

1 Characterization of sulfur and nanostructured sulfur battery
2 cathodes in electron microscopy without sublimation artifacts.

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12 **Abstract**

13 Lithium sulfur (Li-S) batteries have the potential to provide higher energy storage density at lower
14 cost than conventional lithium ion batteries. A key challenge for Li-S batteries is the loss of sulfur
15 to the electrolyte during cycling. This loss can be mitigated by sequestering the sulfur in
16 nanostructured carbon-sulfur composites. The nanoscale characterization of the sulfur distribution
17 within these complex nanostructured electrodes is normally performed by electron microscopy,
18 but sulfur sublimates and redistributes in the high vacuum conditions of conventional electron
19 microscopes. The resulting sublimation artifacts render characterization of sulfur in conventional
20 electron microscopes problematic and unreliable. Here, we demonstrate two techniques, cryogenic
21 transmission electron microscopy (cryo-TEM) and scanning electron microscopy in air (airSEM),

22 that enable the reliable characterization of sulfur across multiple length scales by suppressing
23 sulfur sublimation. We use cryo-TEM and airSEM to examine carbon-sulfur composites
24 synthesized for use as Li-S battery cathodes, noting several cases where the commonly-employed
25 sulfur melt infusion method is highly inefficient at infiltrating sulfur into porous carbon hosts.

26 **Introduction**

27 Lithium sulfur (Li-S) batteries have the potential to provide greater energy storage density
28 at lower cost than current lithium ion batteries. One of the main challenges to improving the
29 performance of elemental sulfur cathodes for Li-S batteries is dissolution and loss of sulfur, in the
30 form of polysulfides, to the electrolyte during battery operation (Bruce et. al., 2011). Recent
31 research has focused on electrodes which attempt to sequester sulfur in nanostructured host
32 materials, most prominently porous carbons, to prevent the loss of sulfur and associated capacity
33 reduction as the battery is cycled (Ji et. al., 2009; Jayaprakash et. al., 2011; Wang et. al. 2011;
34 Xiao et. al., 2012; Seh et. al. 2013; Zheng et. al., 2013; Song et. al., 2014; Zhao et. al., 2014;
35 Werner et. al., 2015; Sahore et. al. 2015). These electrode materials are typically referred to as
36 carbon-sulfur composites. Accurate characterization of the distribution of sulfur in these
37 composites over 100 nm to sub-nm length scales is critical for developing an understanding of how
38 the level of infiltration of sulfur into the host material relates to battery performance, which will
39 aid in the design of more durable, high energy density Li-S batteries (Ma et. al. 2015).

40 Electron microscopy offers both direct imaging and spectroscopic techniques for
41 characterization of battery electrodes. For reliable characterization of a material using electron
42 microscopy, it is essential that the sample is not altered by conditions in the microscope. However,
43 elemental sulfur readily sublimates under high vacuum conditions similar to those of an electron
44 microscope sample chamber. Sulfur sublimation under high vacuum has been observed in vacuum

45 chamber experiments on bulk sulfur (Nash, 1987), and can be predicted from sulfur’s measured
46 vapor pressure (Ferreira & Lobo, 2011), but the sulfur battery community has only recently begun
47 to become aware of the problem of sulfur sublimation in electron microscopy (Raiß et. al., 2014).
48 As an illustration of this challenge, Figure 1a shows the vapor pressure curve of sulfur, with the
49 conditions of an FEI Tecnai F20 transmission electron microscopy (TEM) sample chamber
50 (8.8×10^{-8} Torr at $\sim 18^\circ\text{C}$ room temperature) indicated. Figures 1b-g show the result of placing a
51 sample of ball-milled sulfur particles into the microscope under these conditions. The sulfur is
52 observed to sublime at a rate of approximately 1 monolayer of sulfur atoms per second, leaving
53 behind only a small residue of “super-sublimated” polymeric sulfur, which remains relatively
54 stable under vacuum. The measured sublimation rate and residual product are fully consistent with
55 previous macroscopic experiments (Nash, 1987).

56 In nanostructured sulfur composites, sublimation effects in high vacuum may be very
57 severe. In TEM for example, exposed nanoscale features of the sulfur distribution in a sulfur
58 battery cathode composite would disappear within minutes at most. Only super-sublimated
59 polymeric sulfur residue (Figure 1e), and sulfur encapsulated by another material lacking large
60 enough pores for sulfur to escape (Zhou et. al., 2014; Kim et. al., 2015), will remain present under
61 vacuum.

