicals, India) and *N, N*-dimethyl formamide (Merck, India) as a solvent or reaction medium. First, 4.43×10^{-3} moles of hydrated tin (II) chloride was dissolved in 25 ml of DMF, then 4.86×10^{-3} moles of thiourea was dissolved in previous solution. Finally the volume

of the solution was maintained to 50 ml by adding extra DMF. The above solution was heated to 180 °C at hot plate with constant stirring for 2 h and then 5.12×10^{-3} moles of sodium sulfide (Na_2S) flakes were added. After addition of Na_2S , a black precipitate was observed in the reaction vessel. The above mentioned mixture was heated for next 2 h and then cooled down to room temperature. The precipitate was centrifuged and washed with water and alcohol. The washed precipitate was dried at 120 °C in vacuum oven for 12 h to get the SnS nanoparticles.

2.2 Synthesis of graphene oxide (GO)

The graphene oxide was synthesised by oxidation of natural graphite flakes in KMnO_4 , H_2SO_4 and sodium nitrite (NaNO_3) using Hummer's method.³⁷ In first step, 2 g of graphite flakes (Sigma Aldrich) were dispersed in to 60 ml of conc. H_2SO_4 (Merck, India) solution and cooled to 10 °C. Then 1 g of sodium nitrate (Merck, India) was added and mixture was stirred vigorously. After 30 min of rotation, 5 g of KMnO_4 was added to the reaction mixture slowly with interval of 5 min. The reaction temperature was maintained at 35 °C. After 2 h of reaction, 200 ml of H_2O was added to the solution followed by 500 ml of 3% solution in water. The precipitate was washed and filtered with hot water. Then oxidised flakes were transferred to pure Milli Q water and sonicated for 2 h to separate the oxidised flakes from the residual graphite flakes. The filtrate was taken for further use as a colloid of GO- H_2O .

2.3 Preparation of GO-DMF colloids

For preparation of GO colloid in DMF, first GO- H_2O colloid (1.17 mg ml^{-1}) was destabilise using ethanol and hydrochloric acid. The filtrate was sonicated by adding 5 ml of ethanol (ACS absolute ethanol for analysis, 1l = 0.79 kg; Merck, Germany) and HCl (35%, 1l = 1.16 kg; Merck India) in GO- H_2O colloid solution. Then solution was centrifuged for 15 minute at speed of 8000 rpm. The GO get settled in the bottom of centrifuge tube (Figure 1). The supernatant has been

removed and precipitated GO was pressed between cellulose filter paper to remove possible water from GO. Then separated graphene oxide (GO) was dispersed in 50 ml DMF and sonicated for 30 min. This colloid of GO-DMF has been used in solvothermal synthesis of SnS/r-GO composite.

2.4 Graphene-tin (II) sulfide (SnS) nanoparticle synthesis

For preparation of graphene-SnS nano-composite (SnS/r-GO), as prepared GO-DMF colloid (50 ml) was mixed with 0.5 g of hydrated tin(II) chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and 0.5 g of thiourea. The mixture was sonicated for 30 min and then kept in a Teflon lined hydrothermal bomb of dimension of 5.5 cm $\times$ 4.3 cm $\times$ 3.4 mm (height $\times$ diameter $\times$ thickness). The vessel was kept at 180 °C for 22 h. After completion of reaction and cooling the reaction vessel, a black precipitate was obtained. The precipitate was washed with water and iso-propyl alcohol (IPA). The washed sample was finally dried in vacuum oven at 120 °C for 12 h to remove the residual solvent.

2.5 Composite characterization

The composite and nanoparticles were characterized by powder X-ray diffraction with Rigaku Smart Lab with the accelerating voltage of 40 kV and Cu-sources target for X-ray generation in the 2θ range of 10°-70°. FT-IR analysis was done with Perkin Elmer with forming the pellet in the KBr and drying pellet in IR. The FT-IR analysis of the colloid destabilization process was studied by adopting slight different methodology from conventional one. Here, the suspension of GO was drop cast on pre-prepared KBr pellet and FT-IR was taken without drying its liquid. UV-Vis measurement were done by Jasco V-530 Spectrophotometer with a dilution of 95% with milli-Q water in a range of 200 nm to 500 nm. The zeta potential measurement were done with ZetaPALS Zeta Potential Analyser, Brookhaven instrument corporation (USA). The Raman spectroscopy of the sample has been performed with Ramnor HG-2S Spectrometer, Jobin-Yvon,

France with a Ar-LASER of 514 nm with power of 5 mW and 20X optical zoom. The JEOL-F2100J with accelerating voltage of 200 kV has been used to do the TEM analysis of the samples. Carbon content of the sample was analysed by CHNS(O) analyser of model FLASH EA 1112 Series, Thermo finnigan, Italy, fitting of XPS spectra were done by selecting background with Shirley algorithm and peaks are fit to a mixed Gaussian and Lorentzian line shape. The quantitative analysis were done with consideration of atomic sensitivity factor.

2.6 Electrochemical characterisation

The electrochemical test of the nanoparticle and the nano-composite have been performed in a lab scale Swagelok type cell assembly and with CR2032 coin cells. The thin film of electro-active material was prepared by mixing SnS nanoparticle and SnS nanoplate samples with carbon black super C-65 (external carbon) and CMC binder with a ratio of (66:24:10) with few drops of water. The slurries of SnS/r-GO composite and pure r-GO were prepared by mixing the material with CMC binder in (90:10) ratio with few drops of water. The slurry was mixed for 30 min and then cast on thin copper foil. Similar process was repeated for preparation of PVDF based electrode except the solvent and in this case *N*-methyl pyrrolidone (NMP) solvent was used. These films were dried in vacuum oven at 120 °C for 12 h. The half cell assembly was done in a Swagelok type of cell and metallic lithium works as a reference as well as counter electrode. The electrochemical test were performed at Biologic VMP3 and Arbin, USA work stations. The cyclic voltammetry (CV) has been performed with a scan rate of 0.1 mV s⁻¹. The galvanostatic charge discharge experiments were performed at different current rates like 160 mA g⁻¹, 300 mA g⁻¹ and 500 mA g⁻¹, respectively. The potential window for all the electrochemical measurement was 0.01 V to 2.5 V against Li/Li⁺ at 20 °C. The loading of electro-active material for SnS/r-GO composite with CMC binder was 1.092 mg cm⁻², 1.008 mg cm⁻²,

