

Supporting Information

Probing the Polysulfide Confinement in Two Different Sulfur Host for Mg|S Battery Employing Operando Raman and Ex situ UV-Visible Spectroscopy

Ravindra Kumar Bhardwaj^{†1}, Ruth Gomes^{†1} and Aninda J. Bhattacharyya^{1*}

[†]RKB and RG contributed equally to this work

¹*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bengaluru-560012, India*

*Email: anindajb@iisc.ac.in

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Section S1

Materials. Multiwalled carbon nanotubes (inner and outer diameter ~10 and ~20 nm respectively, length 1–10 μm , purity >90%) are purchased from Sun Nanotech Co., Ltd. Toray carbon paper (PTTFE treated TGP-H-60) is obtained from Sri Tirumala Chemicals, India. Doubly sublimed sulfur (Sigma-Aldrich, assay $\geq 99.5\%$) is used for its loading inside the host materials. All other solvents and acids used for the preparation of the cathode materials are of analytical grade obtained from SDFCL and SD Fine-Chem Limited and are used without further purification. For the electrolyte preparation, magnesium bis(hexamethyldisilazide) (97%), aluminium chloride (> 99.99%), magnesium chloride ($\geq 98\%$) and tetraglyme (anhydrous, ≥ 99) are obtained from Sigma-Aldrich. Magnesium foil of thickness 0.25 mm (purity 99.9%) is purchased from Goodfellow Cambridge Limited.

Preparation of Toray Carbon/Sulfur (TC-S) Composite cathode material. Figure 1a shows the preparation of TC-S cathode. The Toray carbon paper is cut into circular disk and placed on a Büchner funnel connected to a suction pump. For a target loading of 3 mg cm^{-2} , the required amount of doubly-sublimed sulfur is taken in the beaker and 50 ml of ethanol is then added to it. The solution is sonicated for 30 min to make a homogeneous dispersion and added slowly to the Büchner funnel with the Toray carbon paper. Due to the high pressure of the suction pump, sulfur particles are encapsulated into the vacant space of the randomly oriented nanofibers as seen in the SEM image (Figure 2d). The final product is then dried in a vacuum oven at 80 $^{\circ}\text{C}$ for 24 h. The areal loading of sulfur is calculated from the increase in weight.

Preparation of CNT-S cathode materials. Figure 1b shows the preparation of CNT-S cathode. The ends of the carbon nanotubes are cut open using a procedure reported previously with minor modifications.³⁹ Typically, 50 mg of CNT is taken in a 25 ml round bottom flask and 1.13 g of conc. HNO_3 is added to it. The mixture is then refluxed for 5 h in 140 $^{\circ}\text{C}$ and the product is washed with water to bring the pH down to 7. It is then washed with CHCl_3 and

dried in a vacuum oven at 80 °C. Finally, the product is heated in a tube furnace at 600 °C under Argon atmosphere for 2 h. Sulfur is incorporated inside the nanotubes using a modified pressure induced melt-diffusion technique, where the end opened CNT (activated at 80 °C under vacuum for 1 h) and the doubly-sublimed sulfur are ball-milled in a ratio of 1:20 and evacuated for 1 h in a quartz boat. This is then heated in a tubular furnace at 150 °C for 1 h and then vacuum is released by passing N₂. The gas flow is continued for 4 h at 150 °C and the final sulfur loaded CNTs are collected and washed several times with toluene to remove the excess sulfur which is present outside the nanotubes.

Physical characterization. The powder X-ray diffraction (PXRD) data are collected using PANalytical diffractometer using Cu-K α radiation, (wavelength= 0.1542 nm). Thermogravimetric analysis data are collected on Metler Toledo TGA/SDTA851^e by heating the samples from room temperature to 600 °C, at a heating rate of 5 °Cmin⁻¹ under N₂ atmosphere. Scanning electron microscopy for morphological analysis are performed using Ultra55 FE-SEM Karl Zeiss EDS. UV-VIS absorption spectroscopic data are recorded using the Auto lab AU00064 UV-VIS spectrometer. The Raman spectra of the cathode materials are recorded using Dilor LabRAM confocal micro-Raman spectrometer equipped with a 100 \times objective, HeNe laser (632.8 nm, 7mW), 600 grooves/mm grating and a Peliter-cooled CCD detector with a beam spot size of 2 μ m.

Electrochemical Characterization.

The Mg|S batteries are assembled at 25 °C in an Argon-filled glovebox (MBraun) (H₂O < 0.5 ppm, O₂ < 0.5 ppm) in a coin type half-cell using magnesium foil as the counter and reference electrodes and Whatman glass fiber as the separator and TC-S and CNT-S as cathode. For the TC-S cathode, circular disks are cut from the sulfur loaded (3 mg cm⁻²) Toray carbon paper. The CNT-S cathodes are cast on Inconel-625 current collector using 8:1:1 weight ratio of CNT-

S, conductive carbon black and polyvinylidene fluoride binder. N-methyl-2-pyrrolidinone is used for making the slurry. The sulfur loading on CNT-S cathode is kept same as TC-S cathode (3 mg cm^{-2}). For the electrolyte preparation magnesium-bis(hexamethyldisilazide) (1.24 g) is taken in 4 mL of tetraglyme and stirred inside the glovebox for 1 h followed by a slow addition of AlCl_3 (0.96 g) to the magnesium-bis(hexamethyldisilazide)-tetraglyme mixture. Stirring is continued for 36 h at room temperature and finally MgCl_2 (0.34 g) is added. The mixture is then allowed to stir again for another 48 h before using for battery assembly. Cyclic voltammetry is carried out using CHI645D instrument at 0.25 mV/s scan rate. The galvanostatic charge/discharge cycling of the as-assembled Mg|S batteries are performed using Arbin Instruments (model BT 2000) Corp., U.S. The electrochemical impedance spectra are performed using a BioLogic Science instrument SP300 in the frequency range 1 MHz to 1 Hz at amplitude 5 mV.