62 In scanning electron microscopy (SEM), the sample is typically held at a higher pressure
63 than in TEM. However, a recent study has observed that even in the vacuum of an SEM sample
64 chamber ($\sim 10^{-6}$ Torr), sulfur sublimation artifacts occur, including the redistribution of sublimated
65 sulfur into the pores of nearby carbon particles. The study concluded that characterization of
66 sulfur/carbon composite materials by vacuum-based methods, including SEM, is very challenging,
67 and results might be misleading (Raiß et. al., 2014). Sulfur sublimation and the resulting artifacts,

68 including sulfur redistribution, present a serious problem for accurate characterization of the
69 inherent sulfur distribution in battery cathodes in electron microscopy. This may be impeding the
70 scientific community's efforts to gain a systematic understanding of how sulfur distribution in
71 different carbon-sulfur composites relates to their performance in batteries. More reliable
72 alternative techniques for sulfur characterization that suppress sublimation are clearly needed.

73 The sulfur vapor pressure curve (Figure 1a) indicates that sulfur has an equilibrium vapor
74 pressure of $\sim 6 \times 10^{-7}$ Torr at 18°C. This means that at 18°C, a sulfur particle will sublime until
75 the partial pressure of sulfur surrounding the particle reaches 6×10^{-7} Torr. If a sample chamber is
76 pumped to too low a pressure, sulfur will not be able to reach equilibrium, and will sublime
77 continually. To avoid sublimation artifacts, either the ambient pressure during imaging must be
78 increased to a level much greater than sulfur's equilibrium vapor pressure, or the ambient
79 temperature must be reduced to much less than 18°C. In this paper, we demonstrate
80 characterization of sulfur and nanostructured carbon-sulfur composite materials in vacuum at low
81 temperature using cryo-TEM, and at atmospheric pressure at room temperature using airSEM.
82 Sulfur sublimation artifacts are not observed using either technique. Our results demonstrate that
83 sulfur infiltration by melt infusion is significantly more efficient in activated porous carbons than
84 in non-activated porous carbons, carbon nanotubes, and hollow carbon spheres, all of which have
85 recently been investigated as Li-S battery electrode materials. Adoption of cryo-TEM, airSEM,
86 and other similar techniques, for more reliable characterization of the sulfur distribution in
87 different carbon-sulfur composites will enable scientists to observe the inherent sulfur distribution
88 in their composite materials, providing important insight and feedback to guide the design of
89 improved Li-S batteries.

90 **Experimental**

91 Cryo-TEM is a well-established method for imaging hydrated biological samples that
92 cannot be exposed to vacuum at room temperature (Dubochet & McDowell, 1981; Adrian et. al.,
93 1984; Kourkoutis et. al. 2012). Cryogenic cooling of sulfur cathode samples inside the microscope
94 was achieved using a Gatan model 626 cryo-holder (Gatan, Inc., Pleasanton, CA, USA), with
95 liquid nitrogen as the cryogen. The cryo-TEM loading method for sulfur cathode samples is
96 simpler than for biological samples, since the sulfur need only be cooled prior to loading into the
97 microscope column, whereas biological samples must be vitrified. Carbon-sulfur composite
98 particles were dispersed from an ethanol solution onto TEM grids, which were then allowed to dry
99 in air. The cryo-holder was cooled so that the tip temperature was $\sim -173^{\circ}\text{C}$. The sample TEM
100 grids were loaded into the cryo-holder under nitrogen gas near liquid nitrogen temperature. An
101 FEI Tecnai F20 STEM/TEM (FEI Company, Hillsboro, OR, USA) equipped with cryogenically
102 cooled beryllium blades, and operated in scanning TEM (STEM) mode at 200 kV was used to
103 image the samples. An Oxford Instruments XMAX detector (Oxford Instruments PLC, Tubney
104 Woods, Oxfordshire, UK) was used for x-ray energy dispersive spectroscopy (XEDS), and a Gatan
105 865 HR-GIF spectrometer was used for electron energy loss spectroscopy (EELS) acquisition.

