Antimony sulfide nanorods decorated onto reduced graphene oxide based anodes for sodium-ion battery

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Abstract: Rechargeable batteries have wide applications starting from electronic devices, hybrid electric vehicles to stationary electrical energy storage (EES) systems where the primary need is that battery should have high energy density and operate for longer duration. However, the technologically superior advanced Li-ion batteries (LIBs) developed for portable electronics and electric vehicles are still under consideration for the stationary EES stringent requirements of low cost and safety. Therefore, there is clear a need to exploit alternative battery chemistries that can exhibit similar energy density but improved performance compared to competitive LIB systems. Keeping in that mind, we have explored novel high capacity antimony based anodes (Sb 2 S 3) which can offer a practical capacity ~400-600 mAhg -1 , excellent Coulombic efficiency (≥99%) and cyclability (~100 cycles). Sb 2 S 3 , and Sb 2 S 3 /rGO based nanocomposite anodes were developed by facile hydrothermal method and thoroughly investigated for their crystallinity, phase stability, and microstructure using XRD, FESEM/EDS, TEM/HRTEM, FTIR, etc.

The electrochemical sodium storage behavior of the synthesized anodes was examined in CR-2032 type coin cells using cyclic voltammetry (CV), galvanostatic charge-discharge cycles. CV of Sb 2 S 3 /rGO in a sodium-ion cell shows that cathodic (~0.7V, and ~0.4V) and anodic (~0.8V and 1.12V) peaks suggest the reversible formation for NaSb and Na 3 Sb phase(s) during cycling. The preliminary galvanostatic cycling data shows that Sb 2 S 3 , and Sb 2 S 3 /rGO exhibits a decent discharge and charge capacity of ~601 mAhg -1 , ~256 mAhg -1 , 490 mAhg -1 , and ~588 mAhg -1 , respectively under a constant current density of 50 mAg -1 for the first cycle. However, capacity fades in the following cycles warrant further in-depth studies to understand the detail charge storage behavior of the electrodes .

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Why Na-ion batteries?

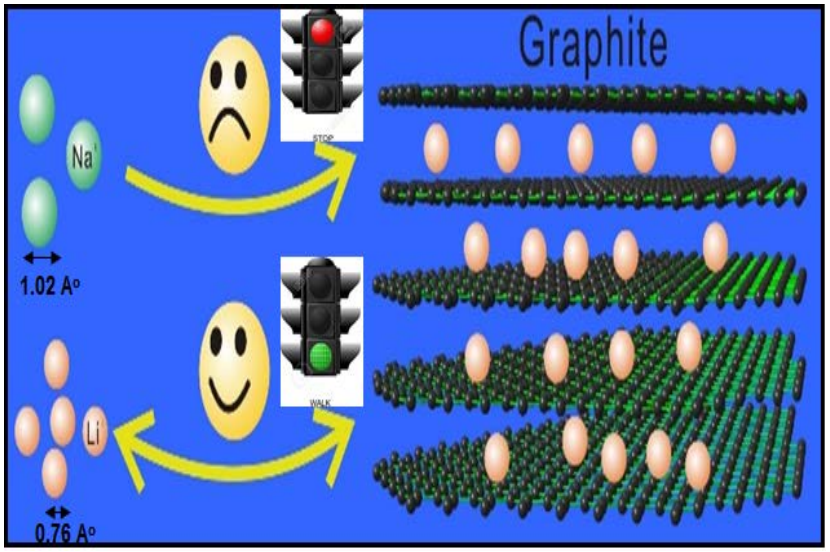
alternative chemistry, cheap, comparable volumetric energy density

Parameter	Lithium	Sodium
Cationic radius (Å)	0.76	1.02
Atomic weight (g mol^{-1})	6.9	23.0
Potential (V vs. SHE)	-3.04	-2.71
Carbonate cost ($/ton)	~6000	~150
Gravimetric capacity ($mAhg^{-1}$)	3862 (Li^{+})	1166 (Na^{+})
Volumetric capacity ($mAhcm^{-3}$)	2046	1129
Coordination Preference	Octahedral and tetrahedral	Octahedral and prismatic