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4 1.168 mg cm⁻² and 1.092 mg cm⁻² for electrodes tested at current rate of 160 mA g⁻¹, 300 mA g⁻¹,
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6 500 mA g⁻¹ and power plot tests, respectively. The loading of electro-active material for SnS/r-
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8 GO composite with PVDF binder was 0.74 mg cm⁻² tested with current rate of 160 mA g⁻¹. The
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10 loading of electro-active material for SnS nanoparticle with CMC binder and bare carbon was
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12 0.532 mg cm⁻², 0.76 mg cm⁻², 0.784 mg cm⁻² and 1.38 mg cm⁻² for electrode tested at current rate
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14 of 160 mA g⁻¹, 300 mA g⁻¹, 500 mA g⁻¹ and power plot tests, respectively. The loading of the
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16 nanoplate electrode and pure r-GO electrode with CMC binder was 0.756 mg cm⁻² and 3.0 mg
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18 cm⁻², respectively, tested at current rate of 160 mA g⁻¹.
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23 **2.7 Ex-situ TEM analysis**

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25 Morphologic changes during the cycling has been analysed with the JEOL FEG-TEM F2100
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27 with the acceleration potential of 200 kV. The Holey carbon grids were used to prepare the
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29 samples. Fresh composite and nanoparticles were dispersed in acetone and sonicated for 5 min
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31 and then drop casted on carbon grids for analysis. The TEM of cycled cell were performed by
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33 removing the used cell electrode and scratching the electrode surface with the tip of micropipette
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35 having acetone solution. The scratched debris has been dropped on holy carbon grid and tested
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37 for TEM analysis.
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42 **3. RESULTS AND DISCUSSION**

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44 Graphitic oxide prepared with Hummer's method, used to disperse in water to get graphene
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46 oxide (GO) nanosheets. Water molecule can act as a better dispersion medium for graphene
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48 oxide (GO) because it is polar in nature due to charged basal planes.³⁸⁻⁴¹ However, use of GO-
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50 H₂O colloid for direct synthesis of the SnS-GO was not achieved so far by most of the
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52 researchers because in aqueous medium, oxidation state of tin precursor changes from Sn²⁺ to
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54 Sn⁴⁺ by formation of its hydroxides which finally lead to the formation of SnS₂ with sulfur
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precursor. To short out this problem in greater extend, we have decided to separate the graphene oxide (GO) from water first and then disperse in a suitable solvent like DMF which does not allow tin to change its oxidation state and easily forms a solution of precursor salt by co-ordination with tin.¹⁷

In literature, separation of GO from water colloid was previously reported by using strong electrolyte or metallic salts such as HCl, LiCl, MgCl₂, CaCl₂ *etc.* These processes are time consuming and have chances to contaminate the GO surface by metallic impurities, which is not a desired output for any electrochemical applications.⁴²⁻⁴⁵ Previous works have also reported the chelation of metallic ions (Li⁺, Mg²⁺, Ca²⁺) with the functional group of the GO sheet or by protonation of GO sheet results in precipitation which usually takes 2 h (metallic chelation) to 72 h.⁴²⁻⁴⁴ Herein, this work, GO-H₂O colloid (Figure 1 a-c) was destabilized by addition of 2.99 mol % of absolute ethanol (C₂H₅OH) and 5.26 mol% of HCl with successive centrifugation. After removal of water, separated GO was sonicated in DMF to get better colloidal dispersion of GO particles in DMF solvent (shown in Figure 1a). The benefit of this process is that the GO obtained by this method can be dispersed in various solvent because the excess water has been removed in shorter time scale. The other major benefit of this process is that the separation occurs at room temperature without any metallic impurity on GO surface.

Figure 1. Process of destabilization of graphene oxide-water colloid and transfer of GO in another solvent DMF, (a) Different Stages of GO colloids, (b) Schematic for ionic equilibrium of GO sheet, and (c) Schematic for molecular change in GO sheets .

The stability of any colloid depends on the charge present on the surface of dispersed particles and the distance between the dispersed particles.^{46, 47} A suitable distance between dispersed particles is maintained (stabilization of colloid) by the balance between the attractive Vander waal forces and repulsive electrostatic forces among colloid particle.⁴⁶⁻⁴⁹ Similarly, GO forms a stable colloid in water due to formation of hydrogen bond (H-bond) between functional groups (C-COOH, C-CHO, C-OH) on basal plane of GO and polar water molecule and the coagulation was restricted by the repulsive forces acting between ionic (C-COO⁻, C-O⁻) functional group (Figure 1b-c).^{50, 40} The functional groups of GO sheets are in ionic equilibrium due to protonated

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4 and de-protonated state in aqueous medium by maintaining a proper pH of colloid.^{40, 44} Herein
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6 this work, GO-H₂O colloid is destabilized after addition of ethanol/HCl, because a strong
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8 electrolyte like HCl will disturb the ionic equilibrium of protonated and de-protonated state due
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10 to common ion effect and ethanol molecule will form H-bond with surface functionalities of GO
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12 sheet (Figure 1c) that will minimize the ionic repulsion among GO sheets. This passivation of
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14 GO surface by ethanol leads to an agglomeration process of GO sheets and by centrifugal force,
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16 GO sheets can easily be precipitated out from water.
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21 To study the GO-H₂O separation behavior, FT-IR, UV-Vis and zeta potential (ζ) with pH
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23 measurements (Figure 2) were performed for the GO-H₂O colloid in pure state, after addition of
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25 ethanol (C₂H₅OH) and hydrochloric acid (HCl) respectively. The primary study start with FT-IR
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27 and that will predict the bonding status of GO in water colloid. The FT-IR spectra (Figure 2a)
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29 shown in the range of 2600 cm⁻¹ to 4000 cm⁻¹, corresponds to O-H stretching modes of various
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31 carboxy, hydroxy functional groups and this range is also characteristics of hydrogen (H)
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33 bonding and non-bonding status of oxygen functional groups.⁵⁰⁻⁵² As per literature, the
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35 characteristic peak of non-hydrogen bonded (O-H) stretch lies at 3600 cm⁻¹ while for H-bonding,
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37 the peak become wider and asymmetric in nature in the lower frequency range *i.e.* showing blue
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39 shift, and *vice-versa* in FT-IR spectrum.⁵¹⁻⁵²
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Figure 2. Effect of C₂H₅OH and HCl addition in GO-H₂O colloid. The study of (a) FT-IR, (b) UV-Vis, (c) Zeta potential (ζ) and pH.

The FT-IR spectrum (Figure 2a) of pure GO-H₂O colloid has a very wide peak centered at ~3408 cm⁻¹ corresponds to (O-H) stretching of GO sheet which is in hydrogen bonded condition. When ethanol (CH₃-CH₂-O-H) has been added to GO-H₂O colloid, the O-H stretching peak get narrows and is shifted to 3465.8 cm⁻¹ and showed a red shift. On further addition of HCl, this shift becomes more prominent and observed at 3442.7 cm⁻¹ in comparison to the pure GO-H₂O colloid. This red shift in the FT-IR frequency can be assigned to reduction in the H-bonding between the functional group attached on GO surface and water molecule. This reduction in H-bonding may be due to non-covalent passivation of GO surface or due to covalent reaction of

ethanol and hydrochloric acid with the functional group of GO sheet which changes the polarity (ionocity) of dispersed colloid.