Operando Raman spectra: An in-house cell is designed to collect simultaneous Raman spectra and electrochemical data (Figure S8). For the *operando* measurements, a hole is punched in the centre of magnesium foil and the separator such that the laser can pass through and directly be incident on the cathode surface. A minimum of 250 μL of electrolyte is added to the separator and the cell is sealed with a transparent lid so that the interior of the cell is visible to the laser beam. For the cell configuration, the cathode is first placed on a stainless-steel base and then the separator and finally magnesium foil are stacked over it. The base acts as the positive terminal and the lid forms the negative terminal of the battery. The study is performed in a Dilor LabRAM confocal micro-Raman spectrometer equipped with a 100 \times objective, HeNe laser (632.8 nm, 7mW), 600 grooves/mm grating and a Peliter-cooled CCD detector with a beam spot size of 2 μm .

Post cycling UV-VIS spectroscopic analysis of the electrolyte. The concentration of the dissolved polysulfide in the electrolyte at various stages of the battery cycling is compared

using UV-VIS spectroscopy. For this the cell after cycling to various voltage, is disassembled inside the glovebox and the separator is collected and dipped in 2 mL of tetraglyme. It is then kept for 3 h for most of the polysulfides to dissolve into the solvent. From the solution, 50 μ L aliquot is collected and diluted with 3 mL of tetraglyme. The control sample for the measurement is prepared by dissolving 120 μ L aliquot from the above prepared stock electrolyte in 3 mL of tetraglyme followed by further 4 times dilution.

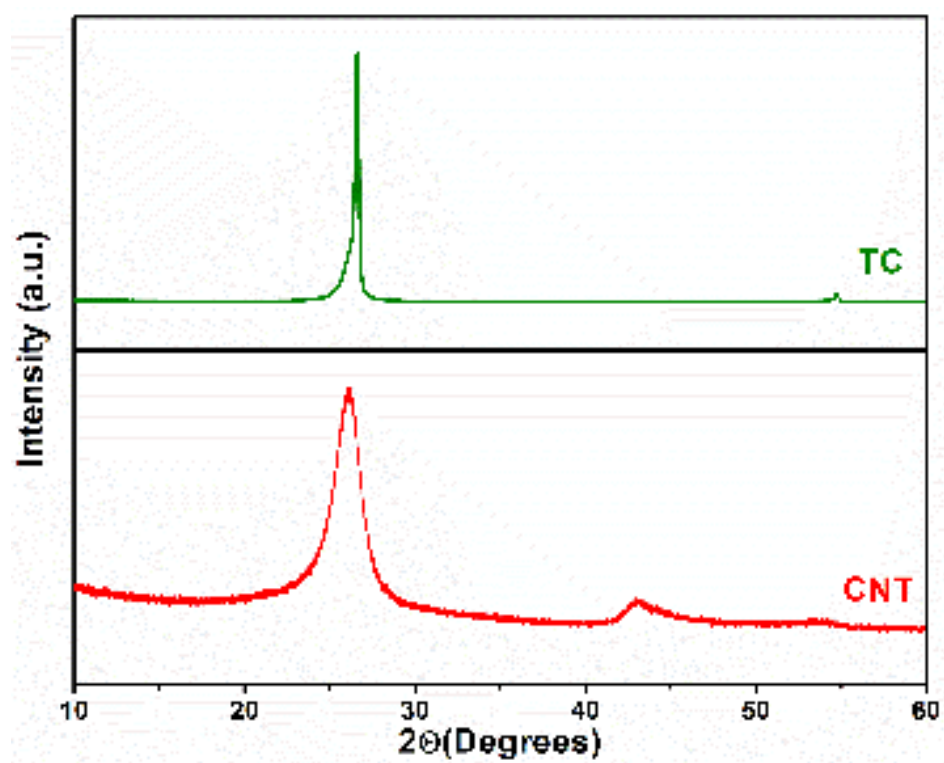


Figure S1. X-ray diffraction pattern of CNT (red) and Toray carbon (green)