106 Experiments in air were performed using a B-nano airSEM (B-nano Ltd. Rehovot, Israel),
107 operated at 30 kV. The airSEM is a relatively new design of electron microscope (a schematic
108 diagram of an airSEM is shown in Supplementary Figure S1), which enables characterization of
109 samples in air, with no sample vacuum chamber (Nguyen et. al., 2013; Solomonov et. al., 2014;
110 Vidavsky et. al. 2014; Nguyen et. al., 2016). Carbon-sulfur composite particles for analysis in
111 airSEM were dispersed onto TEM grids from an ethanol solution and allowed to dry in air, in the
112 same manner as for cryo-TEM. Sample TEM grids were placed directly on top of an airSTEM
113 detector (Nguyen et. al., 2014; Han et. al. 2015; Nguyen et. al., 2016), which was mounted on an

114 optical slide. A white light optical reflectance microscope (Olympus, Centre Valley, PA, USA)
115 was used both for optical imaging, and to set the height of the sample to $\sim 50 \mu\text{m}$ below the electron
116 window, the optimal working distance for airSEM imaging. XEDS maps were acquired using a
117 Bruker XFlash 6160 detector (Bruker Corporation, Billerica, MA, USA).

118 Pure sulfur particles were prepared for analysis by ball-milling sulfur flakes. Carbon-sulfur
119 composites synthesized with ordered mesoporous carbon structures GDMC-15-1600°C and
120 aGDMC-15-10h, were obtained from block copolymer co-assembly and heated to 1600°C to
121 remove any intrinsic microporosity. The high-temperature treatment yielded low oxygen content
122 and surface functionalization (hydrophobic surface). Carbon aGDMC-15-10h underwent
123 activation by heating in CO_2 at 950°C for 10 hours. Sulfur infiltration by melt infusion was
124 attempted at a sulfur:carbon ration of 1:1 by weight. The synthesis, and performance of these
125 mesoporous materials in battery testing is described in detail by Werner et. al. (Werner et. al.,
126 2015). Carbon nanotube – sulfur composite samples, CNT-S, were synthesized using multi-walled,
127 $> 8\%$ carboxylic acid functionalized carbon nanotubes, average diameter $\sim 9.5 \text{ nm}$, length ~ 1.5
128 μm , which were obtained from Sigma Aldrich, and dried before use. Polyethylenimine (PEI)
129 solution (50 wt. % in water) was obtained from Sigma-Aldrich, and PEI was covalently grafted to
130 the carbon nanotubes. Sulfur infiltration by melt infusion was then attempted at a sulfur:carbon
131 ration of 7:3 by weight. Mesoporous hollow carbon sphere – sulfur composites, MHCS-S, were
132 prepared by an organic hard template method. In a typical synthesis, size tunable mono-dispersed
133 melamine-formaldehyde (MF) resin sphere templates (0.5 g) were synthesized by the in-situ
134 polymerization method reported by Xie et al. (Xie et al., 2008). These were then suspended in a
135 50 mL water/ethanol (volume ratio 3/1) solvent containing 0.5 g of Triton X-100 surfactant.
136 Formaldehyde solution (1.0 mL) and resorcinol (0.75 g) were then added to the reaction solution,

137 and stirred for 30 min at 60°C. The solution was subsequently heated for 2 hours at 75°C. The solid
138 product was recovered by filtration and air-dried at 90°C for 8 hours. Mesoporous hollow carbon
139 spheres were formed by carbonization of the as-made resorcinol-formaldehyde encapsulated MF
140 spheres at 950°C for 2 hours under flowing nitrogen gas with a heating rate of 3°C/min. Sulfur
141 infiltration was attempted by melt infusion at a sulfur:carbon ratio of 7:3 by weight.

142 **Results and Discussion**

143 I. Sulfur characterization in cryo-TEM.

144 In order to investigate whether sublimation effects were still apparent at cryogenic
145 temperatures, ball milled sulfur particles, were prepared in an identical manner to those in Figure
146 1, and imaged by cryo-TEM at a temperature of approximately -173°C. A time series of cryo-TEM
147 images from a sulfur particle is shown in Figure 2. No change in the morphology of the particle
148 was observed over a 5-hour period, in stark contrast to the sulfur particle imaged by standard room
149 temperature TEM shown in Figure 1, which sublimated and disappeared in under 40 minutes. The
150 cryogenically cooled sulfur remained stable enough under the electron beam to allow imaging in
151 annular dark field (ADF) cryo-scanning TEM (cryo-STEM, Figure 2d) and XEDS mapping
152 (Figure 2e). The suppression of sulfur sublimation by cryogenic sample cooling demonstrates that
153 cryo-TEM is a viable method for both imaging and spectroscopic characterization of composites
154 containing elemental sulfur such as carbon-sulfur nanocomposites for advanced lithium batteries.