Therefore to confirm the chemical status of basal plane of GO in GO-H₂O colloids, UV-Vis spectra (Figure 2b) were taken in similar conditions mentioned above. The UV-Vis spectra show a peak at 233 nm and a successive shoulder peak at 304 nm which corresponds to the ($\pi \rightarrow \pi^*$) transition of C-C bonds from aromatic basal plane of GO and the ($n \rightarrow \pi^*$) transition of C=O groups of the GO.^{38, 43} For all three samples, the peak positions remained the same and do not show any shift. Thus, UV-Vis spectra conclude that the basal plane and C=O remains unaffected due to addition of ethanol and HCl, therefore no covalent functionalization of the GO sheet occurs during the process. Thus, the UV-Vis experiment depicts the possibility of non-covalent passivation of GO sheet by addition of ethanol and HCl and that need to be further justified.

Therefore, to get more information about the change in the surface charge of GO sheet, zeta potential (ζ) and pH measurement (Figure 2c) experiments were performed for all the three conditions mentioned above. The zeta potential (ζ) of pure GO-H₂O colloid was found to be -25.29 mV at pH $\sim$ 3.1, which is in a good agreement with the existing literature and it is believed that, at this surface charge, the colloid will remain stable.^{39, 40, 53} On addition of the ethanol in GO-H₂O colloid, pH changes to 3.4 and zeta potential (ζ) reduces to -16.81 mV and on further addition of HCl, pH reaches to $\sim$ 1 and similarly zeta potential (ζ) shifted to much more closer to zero value (-5.4 mV). This reduction in charge on GO sheet will lead to a faster attraction of colloid dispersion (*i.e.* coagulation) in polar solvent. Reduction in charge density also results in reduction of H-bonding with polar solvent molecule (H₂O) at GO surface and that can be responsible for destabilization and precipitation of GO in H₂O colloid.

It is known that when ethanol ($\text{CH}_3\text{-CH}_2\text{-O-H}$) is mixed with water (H-O-H), it forms H-bonding between ethanol molecule more frequently than water-ethanol and results in polymeric ethanol ($\text{C}_2\text{H}_5\text{OH}$)_n chains.⁵⁴⁻⁵⁶ This phenomenon resulted in the formation of hydrophobic core of ethyl groups ($\text{CH}_3\text{-CH}_2\text{-}$) in the inner surface of polymer and hydrophilic groups (-O-H) orient outside of the polymer which form hydrogen bonding with water molecule.⁵⁴⁻⁵⁵ This preferential selection of molecule for H-bonding was governed by the degree of polarization of (-O-H) which depends on partial charge of oxygen. Herein, the (Mulliken) partial charge on ethanol oxygen (-0.787) is larger than that of (Mulliken) partial charge on oxygen (-0.634) of water.⁵⁷⁻⁵⁸ This charge difference will force the ethanol to get polymerize by H-bonding, preferentially among ethanol molecules rather than the H-bonding between water and ethanol. This way ethanol polymer ($\text{C}_2\text{H}_5\text{OH}$)_n, creates a hydrophobic core, the outer surface of which will partially experience H-bonded with water. Eventually, the chain length of the ethanol polymer ($\text{C}_2\text{H}_5\text{OH}$)_n depends on the concentration of ethanol in H_2O . It is reported that if the concentration of ethanol in H_2O is above > 4 mole %, the higher chain length will form and the length will be very small, if the concentration is below to 4 mol %.^{54, 56} Here in our case, the added ethanol was ~ 2.99 mol%, which leads to the formation of smaller chains of ethanol (monomer, dimer *etc.*) by hydrogen bonding among ethanol O-H groups. Smaller chain length polymers will have tendency to form H-bonding in compare to larger one with the rest of the colloids. In addition of ethanol to GO- H_2O colloids, hydroxyl (-O-H) group of small polymeric ethanol will attract the hydroxyl (-O-H) group of GO sheet in place (-O-H) group of H_2O to form hydrogen bond. This preferential selection will be again based on the partial charges on the oxygen atom of water, ethanol and GO functional groups. GO surface is mainly accompanied by hydroxyl (-OH) and carboxylic (-COOH) functional groups which are attached to the pentagonal/hexagonal cyclic

1 aromatics basal plane.⁵⁰ Currently, we are unable to find any literature report about the
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3 information of partial charges on the GO functional groups. Therefore, as a reference point,
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5 phenol group (Ph-OH) and benzoic acid (Ph-COOH) are considered as a structural analogue to
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7 GO and partial charge of its oxygen can be considered for comparison. The (Mulliken) partial
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9 charge on oxygen of phenol is -0.750 and that is almost equal to ethanol and higher than H₂O.⁵⁸
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11 The Mulliken partial charges on (-O-H) group of benzoic acid is -0.66 which is slightly higher
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13 than oxygen of water.⁵⁹ After the H-bond formation between (-O-H) group of GO functional
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15 group and with (-O-H) group of ethanol, core of ethanol will be outside (Figure 1c) and can act
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17 as a hydrophobic layer on GO sheet. This condition of bonding will result in reduction of total
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19 number of hydrogen bonds initially present. Due to preferential formation of H-bonding between
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21 (-H-O) group of ethanol and (-O-H) group of GO (because of higher Mulliken partial charge on
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23 oxygen atoms) there will be a marginal decrease in overall H-bonding with water (-O-H) group.
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25 Involvement of (-O-H) groups of GO sheet in H-bonding with ethanol will disturb the ionic
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27 equilibrium existing between GO functional group and solvent medium (Figure 1b). So, to
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29 maintain the dynamic equilibrium, again remaining enolate (-C-O⁻) and carboxylate (-C-COO⁻)
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31 groups on GO surface will get protonated by the solvent and the resultant pH of the colloid will
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33 increase. This H-bonding will also results in minor passivation of GO surface and the surface
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35 charge gets decrease. Therefore, as we observed on addition of ethanol resulted in decrease in
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37 zeta potential and slight increase in pH and that is justified at this point.
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50 Further addition of HCl to ethanol-GO-H₂O colloid, HCl will act as a strong electrolyte
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52 in water and due to common ion effect (H⁺), most of the ionic groups on the GO surface will be
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54 protonated by shifting the ionic equilibrium.⁴⁴ Now the protonated group will also form bonding
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56 with remaining ethanol in the colloid. This equilibrium shifts and further passivation due to
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ethanol resulted in huge reduction in surface charge (ζ) from -16.81 mV to -5.4mV and pH to 1. This change in the surface charge with extent of hydrogen bonding, results in the agglomeration of the GO and at this stage the coagulation of the colloid was visible. An additional centrifugation step is used to separate completely GO from H₂O.