Tarascon J.M.; *Philosophical Trans Royal Soc. A*, 368, (2010), 3227-41

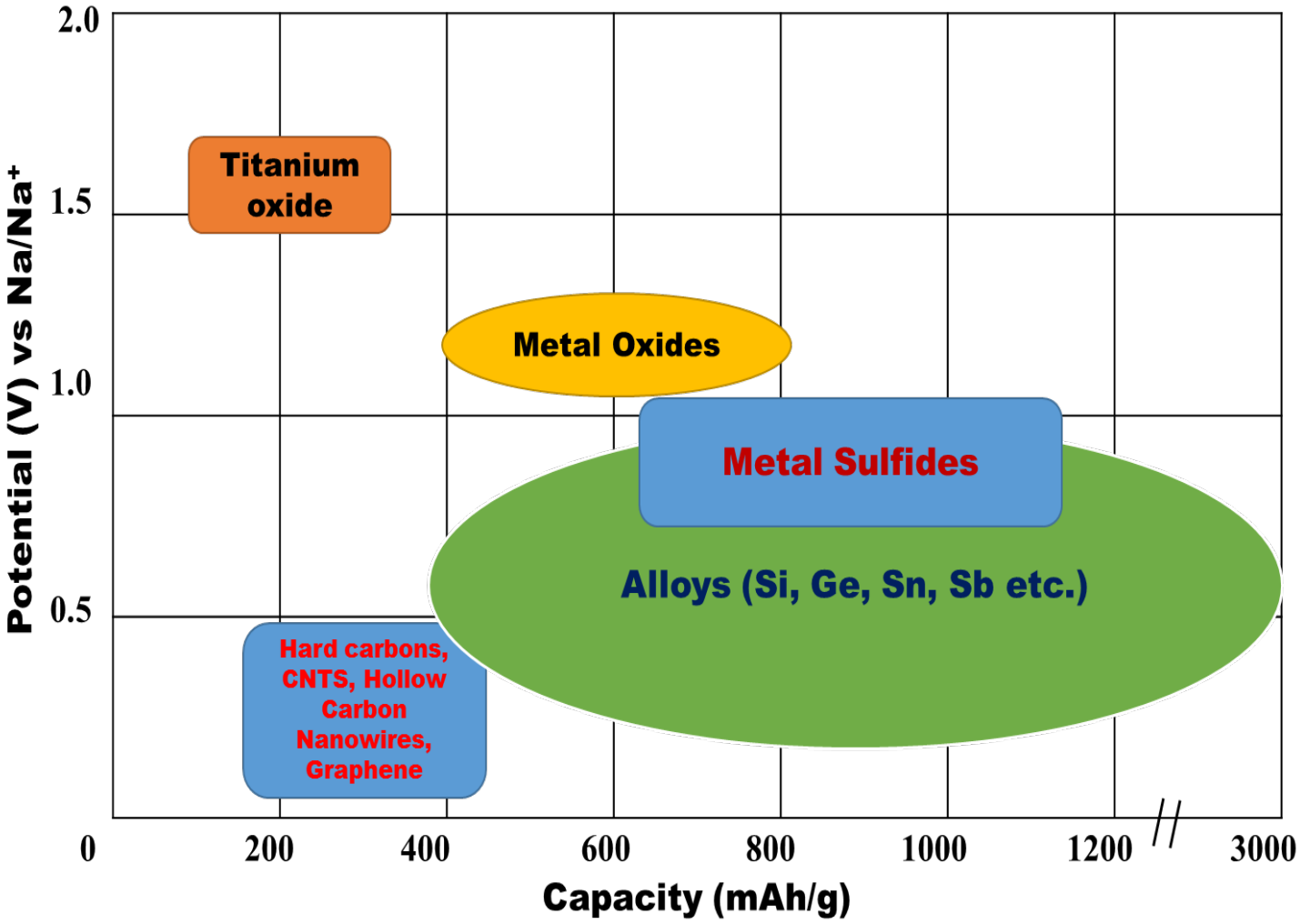
Challenges for Na-ion Negative Electrodes

- Graphite is the material of choice in current LIBs because the interlayer spacing offer's smaller size lithium ions to diffuse in and out.
- Na-ion can't be reversibly alloyed/de-alloyed with graphitic carbon (Na-C)
- Sodium cannot be reversibly alloyed/de-alloyed with silicon also (Na-Si)
- Hard carbon can deliver specific capacity ~50-300 $mAhg^{-1}$
- In hard-carbon Na metal plates which is a fire hazard and forms sodium alkyl carbonates which reduces the stability of electrolytes and solvents



Intercalation mechanism of Li-ion and Na–ion in graphite structure

Metal (Sb, Sn etc.) based anodes for Na-ion batteries



Electrochemistry of Sb based anodes for Na-ion batteries

- **Antimony (Sb) and antimony sulfide (Sb_2S_3) appears to be a promising system for SIB**
- **Sb can react with 3-Na and form Na_3Sb alloy and in turn can offer a theoretical capacity ~ 660 $mAhg^{-1}$, Sb_2S_3 can offer a theoretical capacity ~ 946 $mAhg^{-1}$**