155 Having established that sulfur sublimation is suppressed at cryogenic temperatures, we
156 used cryo-TEM to analyze the sulfur distribution within three different carbon-sulfur
157 nanocomposite materials recently investigated for Li-S battery electrodes. The first two samples,
158 GDMC-15-1600°C and aGDMC-15-10h, are examples of ordered carbon nano-networks (Werner

159 et. al., 2015). These have attracted interest as sulfur battery cathode materials due to the potential
160 of sequestering sulfur in the pores of a torturous carbon network. GDMC-15-1600°C and aGDMC-
161 15-10h were prepared in an identical manner except that, prior to sulfur melt infusion, aGDMC-
162 15-10h underwent an additional activation procedure to substantially increase its microporosity
163 and associated surface area, whereas the non-activated carbon, GDMC-15-1600°C, exhibits very
164 little microporosity (see Experimental). The third sample, CNT-S used a network of carbon
165 nanotubes as the host material for sulfur. Carbon nanotubes have attracted interest as Li-S battery
166 electrodes due to the potential to sequester sulfur inside the body of the nanotubes (Fujimori et.
167 al., 2013; Kim et. al., 2015). In each of our three samples, successful melt infusion would ensure
168 that electrically insulating sulfur is in contact with electrically conducting carbon at the nanoscale.
169 Cryo-STEM imaging and XEDS maps of the activated C-S composite aGDMC-15-10h (Figure
170 3a), showed a high degree of infiltration of sulfur into the carbon following melt infusion.
171 However, in the non-activated C-S composite GDMC-15-1600°C we observed that a majority of
172 the sulfur had not infiltrated the carbon, and remained external to the carbon particles (Figure 3b).
173 External sulfur particles typically had a diameter of several μm or larger. In reported battery
174 performance tests, the activated carbon aGDMC-15-10h outperformed its non-activated
175 counterpart GDMC-15-1600°C in terms of initial capacity, capacity retention over cycling, and
176 rate capability (Werner et. al., 2015). This may be partly explained by our observation that sulfur
177 infiltration was much more successful in the activated carbon aGDMC-15-10h than the non-
178 activated carbon GDMC-15-1600°C, because the external sulfur particles observed in GDMC-15-
179 1600°C would be in poorer electrical contact with the carbon, and more exposed to dissolution and
180 loss to the electrolyte in the form of polysulfides during battery cycling.

181 High magnification STEM imaging and EELS spectra of sample CNT-S indicated that little
182 or no sulfur had infiltrated into the carbon nanotubes, which had remained hollow (Figure 3c).
183 XEDS mapping of sample CNT-S at low magnification showed that much of the sulfur in the
184 composite remained external to the nanotube network after melt infusion, forming particles several
185 microns in diameter (Figure 3d), in a similar way to the sulfur in sample GDMC-15-1600°C. X-
186 ray sum spectra from the datasets used to generate element distribution maps contain information
187 about the relative quantities of carbon and sulfur in the field of view that are not evident from x-
188 ray maps alone. The x-ray spectra used to generate the maps in Figure 3 are shown in
189 Supplementary Figure S2. Each of these spectra show a strong sulfur peak relative to the carbon
190 peak, indicating significant quantities of sulfur in the field of view. Our results show that the degree
191 to which sulfur infiltrates into carbon host particles can vary significantly depending on the
192 porosity and structural characteristics of the carbon host, and how the carbon was prepared. In this
193 case, sulfur infiltrated far more efficiently into the activated, high-surface area carbon aGDMC-
194 15-10h exhibiting both 15 nm mesopores and a large fraction of small micropores (< 4 nm), than
195 into the non-activated carbon GDMC-15-1600°C, exhibiting only 15 nm mesopores, or into a
196 network of carbon nanotubes. In a related cryo-TEM study of sulfur infusion into highly porous
197 carbons synthesized by ice templation, sulfur was observed to have infiltrated far more efficiently
198 into activated carbon 20-2-1.5-80S exhibiting both mesopores and micropores, than into non-
199 activated carbon 20-2-0-80S, exhibiting only mesopores (Sahore et. al., 2016), a very similar trend
200 to the results described above.