After water removal, separated GO was further dispersed in DMF as mentioned in experimental section. Now, GO-DMF colloid has been used further to synthesize SnS composite by solvothermal method. The sulfur source used in the process was thiourea SC(NH₂)₂. During the reaction, H₂S is formed which leads to the sulfurization of tin and also plays a crucial role in GO reduction process to reduced graphene oxide (r-GO) at solvothermal temperature.⁶⁰⁻⁶¹ The reaction proceeds in DMF in the solvothermal environment that does not allow Sn²⁺ to oxidize further to Sn⁴⁺ ions. The reaction has followed as shown in scheme 1.

Scheme 1. Reaction of hydrated tin (II) chloride with thioiurea in N, N-dimethyl formamide solution.

Furthermore, to study the role of GO, in SnS nanoparticles distribution and morphology onto its surface, a similar solvothermal reaction was carried out without addition of GO in DMF. It can clearly be observed here that when the GO is not present in solvothermal vessel, SnS has formed with a 2D nanoplate morphology (Figure 3 a-b). Therefore here it can be concluded that the GO is also playing a role in nucleation process of SnS nanoparticle growth on its surface and most probably due to its diversity of functional group on its surface.

Figure 3. Impact of Graphene oxide (GO) on crystallisation of SnS during synthesis, (a) SnS nanoplates, and (b) SnS nanoparticle/r-GO composite.

To compare the role of graphene in electrochemical stability of the SnS, a bare nanoparticle of SnS was also synthesized. The preparation of the SnS nanoparticle has been performed with simple precipitation route in DMF reaction medium. The reaction scheme followed for the nanoparticle formation is shown in scheme 2

Scheme 2. Reaction of hydrated tin chloride with sodium sulfide

The precipitate of SnS nanoparticle, SnS nanoplate and SnS/rGO composites were further used for electrochemical tests.

3.1 Electrode material characterization and analysis

Phase identification of SnS nanoparticles, SnS nanoplate and SnS/rGO composite have been analysed by powder X-ray diffraction (PXRD).

Figure 4. Powder X-Ray diffraction pattern (PXRD) of SnS/r-GO composite, SnS nanoplate, SnS nanoparticles, r-GO and JCPDS card (01-075-2115) for SnS.

The PXRD patterns (Figure 4) of all SnS nanostructures and its composite sample matches well with the JCPDS file No. 01-075-2115 which reveals the presence of SnS with *Pnma* space group. There are some minor hump in SnS/r-GO PXRD pattern at 2θ of 26.57°, 33.84° and 50.85° (marked with star) corresponding to the formation of amorphous SnO₂. Quantification and reason for the formation of SnO₂ is further discussed in X-ray photoelectron spectroscopy (XPS) section. The PXRD patterns of the SnS nanoplates, synthesized without GO also has some minor

peak at 2θ of 26.57° , 30.7° and 44° corresponding to formation of SnS_2 as an impurity phase. The PXRD of graphene (r-GO) prepared with same solvothermal condition has shown (Figure 1) a wide peak at 2θ of 26.5° and 43.43° corresponding to the (002) and (101) planes, respectively of graphite. This widening of 26.5° may be due to stacking of graphene layers during the reduction and drying in vacuum oven.⁶² The peak is wider in nature because r-GO stacking will occur randomly during the reduction process and can generate a wide range of d-spacing between layers.

Figure 5. Raman spectra of SnS/r-GO composite, reduced graphene oxide (r-GO), graphene oxide (GO), SnS nanoplate and SnS nanoparticle.

To complete the characterization, Raman spectroscopy has been performed to compare the graphene oxide, SnS/r-GO composite, SnS nanoparticle and SnS nanoplate morphology for qualitative analysis of phase and carbon. The D-band (A_{1g} mode), G-band (E_{2g} mode) and D'

band of the graphene were observed at 1348 cm^{-1} , 1582 cm^{-1} and 1612 cm^{-1} (Figure 5) for SnS/r-GO composite, r-GO and GO.⁶³ Reduction of graphene oxide (GO) during solvothermal treatment can be confirmed here with the relative increase in the D-band intensity in compared to r-GO and SnS/r-GO. The I_D/I_G ratio for SnS/r-GO nano-composite, reduced graphene oxide (r-GO) and for graphene oxide (GO) was found to be 1.73, 1.44 and 1.03, respectively. The I_D/I_G intensity ratio has increased significantly from reduction of GO to r-GO. The increase in I_D/I_G ratio also indicates that solvothermal process has played a crucial role in removal of the functional group from GO surface and generated more disorder in basal plane of GO, which resulted in increase of Raman D-band intensity in SnS/r-GO composite and r-GO. It is also noticed that the I_D/I_G ratio of composite SnS/ r-GO is higher than the pure r-GO. This may be attributed to a better distribution of SnS nanoparticle in between the layers of r-GO which make defect bonds at thier nucleation center at the surface to vibrate more generously in comparison to r-GO where layers stacked to each other. The lower frequency region ($< 600\text{ cm}^{-1}$) of Raman spectra (Figure 5) shows the peaks for A_{1g} B_{1u} and B_{3g} mode at 212 cm^{-1} , 187 cm^{-1} and 170 cm^{-1} for SnS respectively.⁶⁴ Another peak at 312 cm^{-1} corresponds to A_{1g} mode of SnS_2 which is present as impurity in SnS nanoparticle and SnS nanoplate, whereas in case of SnS-rGO the same peak is completely absent.⁶⁵ The formation of such a small amount of SnS_2 is a common phenomenon when water is present in hydrated tin(II) precursor salt.²⁷ Therefore from Raman spectra one can conclude that using this synthesis process of making SnS/r-GO composite, the SnS_2 impurity phase is not formed.

To study the nature of functional groups present on the surface of GO before and after reduction process, FT-IR experiments (Figure 6) were performed on samples containing graphene oxide (GO), reduced graphene oxide (r-GO) and SnS/r-GO composite, respectively.

Sample containing GO has shown the stretching frequencies for (-O-H) of acid and alcoholic group at 3440 cm^{-1} which is asymmetric in nature towards lower frequency range. Similarly, the peak at 2854 cm^{-1} associated with (-C-H) stretch of aldehyde and peak at 2920 cm^{-1} associated with (-C-H) stretch of (-CH₃) terminal bonds were also observed in all samples.

Figure 6. FT-IR spectra of graphene oxide (GO), reduced graphene oxide (r-GO) and composite of SnS/r-GO.