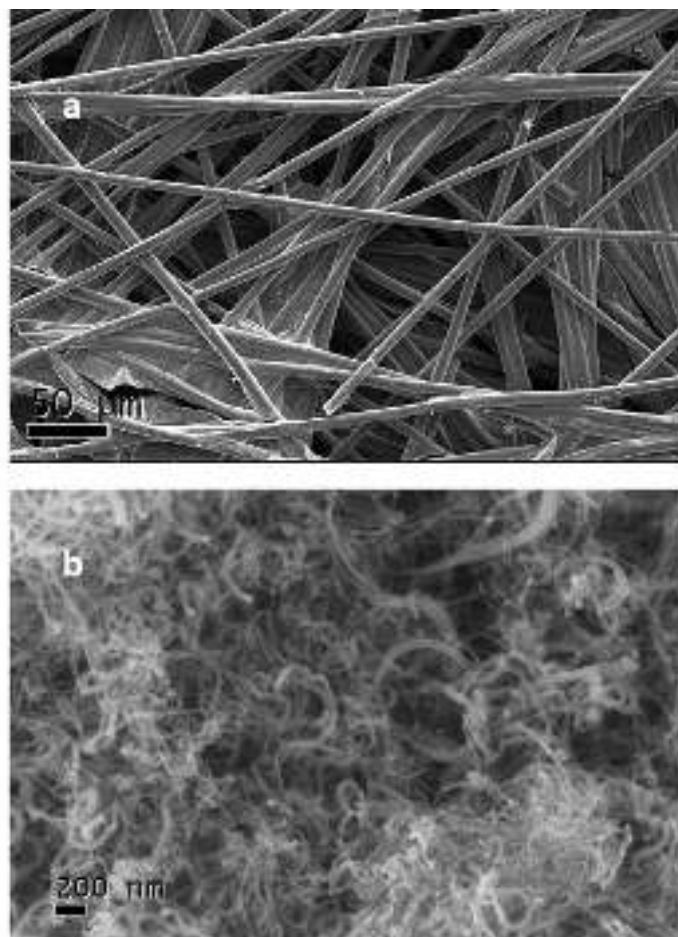


Figure S2. Scanning electron microscopy (SEM) of (a) bare toray carbon paper and (b) bare carbon nanotubes.

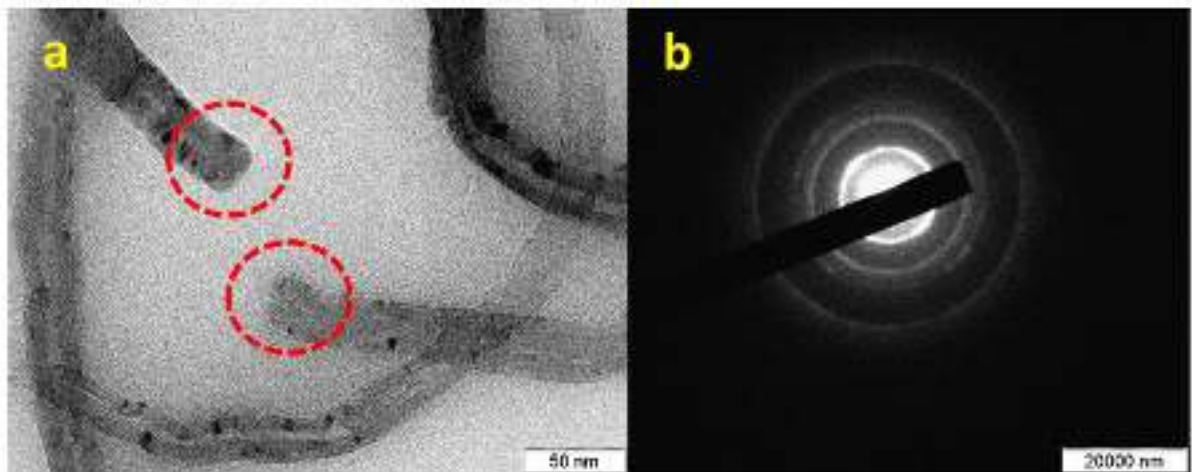


Figure S3. (a) Transmission electron microscopic (TEM) image of bare carbon nanotubes (open ends marked with red circles), (b) SAED pattern showing the amorphous nature of CNT.

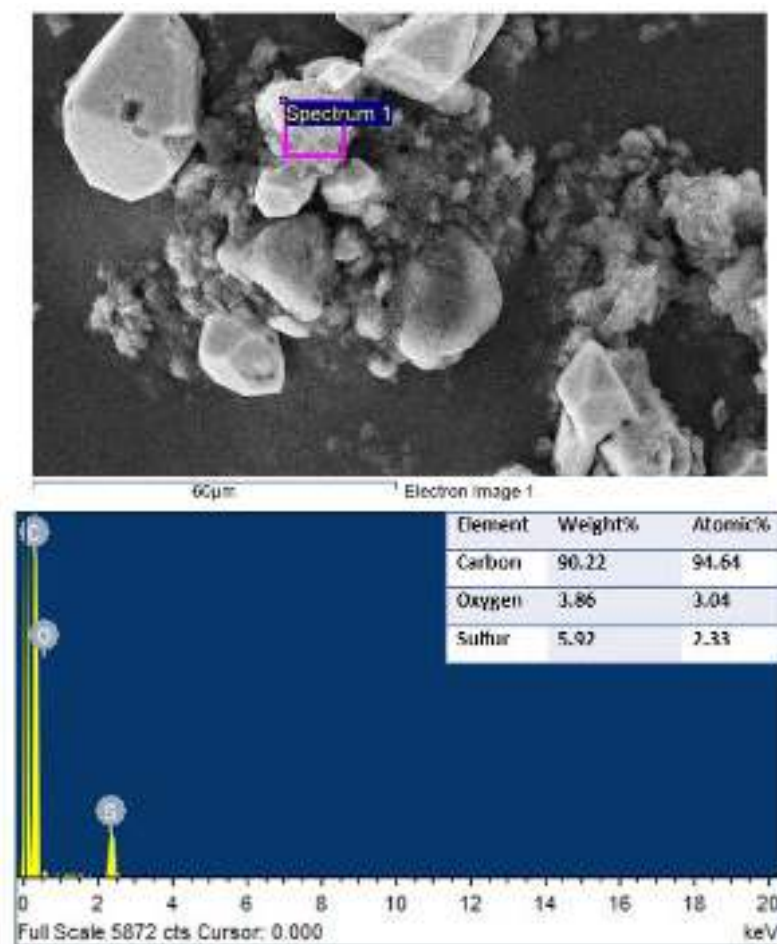


Figure S4. Energy dispersive Spectra (EDS) of CNT-S (below) in the selected region of above image. The percentage of different elements are provided in inset.