201 II. Sulfur characterization in airSEM.

202 An alternative approach to cryogenic cooling to avoid sulfur sublimation is to keep the
203 sample at room temperature, but increase the pressure around the sample, for example by imaging

204 the sulfur at atmospheric pressure. The recently developed airSEM by B-nano enables correlative
205 optical and electron microscopy of samples in air, with no vacuum specimen chamber, by using
206 an electron transparent silicon-nitride window to separate the sample in air from the electron optics
207 in vacuum (Solomonov et. al., 2014; Vidavsky et. al. 2014; Nguyen et. al., 2016). Our cryo-TEM
208 observations of external sulfur particles several μm in diameter in carbon-sulfur composite samples
209 suggested that correlative optical-electron microscopy would be a useful method of high-
210 throughput characterization of these materials. Optical microscopy can screen samples for large
211 external sulfur particles, since external sulfur (yellow) is optically distinct from carbon (black).
212 Electron microscopy and XEDS can then be used to image carbon particles at higher magnification
213 to analyze the degree of sulfur infiltration into the carbon, and investigate nanoscale features of
214 the sulfur distribution.

215 As a demonstration of this technique, we used airSEM to investigate the distribution of
216 sulfur in sample MHCS-S, a composite of sulfur and 3 μm diameter hollow carbon spheres with
217 porous shells. These have attracted interest as candidate materials for Li-S batteries because of the
218 potential for large quantities of sulfur to be sequestered in both the porous shell, and in the hollow
219 interior of the sphere, though some recent studies have questioned whether melt infusion is actually
220 successful at infiltrating sulfur into the hollow interior (Jayaprakash et. al., 2011; He et. al., 2013).
221 In our sample, sulfur infiltration was attempted by melt infusion at a ratio of 7:3 sulfur to carbon
222 by weight prior to imaging, sufficient to ensure that both the pores in the shell wall, and the interior
223 cavity could be filled if melt infusion was successful.

224 Particles of external sulfur were identified by optical microscopy (Figure 4a). Closer
225 inspection of a $\sim 30 \mu\text{m}$ wide external sulfur particle (Figure 4b) with airSEM, using a bright-field
226 STEM detector positioned directly below the sample (Nguyen et. al., 2014; Han et. al. 2015;

227 Nguyen et. al., 2016), shows a morphology that suggests this particle was formed by freezing from
228 a liquid state. XEDS mapping confirmed the identity of the particle as external sulfur (Figure 4c
229 & 4d, spectrum in Supplementary Figure S4a). Clusters of carbon spheres were identified in the
230 optical microscope (Figure 4e) and imaged at high resolution in the airSEM (Figure 4f). The
231 spheres appeared to be unfilled in the airSEM images, suggesting that sulfur had not infiltrated
232 into the sphere interior. This was confirmed by XEDS mapping (Figure 4g & 4h, spectrum in
233 Supplementary Figure S4b). However, XEDS maps did show that sulfur had infiltrated the walls
234 of the spheres, despite not infiltrating the hollow interior as had been intended.

235

236 III. Comparison of airSEM and cryo-TEM

237 The spatial resolution set by electron optics in the airSEM will be more limited than for
238 cryo-TEM. However, an advantage of the airSEM is that samples do not need to be cooled and
239 placed in a vacuum chamber, meaning that airSEM can achieve greater sample throughput.
240 AirSEM will be most suitable for use in conjunction with optical microscopy for high-throughput
241 characterization of samples using a broader field of view where image resolution of < 5 nm is not
242 required, whereas cryo-TEM will be most suitable for characterization of samples that require
243 resolution of finer, nanometer scale features.

244 IV. Limitations due to radiation damage

245 Even after sublimation has been suppressed, radiation damage will ultimately limit the
246 resolution at which sulfur can be characterized in electron microscopy. Electrical insulators, such
247 as sulfur, are vulnerable to ionization damage (Egerton & Malac, 2004). Furthermore, sulfur
248 molecules are weakly bound, making sulfur vulnerable to knock-on displacement damage
249 (Chisney et. al., 1988). When sulfur is imaged at relatively low magnification, as in the results

250 presented in this paper, electron dose is spread over a wide area, and beam damage effects to sulfur
251 will be minimal. However, at high magnification, electron dose becomes more concentrated and
252 radiation damage will cause mass loss from sulfur particles. Radiation damage effects have been
253 observed in Supplementary Figure S5, which is accompanied by further discussion of damage.

254 **Conclusions**

255 The high vapor pressure of sulfur creates a serious risk that sublimation artifacts will lead
256 to a mischaracterization of samples containing sulfur in standard high-vacuum electron
257 microscopy. As a solution to this problem, we have demonstrated that sulfur sublimation is
258 suppressed by cooling sulfur samples below the sulfur sublimation point in vacuum using cryo-
259 TEM, or by using airSEM to image sulfur in air. Both techniques are able to detect features of the
260 sulfur distribution across C-S nanocomposite materials that are extremely challenging to observe
261 reliably in standard electron microscopy due to sulfur sublimation in vacuum and resulting artifacts
262 such as sulfur redistribution. Most notably, in three of the four carbon-sulfur composite samples
263 investigated in this paper, we have directly observed that sulfur infiltration by melt infusion is
264 unsuccessful or inefficient, leaving much of the sulfur external to the carbon host material. It may
265 be of interest for future studies to investigate whether inefficient sulfur infiltration by melt infusion
266 occurs in other composite materials, and to what extent this affects battery performance.