In FT-IR spectra of GO, multiple peaks from 1495 cm^{-1} to 1810 cm^{-1} have been observed and showed the different (-C=O) stretch mode of various functional groups present in GO *i.e.* aldehyde, carboxylic acid and their derivatives, etc. The presence of alcoholic group is also distinct with a peak at $\sim 1161\text{ cm}^{-1}$ for (-C-O) stretch of alcohol (-C-O-H). The basal plane of GO **has** aromatic chain containing double bond which reflects in FT-IR frequency at 1645 cm^{-1} for (C=C) in ring structure. Stretching frequency observed at 1139 cm^{-1} corresponds to (-C-O-) ether

group in basal plane. On solvothermal reduction of the GO, FT-IR spectrum in the range of 1495 cm^{-1} to 1810 cm^{-1} has reduced the presence of multiple peaks corresponding to ($-\text{C}=\text{O}$), considerably and only distinct peak at 1645 cm^{-1} remains visible, which stands for ($\text{C}=\text{C}$) stretch from basal plane of graphene.⁶⁶ Another change observed on reduction of GO is in the asymmetry of the ($-\text{O}-\text{H}$) stretching peak that is reduced and became more symmetric. The FT-IR peaks of SnS/r-GO composite are similar to the r-GO except to the presence of a new peak at 453 cm^{-1} that corresponds to SnS.⁶⁴ Peak at 606 cm^{-1} in the r-GO and SnS/r-GO (as a shoulder peak to SnS) corresponds for C-Cl stretch which arises due to partial chlorination of GO sheet during solvothermal reduction.⁶⁷ The source of the chlorine may be accounted for residual HCl that are added for colloid destabilization process.

To get further insights about the qualitative and quantitative analysis of r-GO and their composite, X-ray photoelectron spectroscopy (XPS) experiment has been employed. The XPS data show the similar results or trends (Figure 7) as predicted by the FT-IR experiment for composite and reduced graphene (r-GO). The survey scan of both the SnS/r-GO composite and r-GO (Figure 7a) show the presence of some common peaks of C(1s), O(1s), Cl(2p) and C(KLL) emission band at their respective positions. The composite survey scan also contained extra emission peak for Sn (4d), Sn (3d_{5/2}), Sn (3d_{3/2}), Sn (3p_{1/2}), Sn(3p_{3/2}) and sulfur (2p) respectively. Quantitative analysis of the r-GO, the XPS spectrum shows the atomic percentage (%) of carbon, oxygen and chlorine found to be 80%, 10% and 6%, respectively. This shows that during solvothermal reduction of GO, reduced graphene (r-GO) get partially functionalised with chlorine as it is also observed in FT-IR spectra (Figure 6) of r-GO and SnS/r-GO. The ratio of carbon to chlorine (C/Cl) in SnS/r-GO composite and r-GO is found to be 10.98 and 13.56, respectively. Similarly, carbon to oxygen ratio (C/O) in r-GO is 5.66 while in SnS/r-GO

composite the ratio is 5.2 (including the oxygen present in form of SnO_2). This shows that the solvothermal reduction and formation of SnS/r-GO composite keeps less oxygen on the basal plane of graphene than that of pure graphene (r-GO). The reason for such precious reduction can be attributed to tin which oxidises from Sn^{2+} to Sn^{4+} and simultaneously reduces the oxygen content (present as functional group) on basal plane of GO.

Figure 7. X-ray photoelectron spectra (XPS) of r-GO and SnS/r-GO composite (a) survey scan (b) Sn $3d_{5/2}$ (c) Sulfur 2p (d) Carbon 1s of r-GO (e) carbon 1s of SnS/r-GO (f) oxygen 2p of r-GO (g) oxygen 2p of SnS/r-GO.

For further detailed analysis, high resolution XPS spectra (Figure 7b-7g) were taken for carbon (C), oxygen (O), tin (Sn) and sulfur (S), respectively. On high resolution XPS analysis of the Sn (3d_{5/2}) peak (Figure 7b) of the Sn shows the presecence of two oxidation states for Sn. The fitted curve of Sn (3d_{5/2}) shows an intense peak at 486.3 eV (Figure 7b, peak 1) corresponding to Sn²⁺ state and another smaller peak at 487.1eV (Figure 7b, peak 2) corresponding to Sn⁴⁺ state. According to the quantitative analysis, Sn⁴⁺ atomic percentage (%) was found to be 10.8% of total tin peak area. This may be a limitation for this process which occurs due to presence of oxygenic functional group on the GO plane. The sulfur (2p) peak at 161.5 eV, (Figure 7e) shows presence of a single oxidation state of sulfur atom and it is S²⁻ oxidation state. After fitting the high resolution spectra of carbon (1s) of both the samples, show four major peaks located at 284.54 eV, 285.31 eV, 286.51 eV and 288.14 eV correspond to sp² carbon, sp³ carbon, C-Cl or C-O and C=O bonded carbon, respectively.⁶⁷⁻⁷⁰ The binding energy position observed at 286.51 eV, (Figure 7c and 7f, peak 3) is unclear at the moment because it can be associated with both the halogenated carbon (C-Cl) or/and epoxide (C-O-C) bonded carbon with oxygen.⁷⁰ Therefore, Sn ions are first attached with the -COO⁻ functional group of GO plane and, by changing their oxidation state, reduce the functional groups. Similarly, on fitting of the high resolution spectra of O(2p) shows 2nd and 3rd peak (Figure 7d and 7g) for r-GO and SnS/r-GO composite, respectively. Both the spectra have two common peaks at 532.3 eV and 533.32 eV corresponding to oxygen attached in the form of C-O and C=O.⁷¹ An extra peak is also present in O(2p) for SnS/r-GO composite at 531.18 eV (Figure 7d; peak 1) which corresponds to oxygen atom attached to Sn⁴⁺ as SnO₂. Therefore from the analysis of FT-IR and XPS spectra, it is clear that the solvothermal reduction of the GO in DMF and thiourea medium are capable of reducing the

major functional group of the GO which is in the form of C=O and this reduction process is more effective in SnS/r-GO composite formation than in r-GO.

Figure 8. Field emission gun-transmission electron microscope (FEG-TEM) image of (a-b) SnS/r-GO nano-composite, (c-d) SnS nanoparticle.

In order to reveal the fine microstructure, detailed electron microscope analysis on SnS/r-GO composite and tin(II) sulfide nanoparticle samples (Figure 8) have been performed with FEG-

TEM and HR (high resolution)-TEM. As shown in image, the SnS nanoparticle are distributed on r-GO surface (Figure 8a and 3) with average particle size of ~5 nm. On other hand, the SnS nanoparticles prepared for electrochemical comparison showed (Figure 8c) separate particles with an average size in the range of 20-30 nm. On high resolution imaging of these SnS nanoparticles, as shown (Figure 8d), show several grain boundaries that ensure that particles are grown together during nucleaion and the grain size as expected 5-10 nm in range. The selected area electron diffraction (SAED) pattern for both the samples have diffuse ring pattern (Figure 8a and 8c; inset) for the [212], [102], [201] and [011] planes respectively. The high resolution images of composite show the presence of [201] plane of SnS in the composite and [011] plane in SnS nanoparticle.