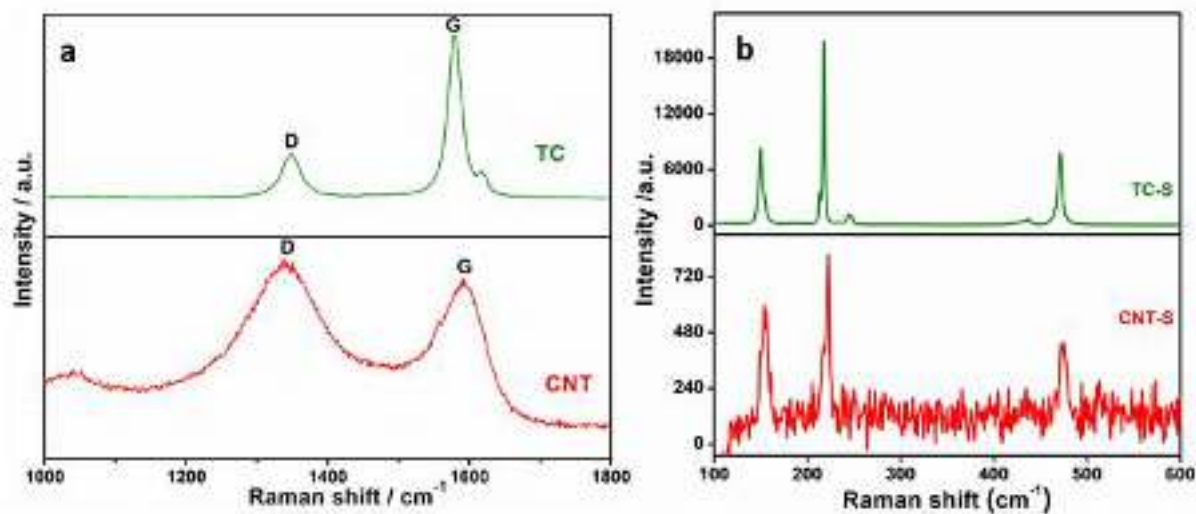


Figure S5. (a) Raman spectra of CNT (red) and Toray carbon (green). (D and G shows the characteristic D and G bands for carbonaceous materials. The intensity of the D and G band is often used to estimate the density of structural defects in carbonaceous materials. calculated I_D/I_G ratio for CNT and TC are 1.08 and 0.29 respectively. High I_D/I_G ratio of CNT suggests the density of structural defects is high in the case of CNT.) (b) Raman spectra of CNT-S (red) and TC-S (green)

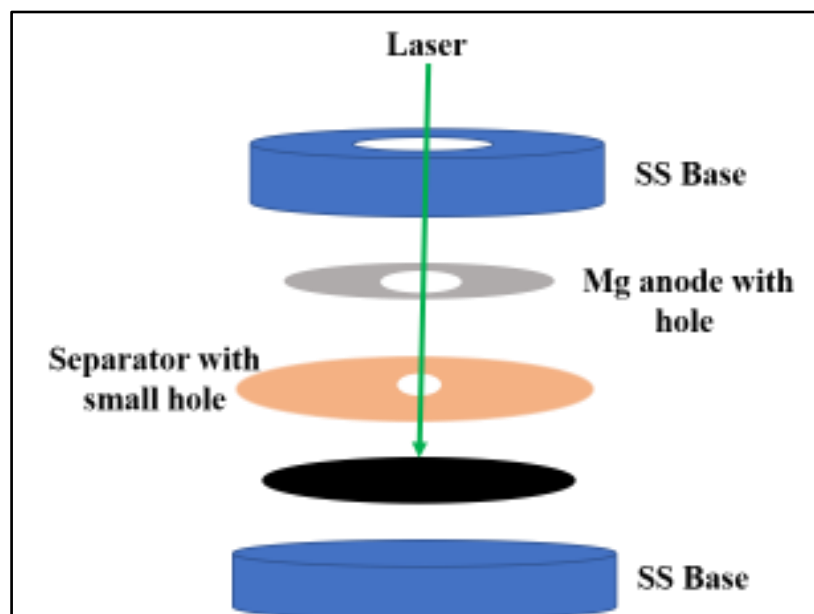


Figure S6. Schematic representation of the Raman cell used for acquiring the Raman spectra