Alloying reaction of Sb anode for SIBs: $Sb + Na^+ + 3e^- \longrightarrow NaSb$

$Sb + 3Na^+ + 3e^- \longrightarrow Na_3Sb$

The reactions between Sb_2S_3 and sodium can be written as follows:

Conversion reaction: $Sb_2S_3 + 6Na^+ + 6e^- \longrightarrow 2Sb + 3Na_2S$

Alloying reaction: $Sb + 3Na^+ + 6e^- \longrightarrow Na_3Sb$

Drawbacks

Intermetallics	V_m (cm^3 mol^{-1})	$(V_m - V_{Sb})/V_{Sb}$ (%)	Gravimetric capacity (mAh g^{-1})
NaSb	~ 35.90	~ 97	~ 220
Na_3Sb	~ 71.45	~ 293	~ 660

V_{Sb} is the molar volume of Sb (~ 18.18 cm^3 mol^{-1})

Critical drawback of metal sulfide system is the inherently sluggish electronic conductivity which impairs the ability of fast Na^+-ion diffusion and reaction kinetics

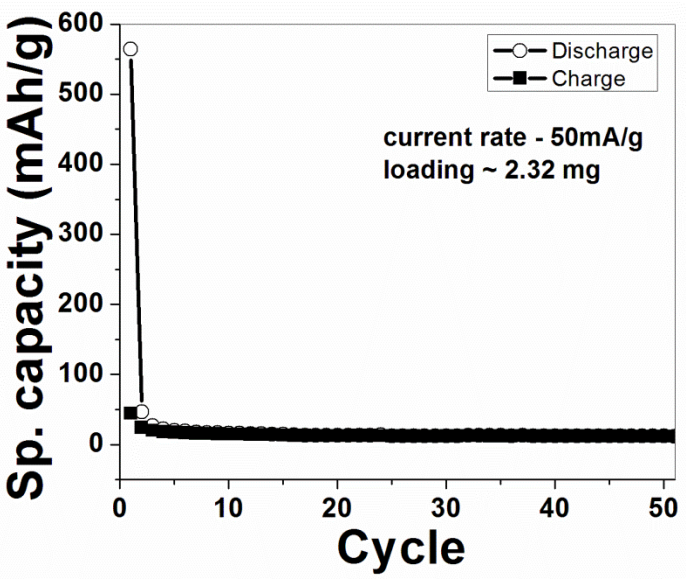
Solution

Synthesis of myriads of nanostructured Sb with inactive matrix (Carbon, graphene, rGO etc.) which will act as buffer or Sb_2S_3 with carbon

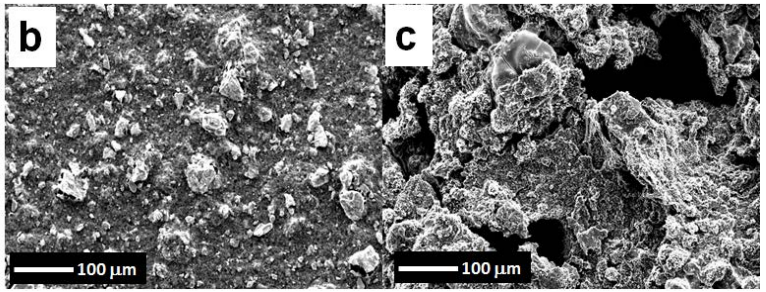
Problem with Sb as an anode for Na-ion battery

$NaClO_4$/1 Molar in EC-DMC electrolyte, cycled between 0.02-1.2 V vs. Na/Na^+, using Cu current collector

