SUPPORTING INFORMATION for

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The Beauty of Frost: Nano-Sulfur Assembly via Low Pressure Vapor Deposition

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Experimental Details.

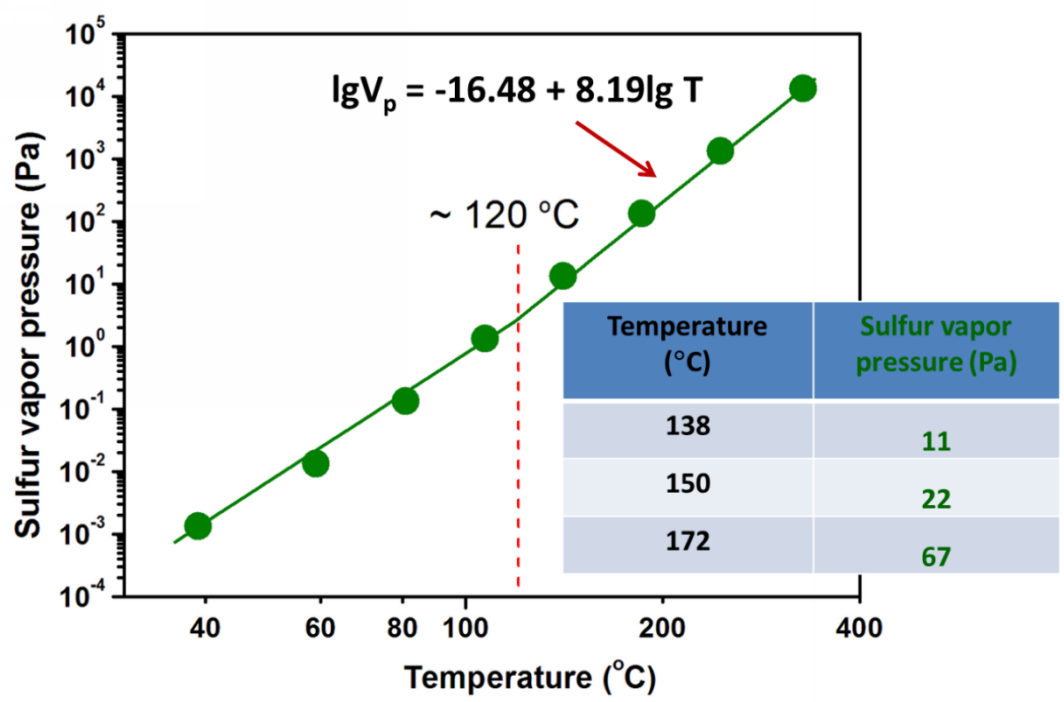
LPVD set-up and deposition operation. The set-up for LPVD is illustrated in Supporting Info. Figure S8. A typical loading of sulfur in the glass container is ca. 10 g. The whole set-up was placed inside a fume hood for all the deposition operation. The surface temperature of the sulfur melt and the temperature of the deposition substrate were measured by an IR-Thermometer. Before placing the deposition substrate onto the top of the container, the temperature of the sulfur melt was stabilized for ca. 25 min. When the temperature reaches its equilibrium state, the cool substrate with room temperature was placed onto the container to trap the sulfur vapor, which starts the count of the deposition time.

Preparation of deposition substrate. (a) Flat glass substrate. Microscope cover glass (24 mm × 60 mm, Fisher Scientific) was cleaned first by DI water with bath sonication for ca. 5 min. and then further cleaned by ethanol also with bath sonication for ca. another 3 min. (b) Carbon nanofiber (CNF) substrate. CNFs (diameter, 100 – 200 nm, length 20 – 200 μm, Sigma Aldrich) was employed as received or treated by surfactant, sodium dodecyl sulfate (SDS). To prepare a CNFs film, the pristine CNFs was first dispersed in ethanol (ca. 0.2 wt%) followed by filtering on a filter paper (ϕ = 70 mm). After the filtering, a layer of CNFs film formed on the top of the filter paper. The resultant CNFs-filter paper was dried and directly employed as the substrate for deposition. Similarly, for the SDS-treated CNFs (CNFs: SDS = 1 : 2), the CNFs was dispersed in DI-water with a concentration of 0.2 wt% and then the dispersion was filtered and dried with the filter paper. For the SDS treated CNFs, to remove possible extra surfactant, the CNFs was cleaned by DI-water during the filtering. (c) Patterned

substrate. A blank CD-ROM (Verbatim, Corp.) was employed as the materials for pattern substrate. To obtain the pattern surface on polycarbonate (PC) side, the label layer, that is, the Al reflective layer was removed by tape. Then, the PC plate with exposed pattern surface was cut to pieces with the size fitting the glass container and cleaned by ethanol and DI water with bath sonication for ca. 5 min.