267 In conclusion, we strongly recommend adoption of cryo-TEM, airSEM for more reliable
268 characterization of sulfur and sulfur battery cathodes. Other techniques that may also be able to
269 suppress sulfur sublimation artifacts could include environmental SEM, cryo-SEM, and
270 environmental-cell TEM. Applying these techniques to Li-S batteries will allow researchers to
271 reliably characterize the inherent distribution of sulfur in their composite electrodes, helping to
272 guide the design of improved lithium sulfur batteries.

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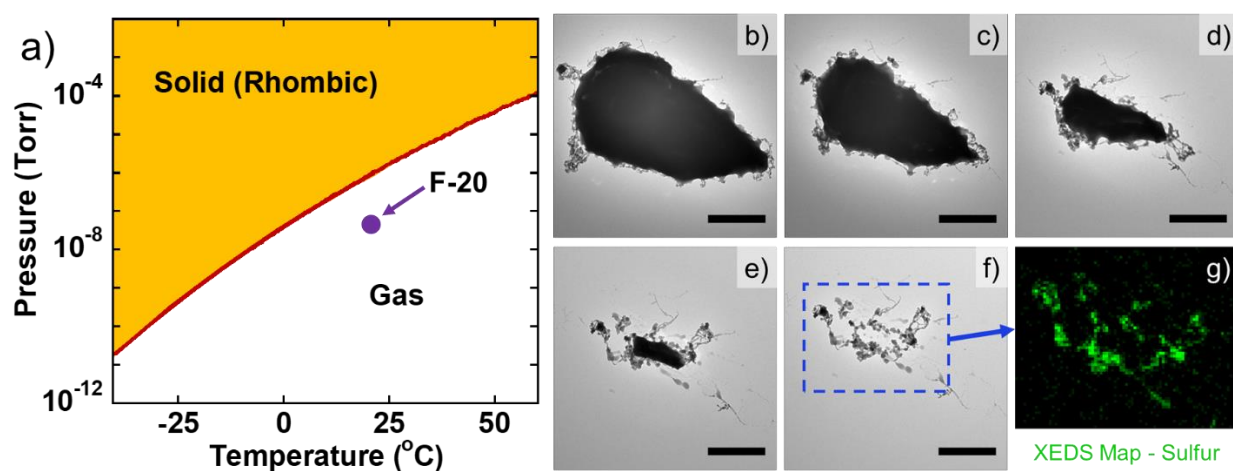
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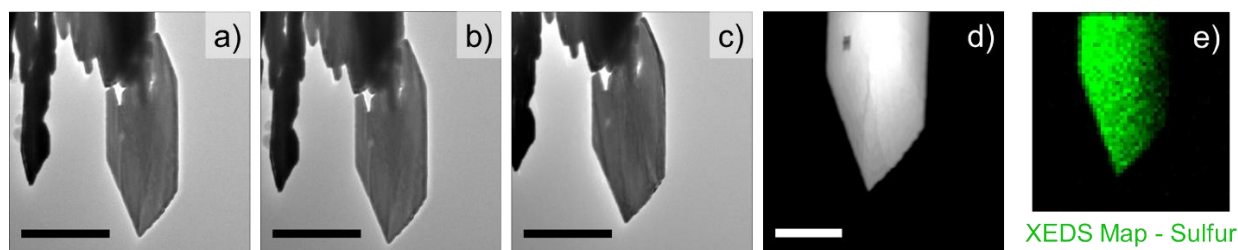
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368 **Figures**