Pure Sb



before cycle **after 50 cycle**

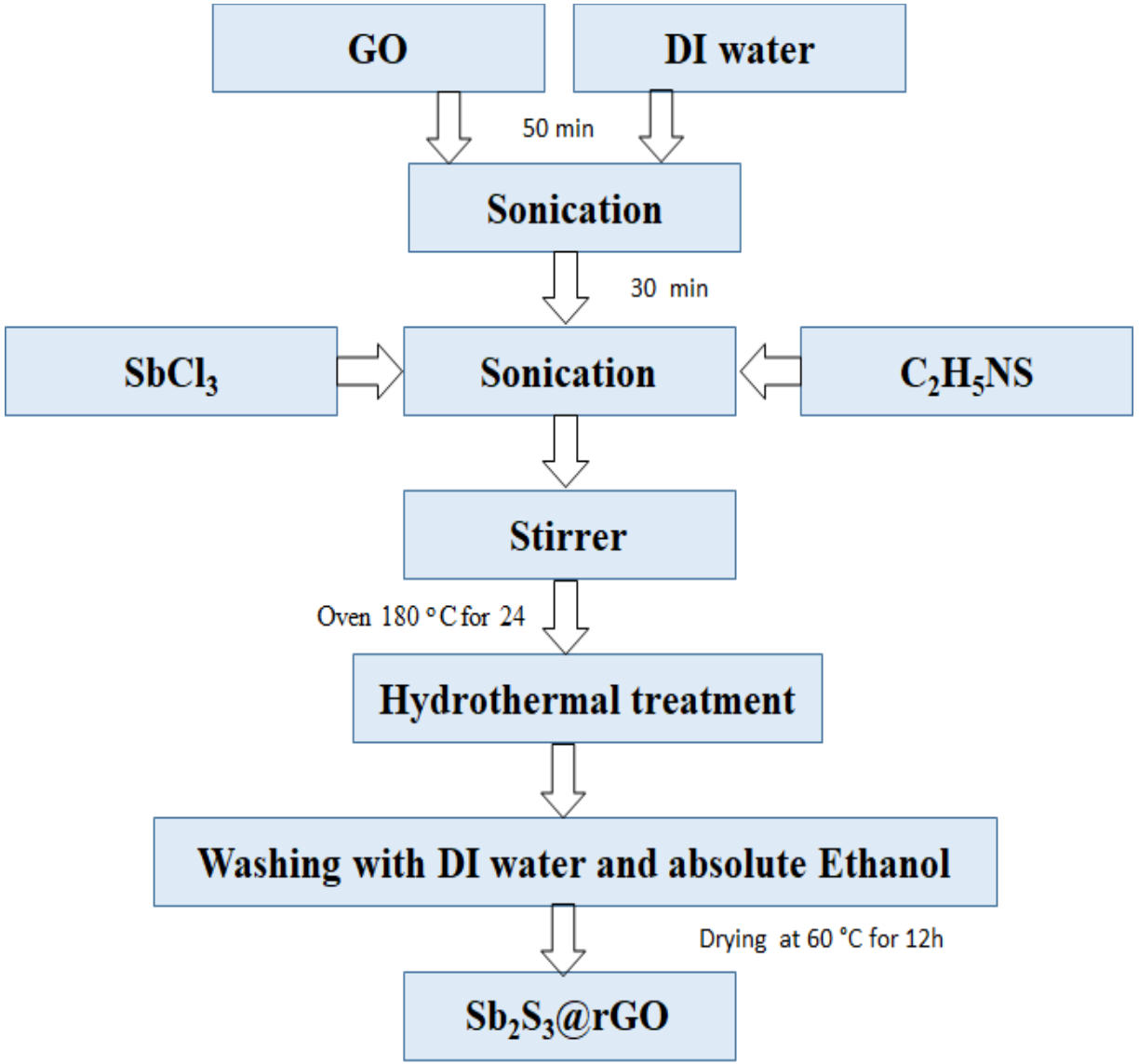


Failure of pure Sb is evident due to large volume expansion and cracking