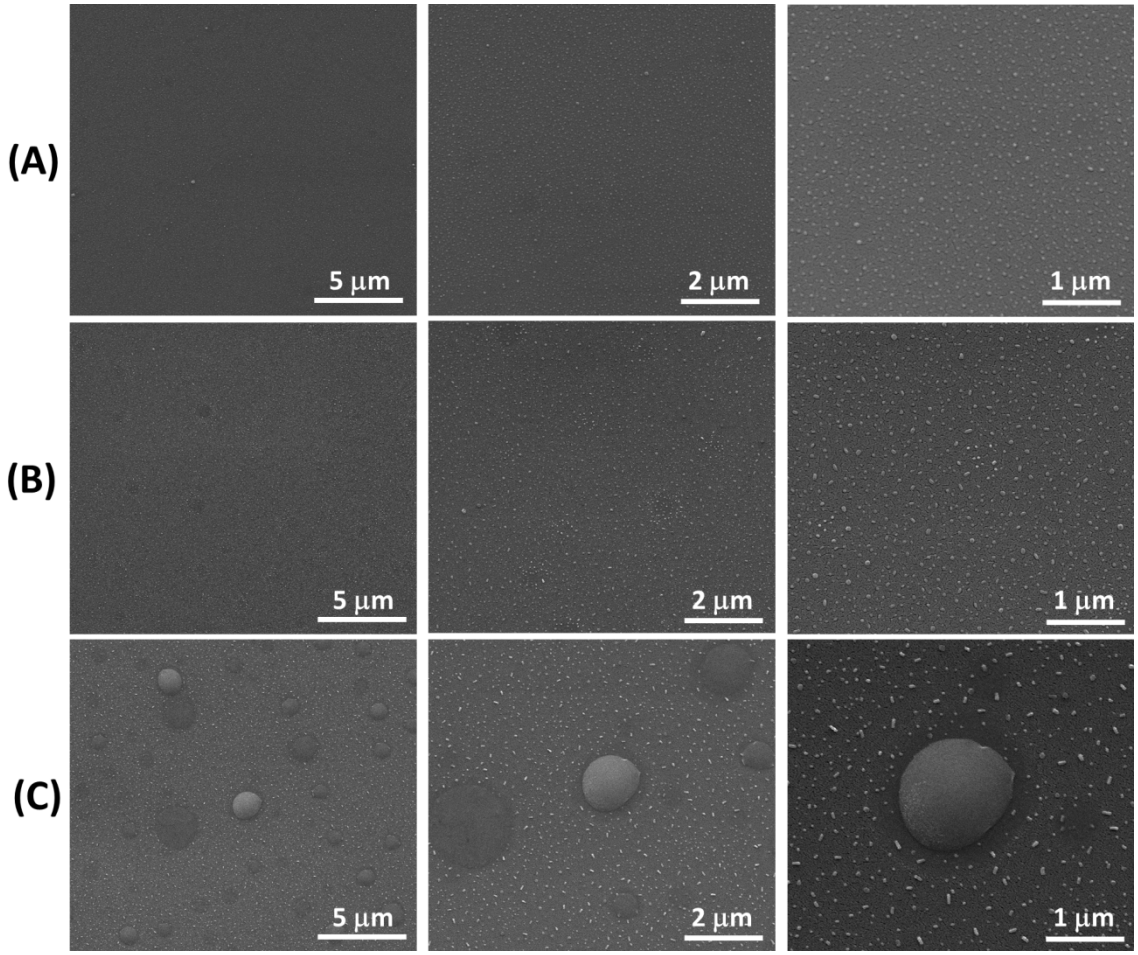
Characterizations. The morphology of substrates and deposition sulfur objects were studied by scanning electronic microscopy (SEM). Based on SEM images, the dimensions of the particles and assemblies were determined by software ImageJ. For contact angle testing, the same substrates as used for the deposition were characterized by an OCA 15 plus Contact Angle Analyzer with DI-water as the droplet. To identify the crystal structures of the deposited sulfur, X-ray diffraction (XRD) was employed. The 2θ range used was from 10° to 80° to cover all the peaks for sulfur material. For sulfur samples deposited on the three different substrates, only the one deposited on carbon nanofibers gave rise to reliable results and others involved strong noises mainly due to the small amount of sulfur materials on the substrates.