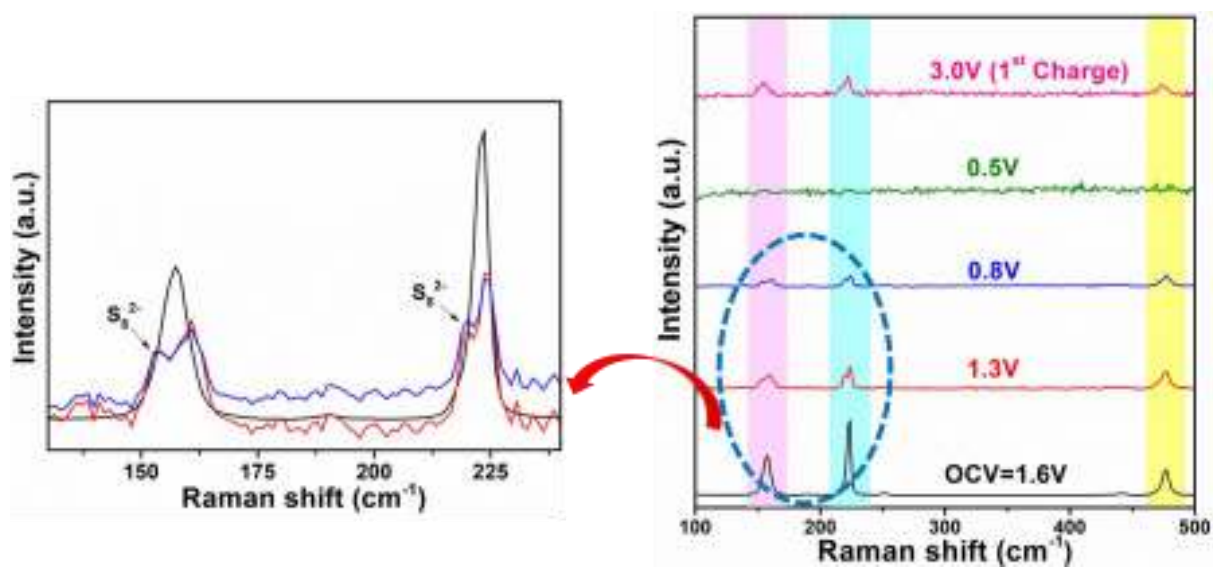


Figure S7: *Operando* Raman spectra of Mg|S cell at different discharge voltages using CNT-S as the cathode. Magnified area shows Raman spectra at 0.8 V (blue), 1.3 V (red) and OCV (black).

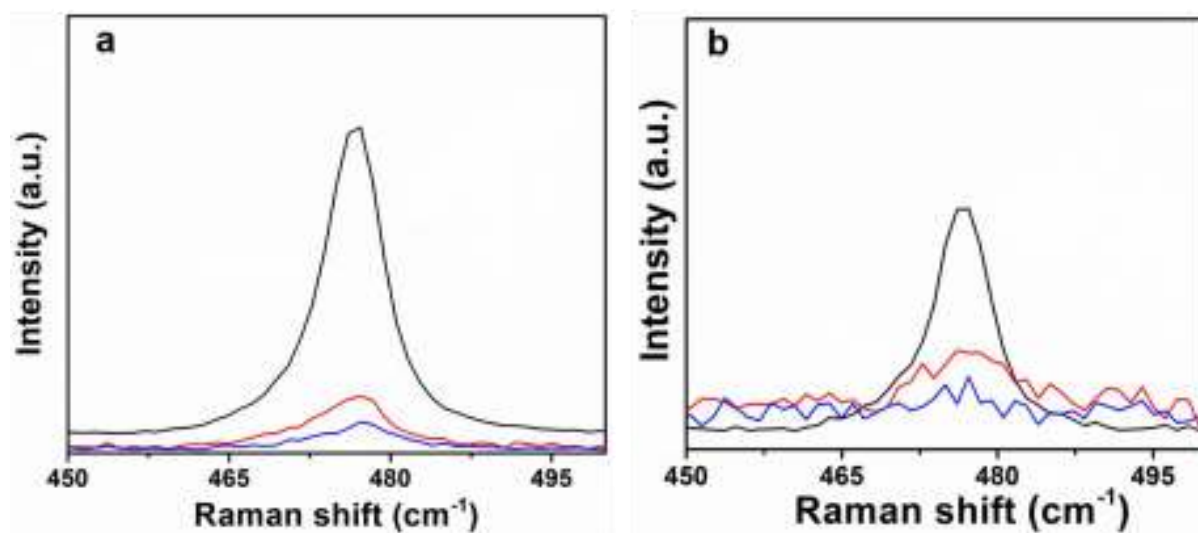


Figure S8. Magnified spectra for the Raman band at 475 cm^{-1} with (a) CNT-S cathode at 0.8V (blue), 1.3 V (red) and OCV (black). (b) C-S cathode at 0.8V (blue), 1.3 V (red) and OCV (black).