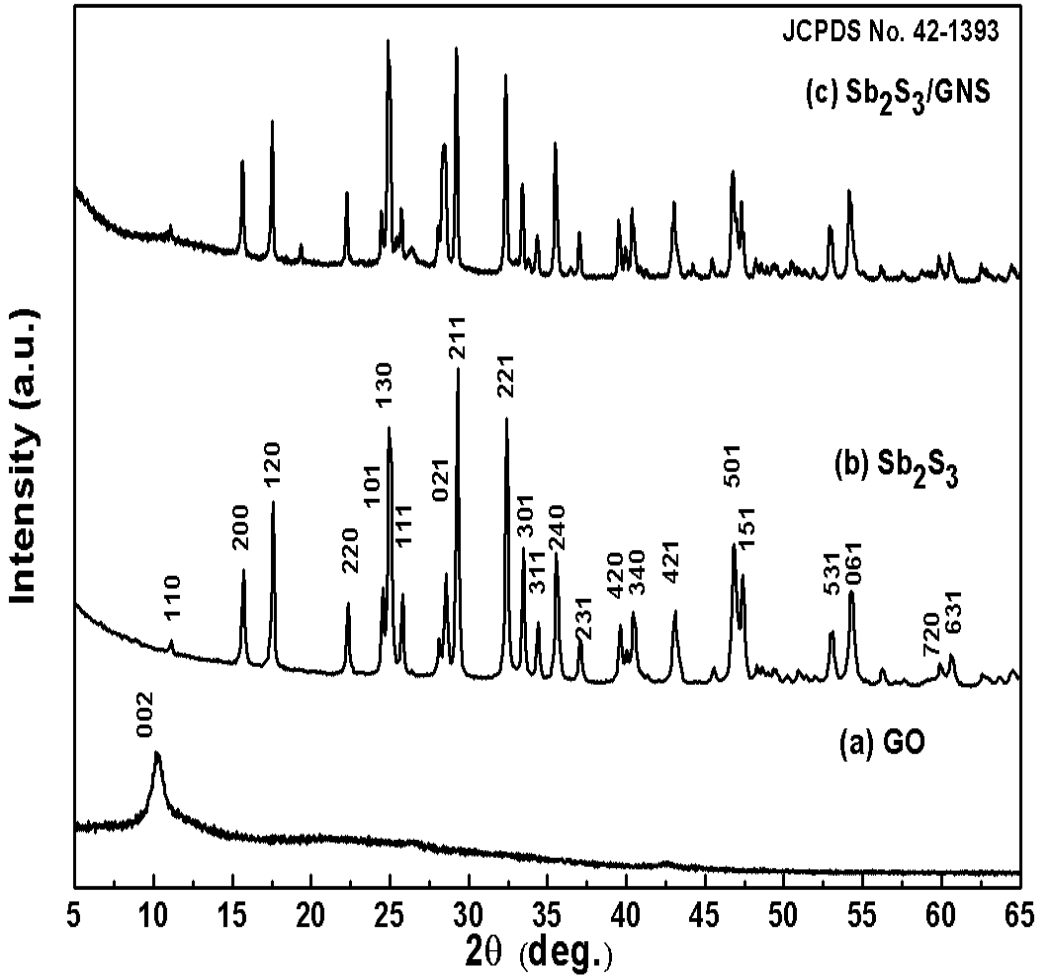
1st cycle discharge capacity ~ 564 mAh/g
1st cycle charge capacity ~ 44mAh/g
1st cycle IL ~ 92%