Supporting Information Figure S1. Temperature dependent behavior of the vapor pressure of elemental sulfur (data are adapted from ref.: Meyer, B. (1976). "Elemental Sulfur." *Chemical Reviews* 76(3): 367-388). The sulfur vapor pressure at the temperatures studied in this work is also calculated via the fitting function of the data above the melting point of sulfur (ca. 120 °C) as indicated in the plot (the results are summarized in the insert table).

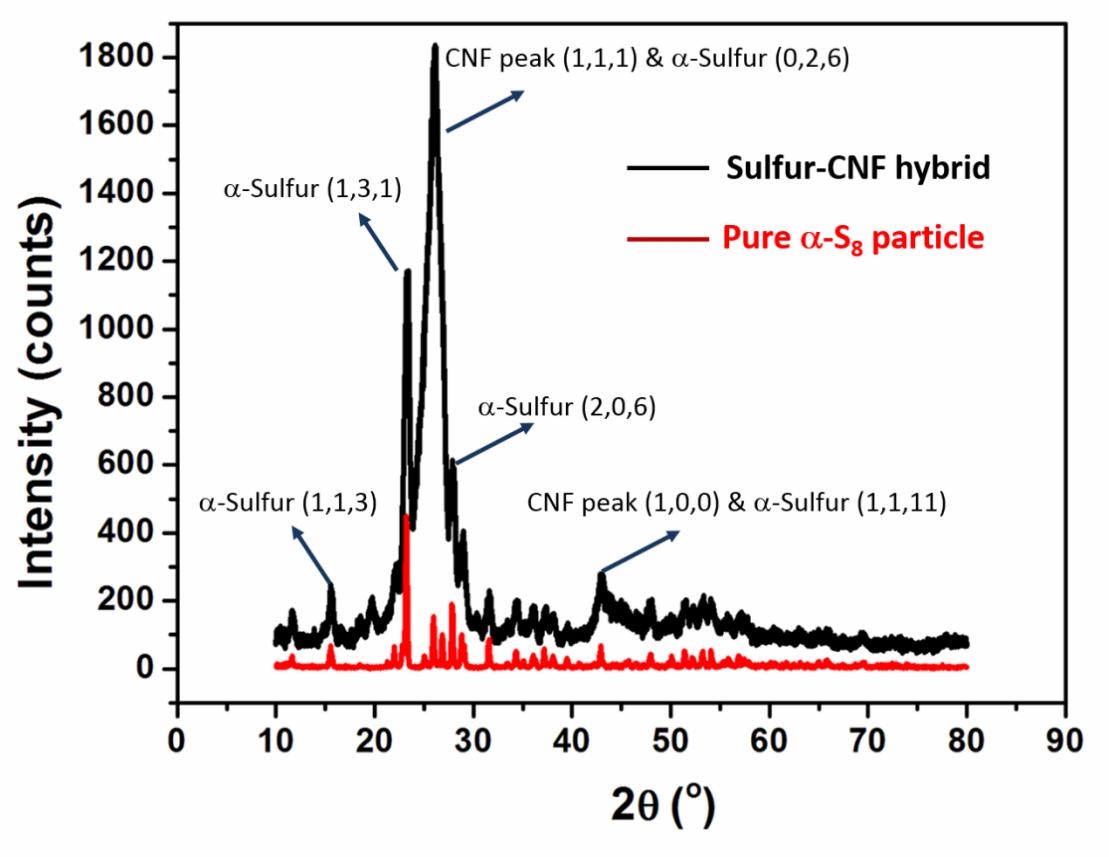


Temperature (°C)	Sulfur vapor pressure (Pa)
138	11
150	22
172	67

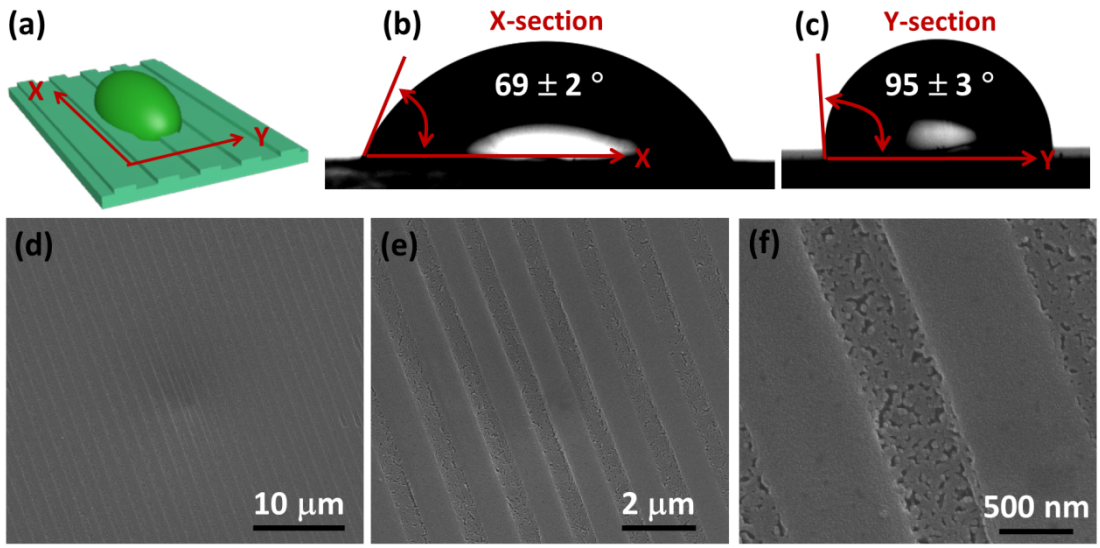
Supporting Information Figure S2. SEM images with different magnifications of the flat glass surface after varying deposition time at 138 °C: (A) 3 s, (B) 10 s and (C) 60 s.



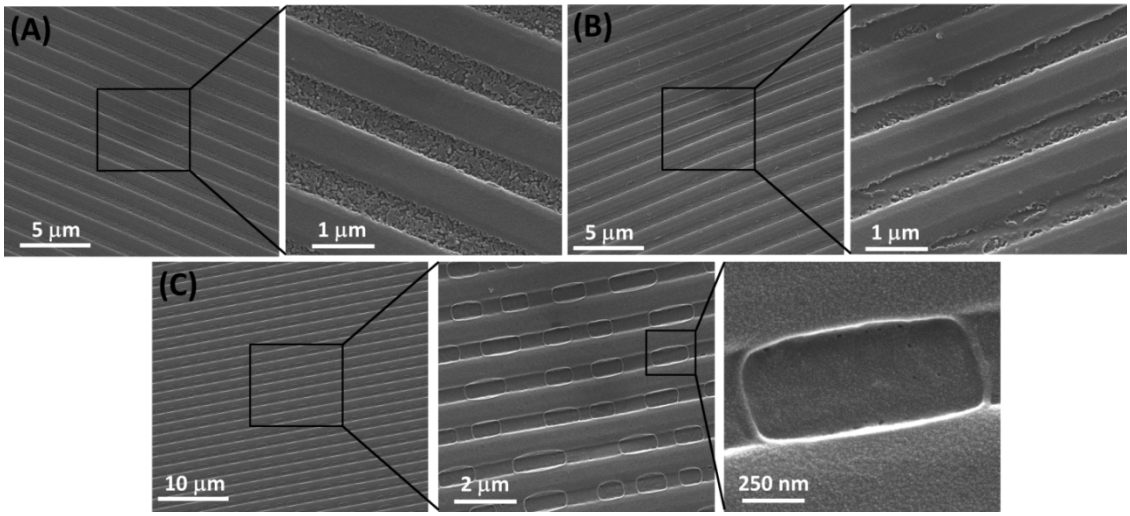