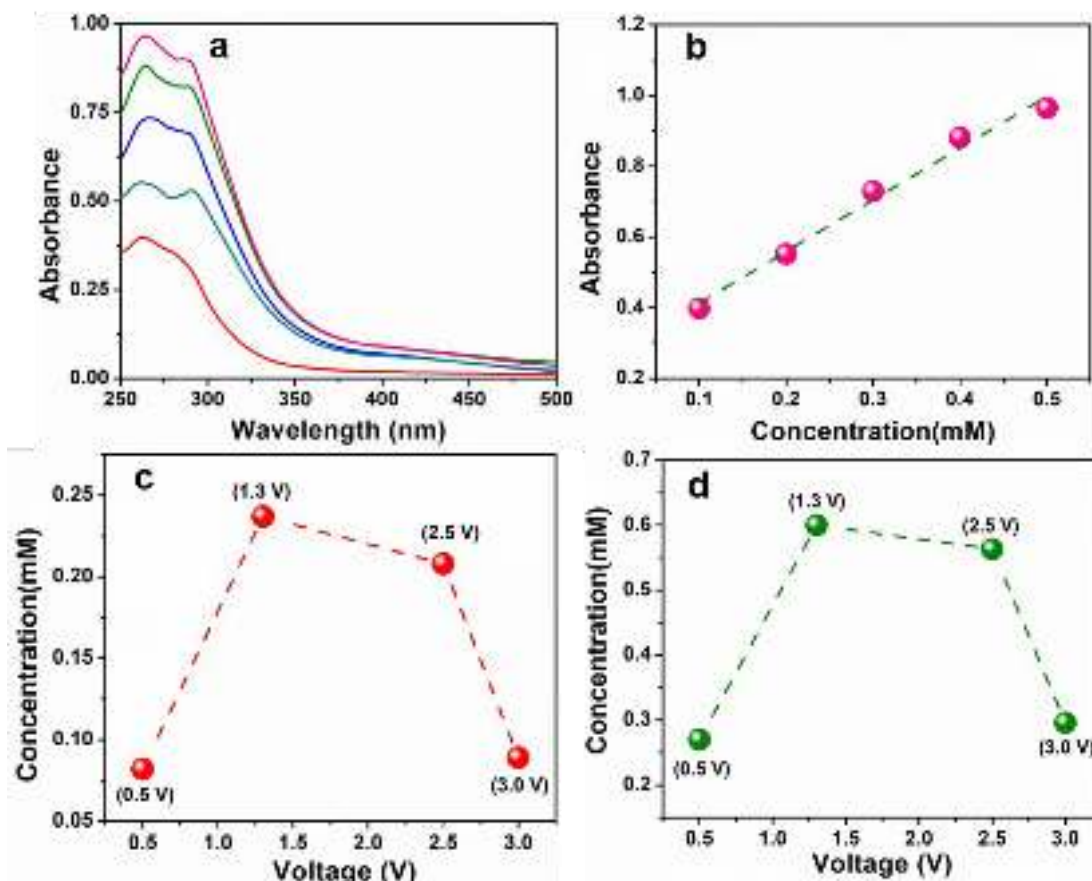


Figure S9. (a) UV-visible spectra of solutions containing different concentrations of MgS_6 , 0.1 mM (red), 0.2 mM (dark cyan), 0.3 mM (blue), 0.4 mM (green) and 0.5 mM (pink). (b) absorbance obtained at 260 nm for MgS_6 as a function of solutions concentration. (c) MgS_6 concentration (obtain from the slope of S8(b) and 4(a) using Beer's Lambert law) for CNTS cathode. (d) MgS_6 concentration (obtain from the slope of S8(a) and 4(b) using Beer's Lambert law) for TC-S cathode.