Therefore, we confine our study on Sb_2S_3 anodes

Hydrothermal synthesis of Sb_2S_3 and Sb_2S_3/rGO

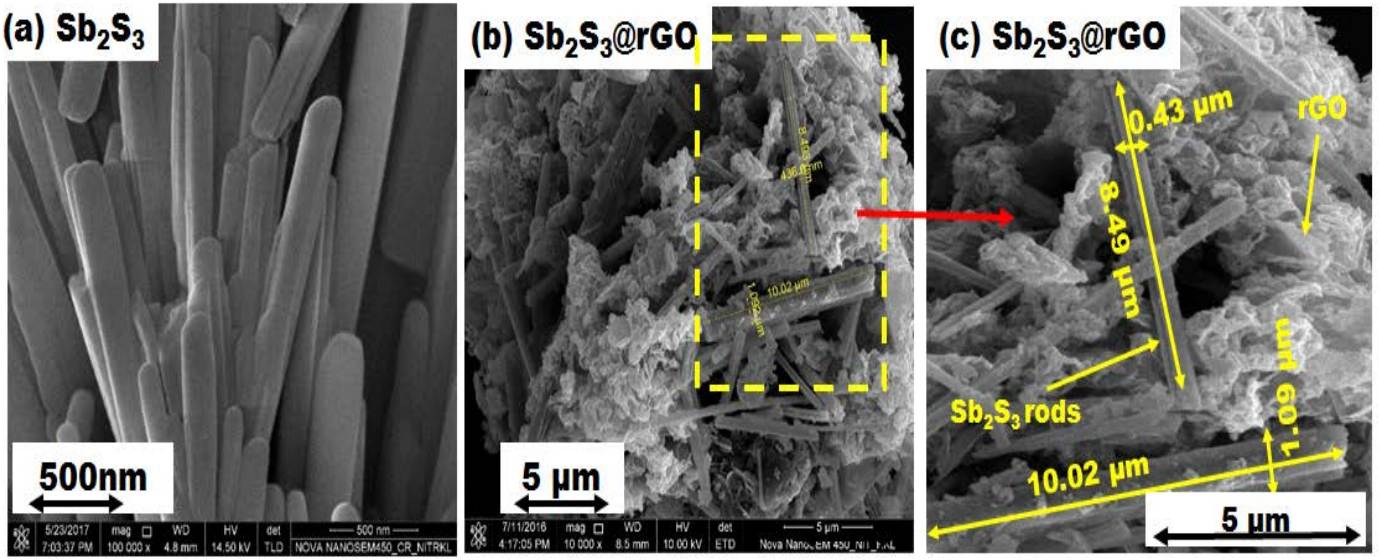


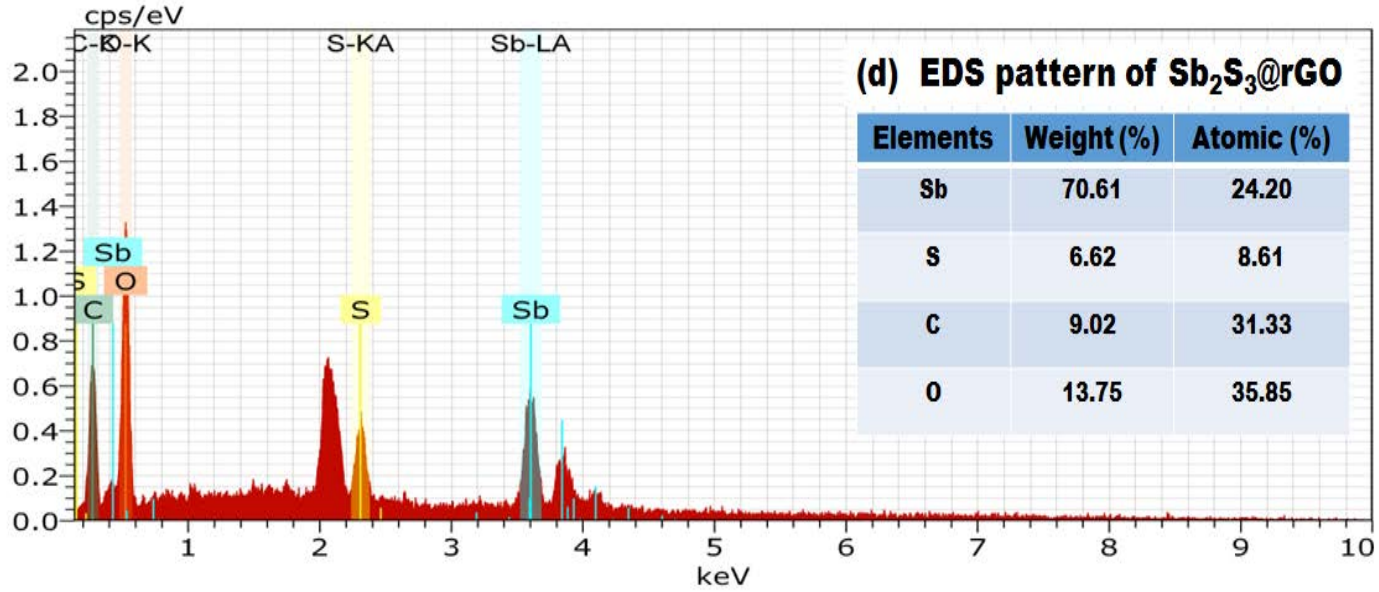
XRD Analysis of Sb_2S_3 and Sb_2S_3 /rGO composite



- **Pure crystalline Sb_2S_3 were formed.**
- **The diffraction peaks can be indexed to Sb_2S_3 phase (Crystal system: Orthorhombic, Space group: Pbnm Space group number: 62), no second phase was found.**