3.2 Electrochemical Characterization and Analysis

Above all SnS nanostructured materials and composite have been tested for electrochemical lithium storage property in a half cell assembly mode against Li/Li⁺ at constant temperature of 20 °C. The carbon content of the SnS/rGO composite has been quantified with the CHN analyser further and found to be 24%. Other electrode films containing nanoparticles and nanoplates were prepared with same carbon content with external conducting carbon (SP carbon). Herein, cell of SnS /r-GO composite and SnS nanoaprticle cells were prepared with PVDF and CMC binders. To find out the possible electrochemical reactions of SnS with Li/Li⁺, cyclic voltammetry (CV) experiment has been performed for nanoparticle and nanoparticle/ r-GO composite (Figure 9 a-d) at a scan rate of 0.1 mV s⁻¹ in a potential window of 0.01V - 2.5 V vs. Li/Li⁺. The CV profile of SnS/r-GO composite and nanoparticle show that the first reduction scan are almost identical for the two binders (PVDF and CMC) with redox peaks positioned around 1.25 V, 1.15 V, 0.7 V, 0.4 V and 0.16 V vs. Li/Li⁺ in reduction scan. The two first peaks correspond to conversion reactions

of SnS to Sn metal, SnO₂ to Sn metal and last three peaks correspond to various steps of tin alloying with Li.^{72-73, 27} Similarly, in oxidation scan, the profile shows the electrochemical reversible reactions and generate peaks for dealloying of Li_{4.4}Sn to Sn at 0.5 V, 0.64 V, 0.75 V and conversion of Sn to SnO₂ at 1.2 V and partial conversion of Sn to SnS at 1.84V vs. Li/Li⁺, respectively.^{27, 31, 72-73} It is noteworthy to mention here that after first reduction-oxidation cycle, the second discharge (reduction) cycle has noticeable change in peak positions depending on carbon support and binders. The second discharge (reduction) peak has little shift toward higher potential and its is due to SEI formation in anode by reaction with electrolyte, which is well documented in the literature.⁷⁴⁻⁷⁵ Moreover, CV profile of SnS/r-GO composite with CMC binder has shown (Figure 9a) a wider redox peak in the first discharge (reduction) cycle for conversion reactions and a small peak for the alloying reactions. This broadening of redox peak in reduction reaction may be attributed to the poor lithium diffusion in the first discharge cycle in electrode matrix. This poor diffusion may be attributed to less swelling of binder (CMC) with electrolyte in presence of functionalised graphene and at present we do not have any reference to justify the statement. In Addition, upon cycling the peak currents are more or less stable at 0.63V, 0.3V, 0.13 V and 0.5 V, 0.64 V, 0.75 V for alloying and de-alloying reactions respectively. For SnS/r-GO, the CV profile, a partial conversion reaction for SnS is also observed at potential 1.84 V (oxidation scan) and 1.2 V (reduction scan) and the intensity reduces with increasing cycle numbers . When the same composite was tested with PVDF binders, the peak positions (Figure 9b) were almost same, however the conversion peak current in first cycle (reduction) was observed to be high and intense at 1.25 V and 1.1 V for SnS and SnO₂ conversion, respectively. In consecutive cycles, all the peak currents have decreased and showing the instability of the electrochemical reactions. Similarly, sample with SnS nanoparticle with externally added carbon

was also tested with CMC and PVDF binders (Figure 9c-d) for comparison. The SnS nanoparticles with CMC binder has shown stable peak current in comparison to PVDF binder electrode. The de-alloying peak for SnS-carbon sample is different in shape than SnS/r-GO composite and visually wider and centered around 0.55 V vs. Li/Li⁺. The outcome of these cyclic voltammerty tests suggest that the cyclic stability is excellent with samples containg CMC binder than that of usual PVDF binder electrode.

Figure 9. Cyclic voltammogram of (a) r-GO-SnS composite with CMC binder (b) r-GO-SnS composite with PVDF binder (c) SnS nanoparticle with CMC binder (d) SnS nanoparticle with PVDF binder; at scan rate of 0.1 mV s⁻¹ against Li/Li⁺ at 20 °C.

Another interesting trend is observed for all four CV profiles in the range of conversion reactions with Lithium. The electrodes prepared with the CMC binder have shown high rate of conversion reaction in the first cycle and in the consecutive cycles, decreasing peak current for the SnS to Sn conversion and *vice-versa* at 1.34 V and 1.9 V, respectively. While in the case of PVDF binder, conversion reaction of SnO₂ to Sn and *vice-versa* has promoted and conversion reaction of SnS + 2Li $\leftrightarrow$ Sn + Li₂S reaction get suppressed.

Figure 10. Galvanostatic cycling performance of (a) SnS/r-GO composite with CMC and PVDF binders at current rate of 160 mA g⁻¹, (b) SnS/r-GO composite, SnS nanoparticle, SnS nanoplate and pure r-GO with CMC binder at current rate of 160 mA g⁻¹, (c) SnS/r-GO and SnS nanoparticle with CMC binder at current rate of 300 mA g⁻¹ and 500 mA g⁻¹ (d) Power plot

performances of SnS/r-GO composite, SnS nanoparticle, SnS nanoplate and pure r-GO with CMC binder, against Li/Li⁺ in potential window on 0.01 V-2.5 V at 20 °C.

At this stage we are not in a position to give the exact reason behind this difference. In current situation, the combination of SnS with r-GO and CMC binder shows excellent result and shows peak for only $\text{SnS} + 2\text{Li} \leftrightarrow \text{Sn} + \text{Li}_2\text{S}$. The SnS/r-GO/CMC composite electrode have almost negligible peak current for $\text{SnO}_2 + 4\text{Li} \leftrightarrow \text{Sn} + 2\text{Li}_2\text{O}$ conversion in discharge and charge cycle after first discharge. This may be a reason for the stability of peak current in the SnS/r-GO/CMC electrode cell. The SnO₂ formation peak (1.1 V) in reverse scan of the CV (oxidation scan) after first reduction scan may be generated due to reaction of Sn with the poly-carbonate electrolyte in the cell.