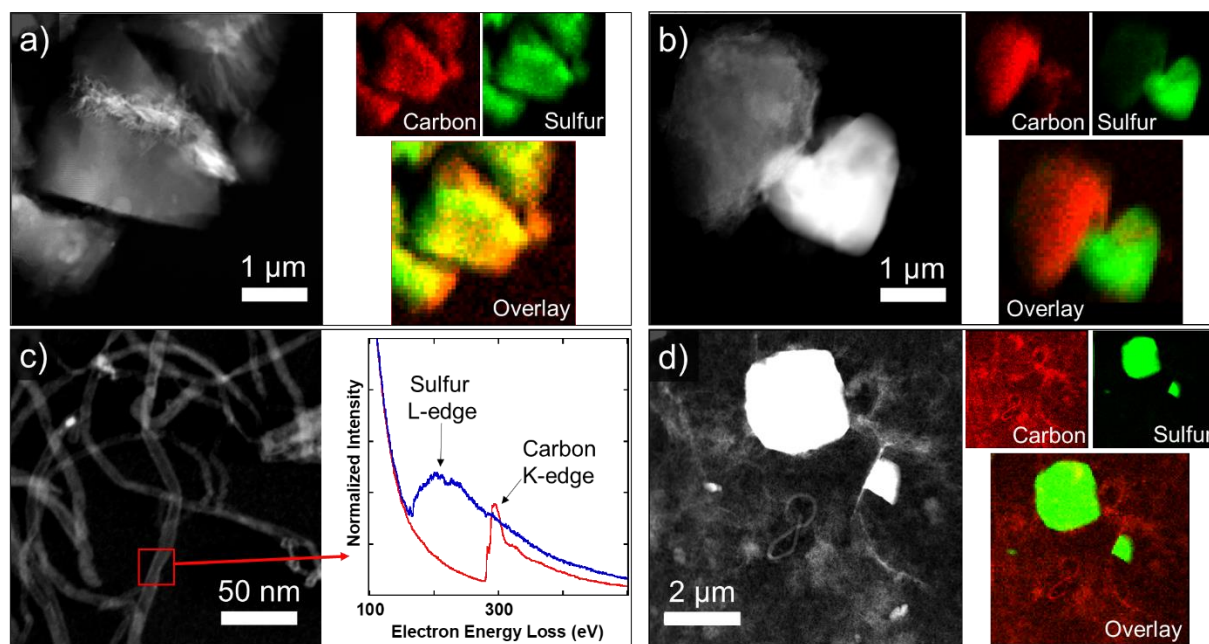


369
370 **Figure 1. a)** Vapor pressure vs temperature for elemental sulfur (Ferreira & Lobo, 2011). Purple
371 marker indicates approximate conditions in specimen chamber of the F20 TEM used for image
372 acquisition. **b) – f)** Sulfur particle sublimating in TEM vacuum chamber at 18°C, at a pressure of
373 8.8×10^{-8} Torr, imaged after (b) 16 min, (c) 21 min, (d) 28 min, (e) 33 min, (f) 40 min under vacuum.
374 Scale bars 1 μm. The particle was not exposed to the electron beam between images. After 40 min,
375 particle has sublimated almost completely, leaving a small residue, which was stable in vacuum.
376 STEM-XEDS map (**g**) indicates that the residue is sulfur. Residue morphology suggests the
377 formation of super-sublimated polymeric sulfur, as expected from the macroscopic experiments of
378 (Nash, 1987).