SEM analysis of Sb_2S_3 and Sb_2S_3/rGO



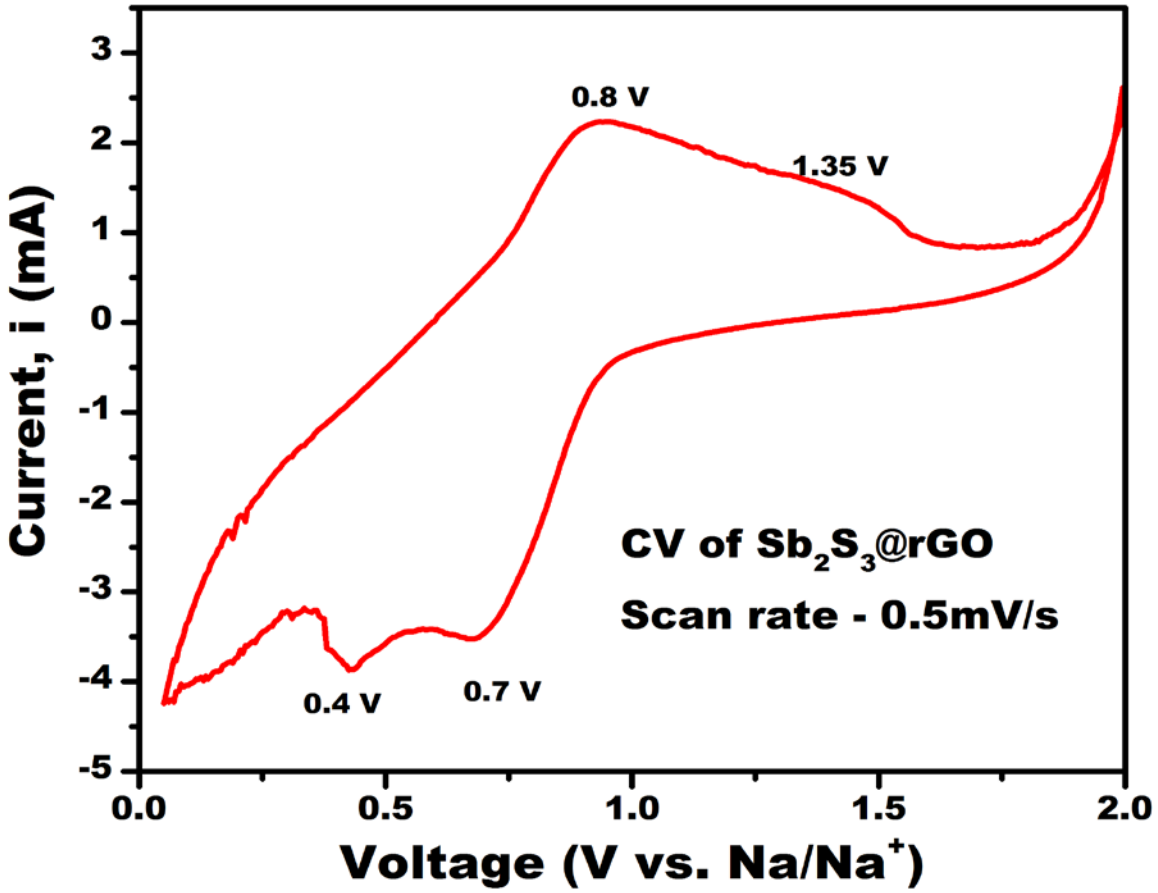


(d) EDS pattern of Sb_2S_3@rGO

Elements	Weight (%)	Atomic (%)
Sb	70.61	24.20
S	6.62	8.61
C	9.02	31.33
O	13.75	35.85

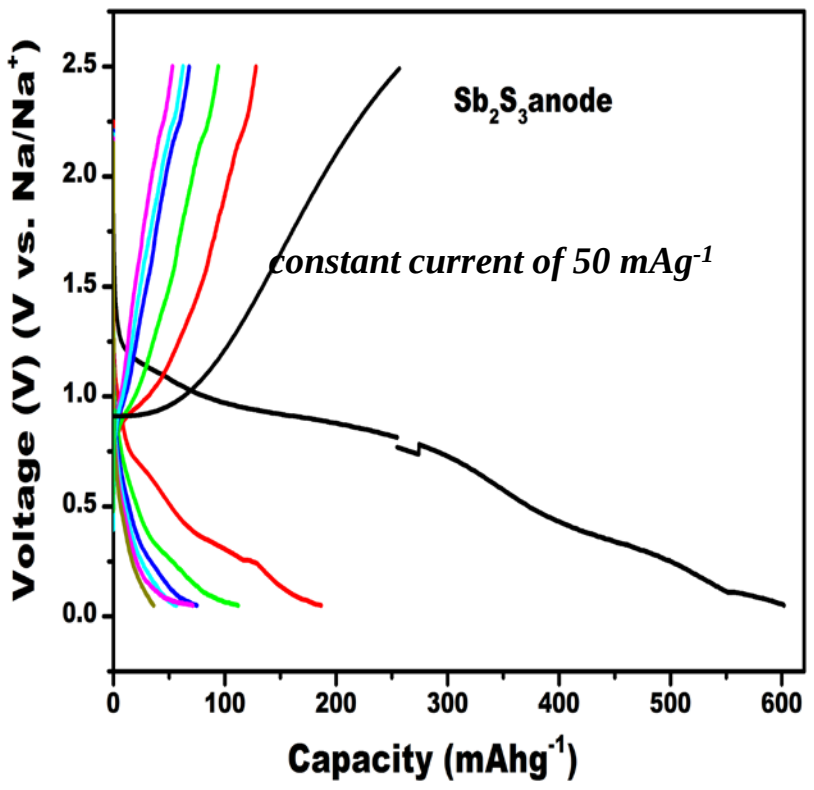
Diameter ranging from **~0.4-1 µm** and length **~8-10 µm**