The charge-discharge profile of all electrodes (composite and nanoparticle) with CMC and PVDF binders were tested in galvanostatic mode (Figure 10 a-d, Figure S1-S2 and table S1) in a half cell assembly against Li/Li⁺. The electrochemical performance of the SnS/r-GO composite with CMC and PVDF binder at a current rate of 160 mA g⁻¹ (Figure 10a) shows the initial discharge capacity of 2090 mAh g⁻¹ and 1878 mAh g⁻¹ with columbic efficiency of 49% and 53%, respectively. This reduction in columbic efficiency can be correlated with the CV peaks, where the first cycle discharge peak current (profile shape) is wider and expected reason could be SEI formation due to surface reaction of electrolyte with carbon and electro-active materials.⁷⁴⁻⁷⁵ The second discharge capacity for SnS/r-GO composite with CMC and PVDF binders were found to be 956 mAh g⁻¹ and 1176 mAh g⁻¹ with the columbic efficiency of 95 % and 88 %, respectively. Here again this is observed as soon as second cycle, as the energy loss is larger with PVDF than with CMC electrode and the columbic efficiency gain is also superior with CMC binder. After fifty continuous galvanostatic charge-discharge cycles, the discharge

capacity with CMC binder was found to be 630 mAh g⁻¹ and with PVDF binder was 470 mAh g⁻¹ with columbic efficiency of 99.23 % and 98.15 %, respectively. The composite electrode with CMC binder has shown 65% retention of discharge capacity with 0.67 % columbic efficiency loss while PVDF binder composite electrode has 40% retention of capacity with 1.85% columbic efficiency loss. Therefore, it is again clear that gain in columbic efficiency and cycle life is better in case of CMC based electrode than in PVDF binder based electrode.

Furthermore, the electrochemical performance of the SnS/r-GO with CMC binder (Figure 10b and S1) is better than that of SnS nanoparticle, SnS nanoplate with externally used carbon and with pure r-GO (Figure 10c) at the same current rate of 160 mA g⁻¹. It is also noteworthy to mention here that the SnS electrodes with external carbon works better with the CMC binder than with PVDF and here a similar trend was also observed with r-GO composite.¹⁷ In comparison to SnS/r-GO electrode, first discharge and second discharge capacity of the SnS nanoparticle, SnS nanoplate and pure graphene (r-GO) electrode with CMC binder were observed (Figure 10b and S1) to be 1694 mAh g⁻¹, 1397 mAh g⁻¹, 784 mAh g⁻¹ and 1286 mAh g⁻¹, 1041 mAh g⁻¹, 137 mAh g⁻¹, respectively. The columbic efficiency of 1st and 2nd cycle of charge discharge of these electrodes were found to be 69%, 89% for SnS nanoparticle, 72%, 89% for SnS nanoplates, 13.6%, 74% for r-GO. After fifty cycle of discharge, the capacity of SnS nanoparticle, nanoplate and r-GO were observe to be 473 mAh g⁻¹, 327 mAh g⁻¹ and 93 mAh g⁻¹ (below to graphite theoretical limit) with the capacity retention of 36.8 %, 31% and 67%, respectively. Therefore, the gain in columbic efficiency and capacity retention data, it can be easily addressed that the SnS/r-GO electrode with CMC binder showed an excellent electrochemical performance in terms of retaining the capacity after the formation of SEI (irreversible loss) compare to SnS nanoparticle, SnS nanoplate and r-GO.

To test the electrolyte and electrode compatibility and robustness of the composite electrode, higher rate charge discharge cycling tests have been carried out with current densities like 300 mA g⁻¹ and 500 mA g⁻¹. The electrochemical performance of the SnS/r-GO composite at current rate of 300 mA g⁻¹ is shown in Figure 10c and the first discharge capacity was found to be 1555 mAh g⁻¹. The second discharge capacity was 828 mAh g⁻¹ and after 50th cycle, the discharge capacity was found to be 612 mAh g⁻¹ *i.e.* capacity retention after second cycle is about 74% at such high rate cycling. In comparison, the electrode of SnS nanoparticle with external carbon and CMC binder at current rate of 300 mA g⁻¹, shows first discharge capacity to be 1343 mAh g⁻¹, second discharge capacity 932 mAh g⁻¹ and after 50th cycle discharge capacity was found to be 477 mAh g⁻¹ which results in a capacity retention of 51%.

On further testing at another high current rate like at 500 mA g⁻¹, the SnS/r-GO electrode has shown first discharge capacity of 1995 mAh g⁻¹, second discharge capacity 980 mAh g⁻¹ and after 50th cycles the discharge capacity was found to be 581 mAh g⁻¹ with capacity retention of 60%. The performance of the SnS nanoparticle at same current rates and with same binder was found to 1420 mAh g⁻¹, 980 mAh g⁻¹ for second discharge and 433 mAh g⁻¹ after 50th cycle with retention capacity after second discharge was 44%. Therefore, from all these rate performance has justified the compatibility of SnS/r-GO electrode with CMC binder over SnS nanoparticle, SnS nanoplate and pure r-GO. The change in capacity after 50th cycle has been found to 2.8% between current rate of 160 mA g⁻¹ and 300 mA g⁻¹, 5% in between current rate of 300 mA g⁻¹ and 500 mA g⁻¹ and 7.7 % in between current rate of 160 mA g⁻¹ and 500 mA g⁻¹. Thus, composite electrode is found to be compatible to these high current rates and losses are due to increase in current rate and that is minimal in comparison to the nanoparticle electrode with external carbon.

To justify the rate capability of material for various battery applications, SnS/r-GO composite, SnS nanoparticle, SnS nanoplate and r-GO has been charged-discharged with successive current rate of 100 mA g⁻¹, 300 mA g⁻¹, 500 mA g⁻¹, 1000 mA g⁻¹ and in second step lower down to 200 mA g⁻¹ and 100 mA g⁻¹ till the completion of 30th cycle. Then all these cells were further charge-discharge at current rate of 300 mA g⁻¹ till completion of 50th cycle. The discharge capacity of SnS/r-GO composite after completion of each consecutive 5 cycles at a fixed current rate, was found to be 882 mAh g⁻¹ (at current rate of 100 mA g⁻¹), 748 mAh g⁻¹ (at current rate of 300 mA g⁻¹), 678 mAh g⁻¹ (at current rate of 500 mA g⁻¹), 576 mAh g⁻¹ (at current rate of 1000 mA g⁻¹), 746 mAh g⁻¹ (at current rate of 200 mA g⁻¹) and 762 mAh g⁻¹ (at current rate of 100 mA g⁻¹) till 30th cycle. Thereafter the charge discharge was carried out at current rate of 300 mA g⁻¹ and complete the fifty cycle after which the discharge capacity after 50th discharge cycle was observed to be 568 mAh g⁻¹. Similarly, the SnS nanoparticle electrode after completion of each 5 cycles at a fix current rate has shown a discharge capacity of 865 mAh g⁻¹ (at current rate of 100 mA g⁻¹), 700 mAh g⁻¹ (at current rate of 300 mA g⁻¹), 583 mAh g⁻¹ (at current rate of 500 mA g⁻¹), 466 mAh g⁻¹ (at current rate of 1000 mA g⁻¹), 596 mAh g⁻¹ (at current rate of 200 mA g⁻¹), 611 mAh g⁻¹ (at current rate of 100 mA g⁻¹) till 30th cycle. Thereafter, the charge discharge was carried out at current rate of 300 mA g⁻¹ until completion of 50th cycle and the discharge capacity after 50th discharge was 311 mAh g⁻¹. The discharge capacity of SnS nanoplate after completion of successive five cycles at a fixed current rate was 776 mAh g⁻¹ (at current rate of 100 mA g⁻¹), 684 mAh g⁻¹ (at current rate of 300 mA g⁻¹), 584 mAh g⁻¹ (at current rate of 500 mA g⁻¹), 394 mAh g⁻¹ (at current rate of 1000 mA g⁻¹), 521 mAh g⁻¹ (at current rate of 200 mA g⁻¹) and 491 mAh g⁻¹ (at current rate of 100 mA g⁻¹) till 30th cycle. Thereafter, the charge discharge were carried out at current rate of 300 mA g⁻¹ until the completion of 50th cycle and the discharge