Supporting Information Figure S3. XRD results for the sulfur deposited on CNFs substrate (for comparison, a pure α-S8 sample was also tested and the result is shown also). Based on the compositions analysis, it turns out that there are 80% S8 and 20% graphite (that is, the CNFs). The XRD data for other sulfur samples is not included due to strong noise issue.



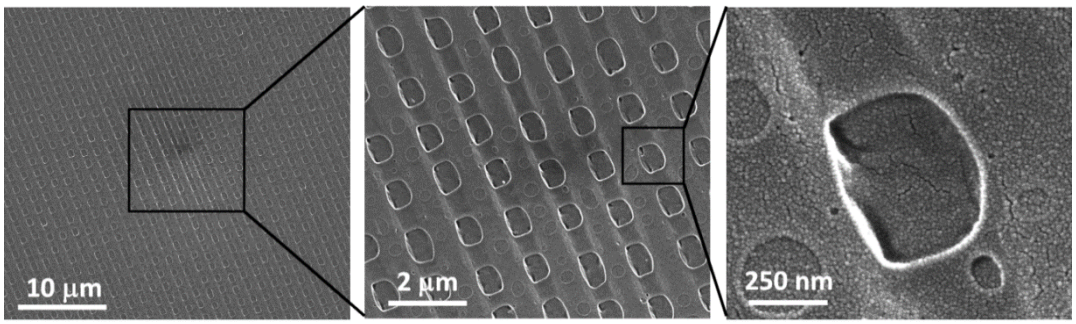
Supporting Information Figure S4. Characterizations of the blank CD-ROM: (a) Schematic of a water droplet on the pattern surface, which shows anisotropic wetting behavior in X and Y direction; (b) and (c), snapshots of the droplet during contact angle testing in X-direction and Y-direction, respectively; (d) – (f), SEM images with different magnifications of the blank CD-ROM with patterned surface.