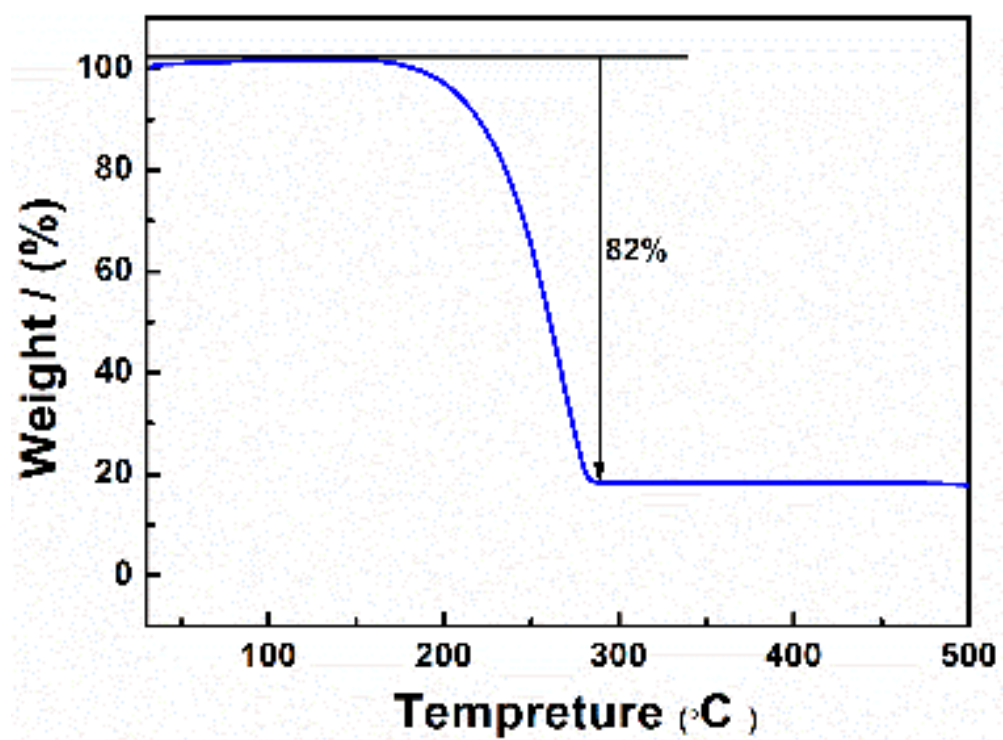


Figure S10. Thermogravimetric analysis (TGA) of CNT-S cathode

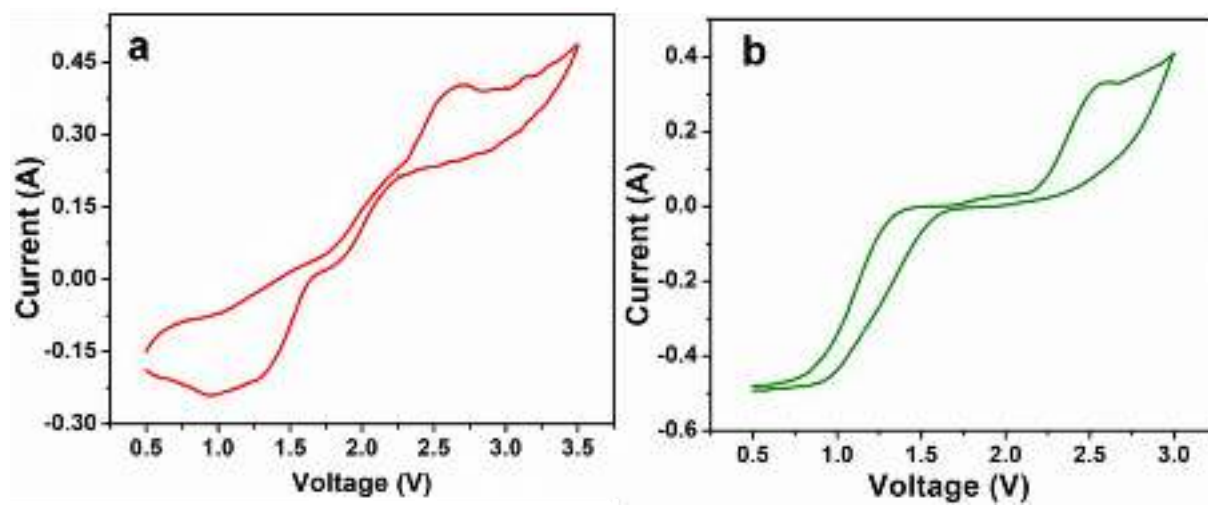


Figure S11. Cyclic voltammetry of Mg|S cell (a) With CNT-S cathode, (b) With TC-S cathode.

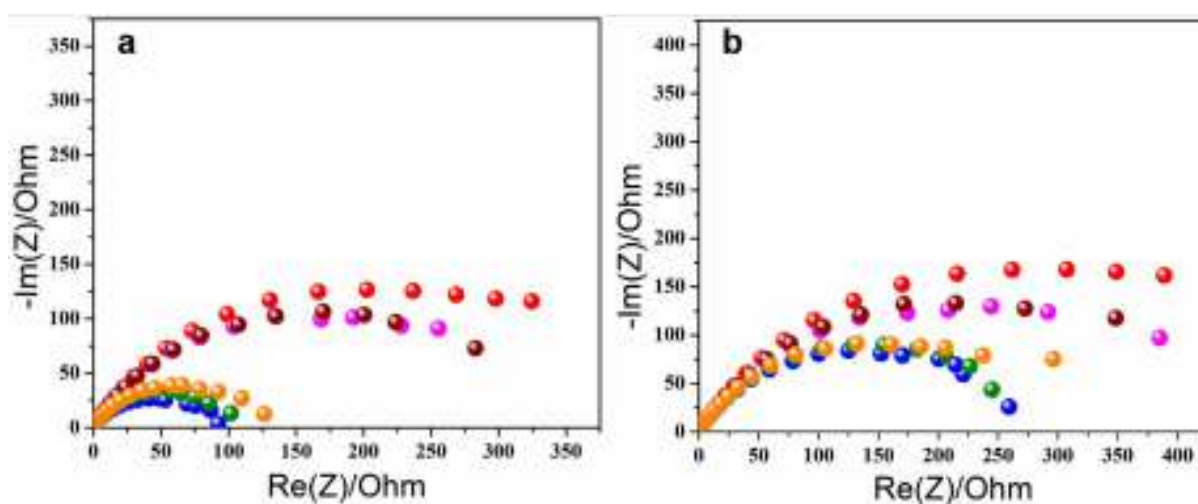


Figure S12. Electrochemical Impedance Spectroscopy (EIS) of Mg|S cell (a) with CNT-S as a cathode OCV (red), 1st discharge(blue), 1st charge(pink) 2nd discharge(green), 2nd charge(brown) and 10th discharge(orange). (b) TC-S as a cathode OCV (red), 1st discharge(blue), 1st charge(pink) 2nd discharge(green), 2nd charge(brown) and 10th discharge(orange).