capacity after completion of 50th cycle was found to be 195 mAh g⁻¹. Similar way, the discharge capacity of only r-GO electrode after completion each consecutive 5 cycles at a fixed current rate was found to be 122 mAh g⁻¹ (at current rate of 100 mA g⁻¹), 48 mAh g⁻¹ (at current rate of 300 mA g⁻¹), 22 mAh g⁻¹ (at current rate of 500 mA g⁻¹), 7 mAh g⁻¹ (at current rate of 1000 mA g⁻¹), 66 mAh g⁻¹ (at current rate of 200 mA g⁻¹) and 81 mAh g⁻¹ (at current rate of 100 mA g⁻¹) till 30th cycle. Thereafter, the same cell was run successively at current rate of 300 mA g⁻¹ until completion of 50th cycle and the discharge capacity after completion of 50th cycle was found to be 16 mAh g⁻¹. It is noteworthy to mention here that the r-GO electrode has completely lost its capacity and performance at high rate in comparison to other tested electrode. In comparison to pure r-GO electrode, all other SnS based electrodes perform satisfactory even with externally added carbon. The performance of the SnS/r-GO composite electrode is excellent than others and the loss due to varying the current rate is also low in case of SnS/rGO. This shows that the SnS/r-GO composite electrode is excellent in capacity regain in successive variable current applications. This retention in capacity and better performance in variable current rates can be attributed to the support provided by the r-GO surface to electro-active nanoparticle and binder. These two helps in maintaining the stresses generated during the electrochemical reaction of SnS with Li. In other words reduced graphene oxide and CMC binder both has played a synergic effect to achieve better electrochemical performance.

3.3 *Ex-situ* TEM analysis of electrode after consecutive cycling

To find out the reason for the performance of the alloying based anode having similar nanoparticle but different binder (CMC & PVDF) and carbon support (SP Carbon and graphene)

the *ex-situ* TEM was performed. Elastomeric binder like CMC has helped to provide better performance in comparison to PVDF electrode in capacity retention and electrochemical performance (cyclic stability) against Li/Li⁺.

Figure 11. *Ex-situ* TEM image of SnS/ r-GO nanoparticle composite with (a) PVDF binder and (b) CMC binder; after 50 cycle of charge discharge at current rate of 160 mA g⁻¹ against Li/Li⁺.

Since binders are elastomers, which participate in managing the mechanical stresses generated due to volume expansion in electro-active material during alloying and de-alloying reaction.^{20, 21,}
³² To find out the reason for this stability in alloying based anode, an *ex-situ* TEM analysis (Figure 11) has been performed on both the electrodes after 50th discharge cycle. The major difference observed with TEM for both the electrodes *i.e.* with CMC and PVDF binder, is on the shape of nanoparticles. Although both the composite were able to maintain a proper distribution of the electro-active particle on r-GO surface after 50th cycle, but the CMC binder has preserved the particle size in a better way than PVDF binder. The rate of amorphousization is larger with the PVDF binder electrode than with the CMC based electrode in presence of graphene, as it was observed previously without use of graphene.²⁷ To study the role of graphene in presence of

CMC binder and SnS/rGO in maintaining the particle size during electrochemical cycling, an *ex-situ* TEM experiments of the SnS nanoparticle electrode with external carbon and CMC binder were imaged after 50th cycle. The result (Figure S2) shows that the particles have were very small in size and randomly entangled in the carbon matrix. Thus, without r-GO matrix, the particles loose its size and shape during alloying-de-alloying reaction (may be due to particle cracking) and that results in loss of capacity. Therefore, from *ex-situ* TEM analysis it is quite clear that CMC binder helped in better performance with r-GO support than with PVDF in maintaining mechanical stress and whickering of electro-active material.

4. Conclusion

Colloid destabilization of graphene oxide has facilitated the solution-phase assembly of reduced graphene sheets and tin (II) sulfide which is used for lithium ion battery anode. For single step SnS r-GO composite preparation, graphene oxide (GO) has been separated from water colloid and transferred to *N, N*-dimethyl formamide media. The hydrochloric acid and ethanol were added and both of them have played a crucial role in separation without changing the functionality of the GO plane. The GO-DMF colloid has resulted in synthesis of SnS nanoparticle anchored r-GO composite with minor impurity of SnO₂. Moreover, this process can be used for preparation of other composite with the oxidation sensitive metals for various electrochemical applications. These composite electrodes can be cycled reversibly in the safe potential zone of 0.01 V-2.5 V and exhibit specific capacity of 630 mAh g⁻¹, which is much higher than those tin sulfide based anode and higher than those of other SnS₂/r-GO-based anode. Moreover, the electrode with interactive binder showed excellent rate capability and present an acceptable cycling performance. It is demonstrated that graphene and graphene-based composites have a great potential applications in lithium ion battery where graphene is not only

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2
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4 fuel electrons to the electroactive species also maintain the proximity between the reactive
5
6 particles and retained particle size (reduce cracking of particles) during high volume change
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8 reaction like alloying-dealloying or conversion.
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10 11 12 ASSOCIATED CONTENT 13

14 15 **Supporting Information.** 16

17 Supporting Information have charge discharge profile of SnS/r-GO composite with PVDF and
18
19 CMC binders, SnS nanoparticle with CMC binder , SnS nanoplate with CMC binder and *ex-situ*
20
21 TEM image of SnS nanoparticle with normal carbon and CMC binder.
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