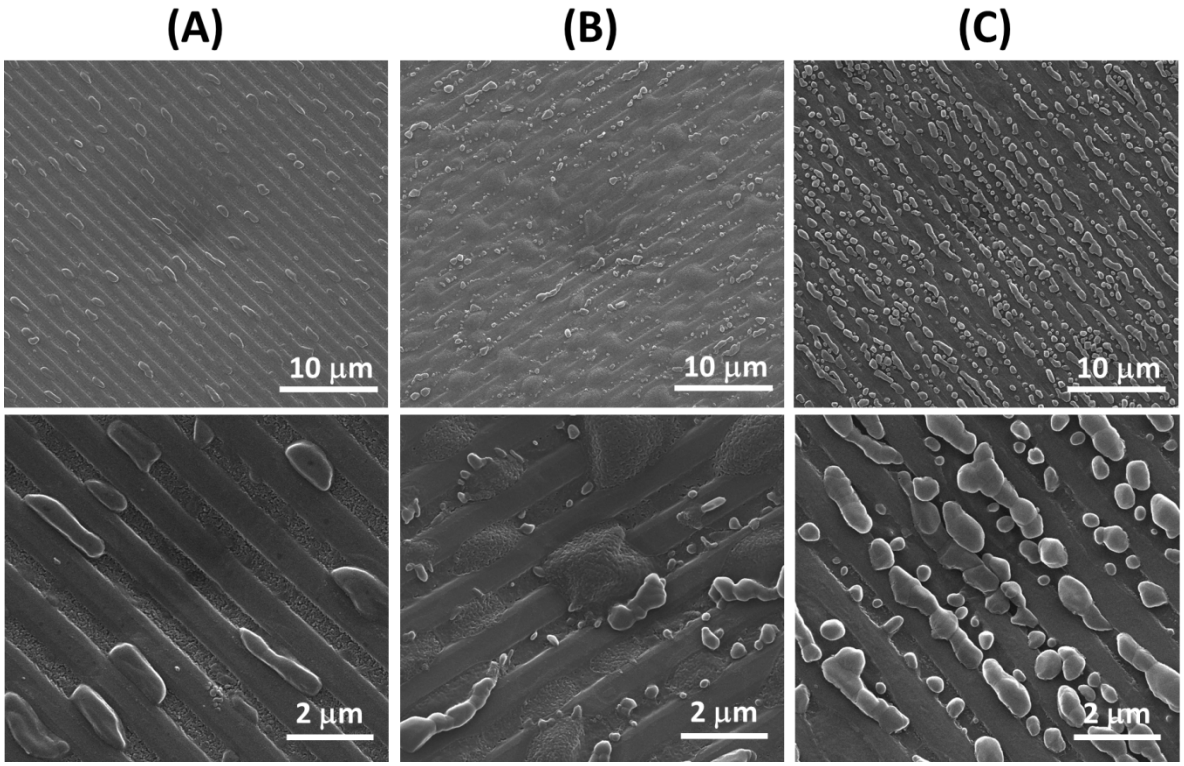
Supporting Information Figure S5. SEM images with different magnifications of the CD-ROM sample after varying deposition time at 138 °C: (A) 10 s, (B) 30 s and (C) 60 s.



Supporting Information Figure S6. SEM images of the deposited sulfur pattern formed on CD-ROM surface with an optimal condition: 150 °C for 60 s.



Supporting Information Figure S7. SEM images of the deposited sulfur on CD-ROM surface at a relative high temperature of 172 °C with varying deposition time: (A) 10 s, (B) 30 s and (C) 60 s.



Supporting Information Figure S8. Schematic of the set-up for LPVD. A circular glass container was employed and its dimensions are shown in the schematic. The typical loading of sulfur in the container is about 10 g. The temperature was adjusted by the hot plate and measured by an IR Thermometer.