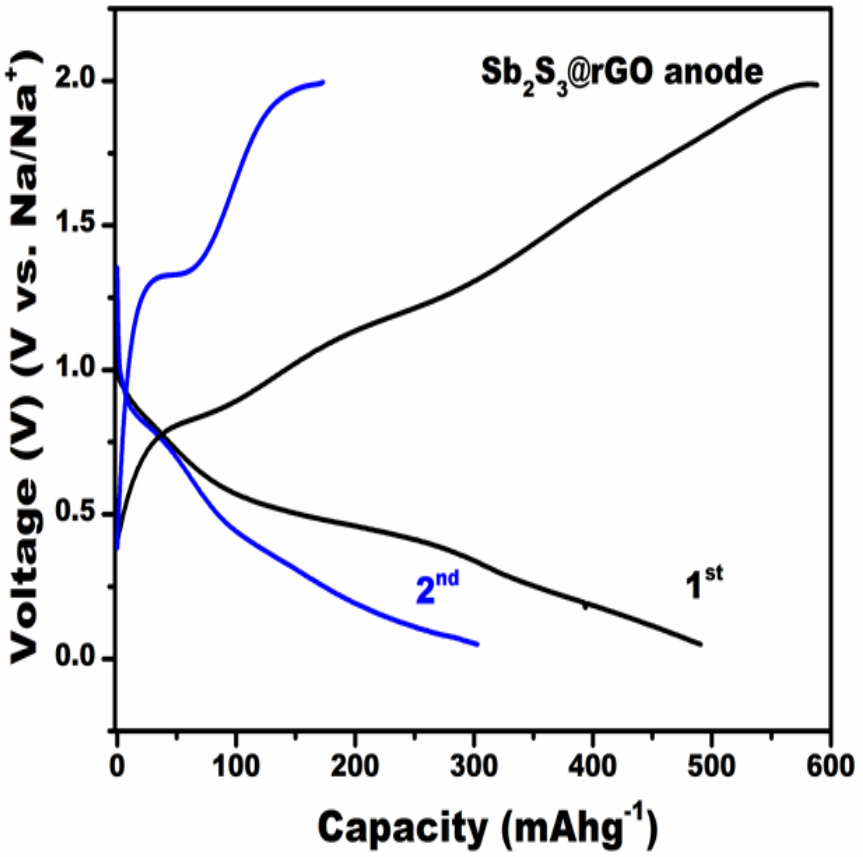
CV shows Sb_2S_3/rGO is electrochemically active



Na-ion can be reversibly cycled, with alloying and de-alloying reactions occurring at 0.7V, 0.4V, 0.8V and 1.35 V respectively.

Galvanostatic cycling of Sb_2S_3 and Sb_2S_3/rGO in a Na-ion cell





1st and 2nd cycle:
discharge capacity ~600, and ~186 $mAhg^{-1}$
charge capacity ~256, and ~94 $mAhg^{-1}$

1st and 2nd cycle:
discharge capacity ~490 and ~302 $mAhg^{-1}$
charge capacity ~588 and ~172 $mAhg^{-1}$

Summary

- Successfully demonstrated the synthesis strategy for Sb_2S_3@C composite anodes for Na-ion batteries.
- The formation of Sb_2S_3 nanoparticles on carbon is confirmed by FESEM and TEM analysis.
- Cyclic voltammetry shows that sodiation and de-sodiation reactions occurs at ~0.7V, and ~0.4V (cathodic) and ~0.8V, and ~1.35V (anodic)
- Galvanostatic cycling data shows that 1st cycle discharge and charge ~capacity of ~383 $mAhg^{-1}$, ~406 $mAhg^{-1}$, 490 $mAhg^{-1}$, and ~588 $mAhg^{-1}$, for Sb and Sb_2S_3 electrodes respectively.

Future Work

- In-depth analysis of various reaction and failure mechanisms of Sb_2S_3 based anodes using electrochemcial impedance spectroscopy of cycled electrodes, in-situ XRD, Raman, XPS study in order to suggest promising strategies for improving their electrochemical performance.

Acknowledgements

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"As Knowledge Increases, Wonder Deepens"
Charles Morgan; 1894-1958; English writer
Thank You For Your Attention