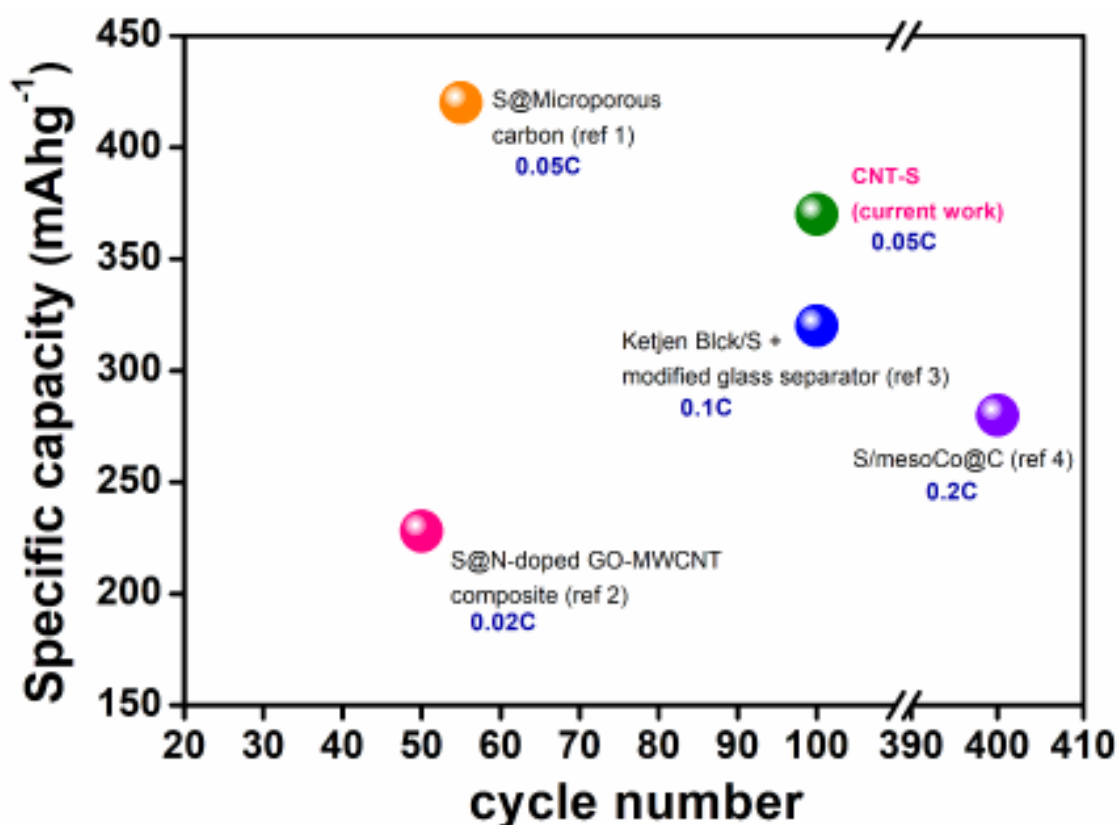


Figure S13. Performance comparison of various recent Mg|S battery reported in literature.

Discussion: Yang et al. used a S@microporous carbon composite (55 wt % sulfur) as the cathode and reported a $\text{Mg}(\text{CF}_3\text{SO}_3)_2\text{-AlCl}_3$ based electrolyte in tetrahydrofuran and tetraglyme solvent.¹ Further anthracene was added to stabilize the Mg^{2+} ions and MgCl_2 was mixed to improve the interface properties. Specific discharge capacity of 420 mAh g^{-1} was obtained after 55 cycles @ 0.5C current rate upon addition of $\text{LiCl/LiCF}_3\text{SO}_3$ additive. A N-doped GO-MWCNT composite was used as a sulfur host by Bhaghavathi et al., where $\text{Mg}[\text{B}(\text{hfip})_4]_2$ in DME solvent as the electrolyte.² At a current rate of 0.02C, discharge capacity of 228 mAh g^{-1} was obtained at the end of 50th cycle. A glass fiber separator modified via electrospun coating of decavanadate-based polyoxometalate (POM) clusters/carbon composite is reported by Ji et al.³ The modified separator demonstrated 320 mAh g^{-1} specific capacity after 100 cycles at a current rate of 0.1C employing $\text{Mg}[\text{B}(\text{hfip})_4]_2$ electrolyte. Sun et al.

reported a specific capacity of 280 mAh g⁻¹ after 400 cycles @ 0.2C current rate using a carbon-confined cobalt in a mesoporous matrix as the sulfur host and MMAC-DME (i.e., MgCl₂ + AlCl₃ + Mg powder in DME + PYR14TFSI) electrolyte.⁴ In the present work we have obtained a very stable discharge capacity of 370 mAhg⁻¹ (100th cycle at 0.05C) with negligible capacity fading. The effect of sulfur confinement inside the host carbon nanotubes are studied using *in-operando* Raman and post cycling UV-Vis spectroscopy and the results are compared with toray carbon paper sulfur cathode material where the sulfur particles are randomly scattered throughout the carbon paper matrix.

Reference

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- 2) Vinayan, B. P.; Euchner, H.; Zhao-Karger, Z.; Cambaz, M. A.; Li, Z.; Diemant, T.; Behm, R. J.; Gross, A.; Fichtner, M. Insights into the Electrochemical Processes of Rechargeable Magnesium–Sulfur Batteries with a New Cathode Design. *J. Mater. Chem. A* **2019**, *7*, 25490–25502.
- 3) Ji, Y.; Liu-Théato, X.; Xiu, Y.; Indris, S.; Njel, C.; Maibach, J.; Ehrenberg, H.; Fichtner, M.; Zhao-Karger, Z. Polyoxometalate Modified Separator for Performance Enhancement of Magnesium–Sulfur Batteries. *Adv. Funct. Mater.* **2021**, *31*, 2100868.
- 4) Sun, J.; Deng, C.; Bi, Y.; Kuang-Hsu, W.; Zhu, S.; Xie, Z.; Li, C.; Amal, R.; Luo, J.; Liu, T.; Wang, D-W. In Situ Sulfurized Carbon-Confined Cobalt for Long-Life Mg/S Batteries. *ACS Appl. Energy Mater.* **2020**, *3*, 2516–2525.