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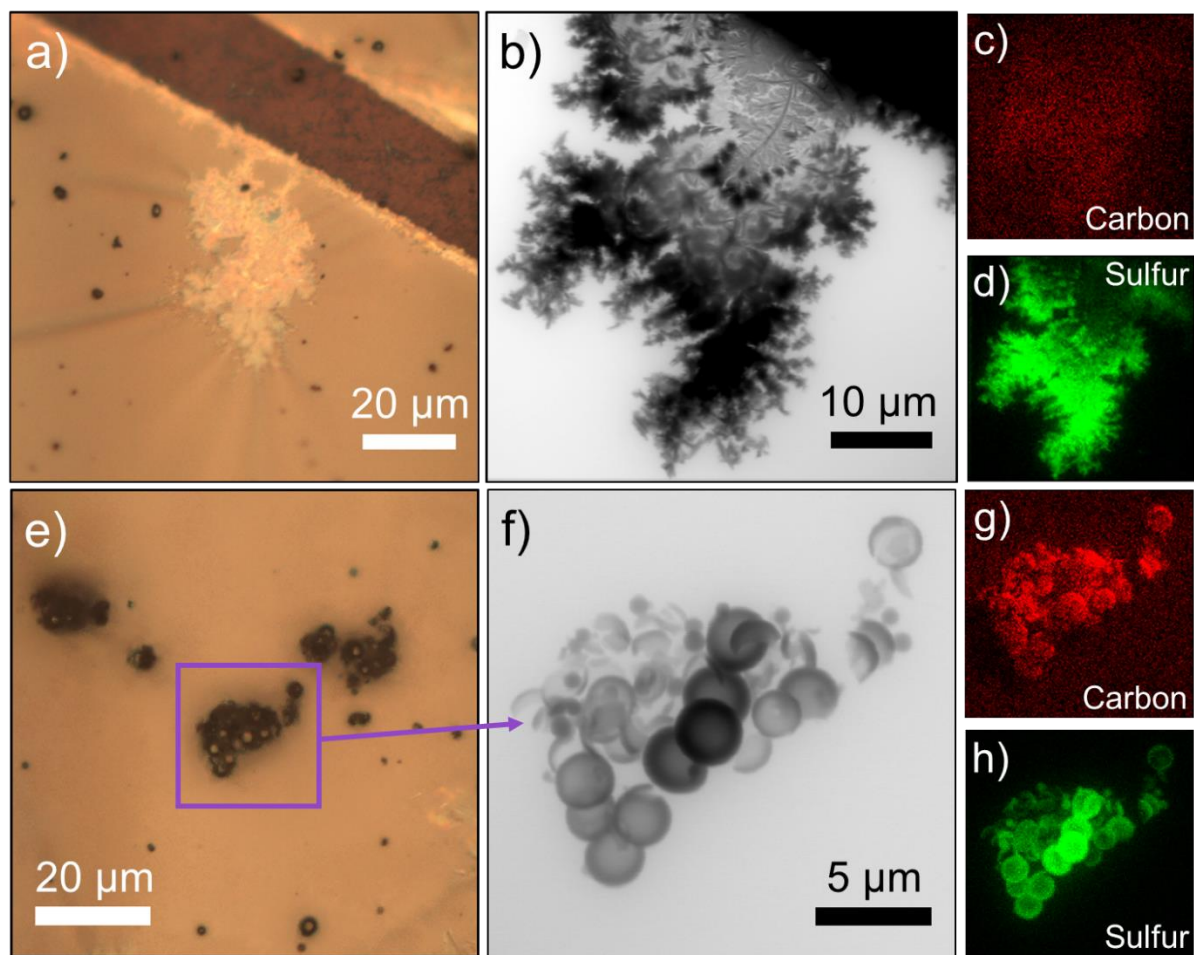
380 **Figure 2.** a) – c) Time series of images of a cryogenically cooled sulfur particle at approximately
 381 -173°C after a) 86 minutes, b) 170 minutes, and c) 311 minutes under 8.8×10^{-8} Torr vacuum. Scale
 382 bars 1 μm . The particle was not exposed to the electron beam between images. No sublimation
 383 effects were observed over a 5 hour period. After 4 hours under vacuum, a HAADF STEM image
 384 (d) (scale bar 500 nm) and STEM-XEDS map (e) were taken from the tip of the particle,
 385 demonstrating the stability of sulfur for STEM imaging and spectroscopic analysis under
 386 cryogenic conditions. Stronger signal on left hand side of particle due to detector geometry.



387

388 **Figure 3.** Cryo-STEM ADF images and XEDS maps of: a) Composite of sulfur and activated
 389 gyroidal mesoporous and microporous carbon aG^DMC-15-10h, showing a high degree and
 390 homogeneity of sulfur infiltration (overlap in carbon and sulfur signals). b) Composite of sulfur

391 and the same gyroidal mesoporous carbon G^DMC-15-1600°C without prior activation and very
392 low microporosity, showing pure sulfur external to the carbon host, indicating poor infiltration
393 efficiency. **c)** Cryo-STEM image of carbon nanotubes after attempted sulfur melt infusion. Tubes
394 remain hollow. EELS spectrum from body of tube (red) on carbon support film shows little or no
395 sulfur L-edge signal. EELS spectrum from an elemental sulfur particle shown for comparison in
396 blue. **d)** Carbon nanotube-sulfur composite CNT-S, also showing most sulfur external to
397 nanotubes.



398
399 **Figure 4.** **a)** Optical microscope image of pure sulfur that has not infiltrated into carbon spheres.
400 **b)** airSEM BF-STEM image of sulfur particle corresponding to that in the optical image. **c) & d)**

401 carbon and sulfur XEDS maps, confirming that the material is bulk sulfur. **e)** Extended depth of
402 field optical microscope image of clusters of carbon-sulfur spheres recorded on the airSEM's
403 optical microscope. **f)** airSEM BF-STEM image of single cluster of carbon spheres from the same
404 region as (b). **g) & h)** XEDS maps showing carbon and sulfur signals that confirm sulfur
405 infiltration into the sphere walls, but suggests no infiltration into the sphere interior.