

Supporting Information

Layered Sulfur Nanosheets Prepared by Assembly of Sulfur Quantum Dots: Implications for Wide Optical Absorption and Multi-wavelength Photoluminescence

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1. Experimental

1.1 Reagents and Materials

All chemicals were analytical reagent-grade and ultra-pure water were prepared with an ultrapurification system (Beijing Shuangfeng Ultrapurification Instrument Plant, Beijing, China). H₂O₂ was purchased from Tianjin Chemical Reagent Plant (Tianjin, China). Polyethylene glycol 400 (PEG-400) was obtained from Guangdong Guanghua Sci. Tech. (Guangdong, China). Sodium hydroxide (NaOH) with 99.99% purity, Nitric acid (HNO₃) with 70% purity were obtained from Aladdin.

A dialysis membrane (1000 KDa) was purchased from Beijing Ruida Henghui Science and Technology Development Co. Ltd.

1.2 Instrument

The surface morphology and structural properties of the sulfur nanosheets (S-NSs) were investigated using field-emission transmission electron microscopy (TEM) (FEI, US, Tecnai G2). Photoluminescence (PL) spectra were recorded by Fluorescence spectrophotometer (LS 55, Perkin Elmer, USA). UV spectra were recorded by UV-vis spectrophotometer (TU-1901, Persee, Beijing, China). The CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.) was used for electrochemical testing. Other instruments included: Ultrasonic Cleaners (KQ-300, 40 KHz, 300 W, Kunshan Ultrasonic Instruments Co. Ltd., China). X-ray diffraction (XRD)(Rigaku corporation, Japan), X-ray photoelectron spectroscopy (XPS) (Kratos Axis Ultra DLD, Japan), Raman Spectrometer(RENISHAW, Britain).

1.3 Preparation of the S-NSs

The detailed preparation process included three steps. The first step aims to dissolve sublimed sulfur. Sublimed sulfur powder (1.4 g) and concentrated nitric acid (70%, 50 mL) were added into a 100-mL round-bottom flask. This mixture was stirred at 70 °C for 48 h. Then the mixture was centrifuged and the resulting precipitates were washed with ultra-pure water twice. These precipitates were then collected and were transferred to 100-mL round-bottom flask. Ultra-pure water (50 mL) and PEG-400 (3.0 mL) were added into the round-bottom flask. This suspension

was stirred for 0.5 h at room temperature. Sodium hydroxide (NaOH 4.0 g) was added into the round-bottom flask and was stirred at 70 °C for 24 h. The sulfur powder gradually dissolved, and the yellow suspension changed to red solution during the heating process. Secondly, after the dissolution of sublimed sulfur, 30% H₂O₂ (2.1 mL) was dropped into the mixture (15 mL, the final concentration of H₂O₂ is 3.7%) under vigorous stirring, resulting in formation of light-yellow transparent sulfur quantum dots colloid. The morphologies of the sulfur quantum dots are observed by TEM, as shown in Figure S1. Lastly, the obtained mixture was then sealed in a 100 mL Teflon-lined autoclave and maintained at 180 °C for 24 h in an oven. In this step, sulfur quantum dots were subjected to assembling and forming multilayer S-NSs. The obtained mixture was dialyzed in ultra-pure water with a dialysis bag (molecular weight cutoff of 1000 KDa) for 24 h to remove small molecules and sulfur quantum dots. The obtained S-NSs dispersed in water were referred as multilayer S-NSs.

Few layered S-NSs or monolayered sulfur nanosheet (sulfurene) were obtained by further sonication exfoliation of the obtained multilayered S-NSs. It is worthy noting that the water temperature will increased above 25 °C after several hours sonication. In the sonication process, in order to make water with constant room temperature, an additional circulation condensate water unit was attached using a long soft plastic tube carried tap water.

1.4 Preparation of the sulfur nanorods

Sulfur nanorods were also successfully synthesized according to the procedure described above for the layered S-NSs (Section 1.3), except that the volume of 30% H₂O₂ dripping into the mixture (15 mL) was 0.35 mL instead of 2.1 mL.

1.5 Cyclic voltammetry of the S-NSs

The Cyclic voltammetry (CV) measurement was conducted with a three-electrode system, a fluorine-doped tin oxide (FTO) electrode working electrode, a platinum wire counter electrode, and Ag/AgCl reference electrode (saturated KCl). The cell contained a solution of 0.010 M HCl in the presence of multilayer S-NSs or a solution of 0.01 M HCl in the presence of sublimed sulfur powder suspension (2.5 mg/mL)

1.6 Characterization methods of the S-NSs

XPS Characterization: The prepared multilayer S-NSs dispersed in water was purified by high speed centrifugation (100000 rpm) in order to remove PEG as much as possible, and then some water was added. And the solution containing the multilayer S-NSs was dropcast on the oxidized silicon surface and then was characterized by XPS.

Raman characterization procedures were carried out by dropping the prepared S-NSs dispersed in water on the surface of the oxidized silicon as a substrate, drying at 70 °C. All data have been normalized to a reference value of 284.8 eV for C-C.

XRD characterization procedures were carried out by dropping the prepared multilayer S-NSs dispersed in water on the surface of the quartz glass as a substrate, drying at 70 °C.

Thermogravimetric analysis (TGA) of the multilayer S-NSs and sublimed sulfur powder were carried out in air at a heating rate of 10 °C/min.

2. Results

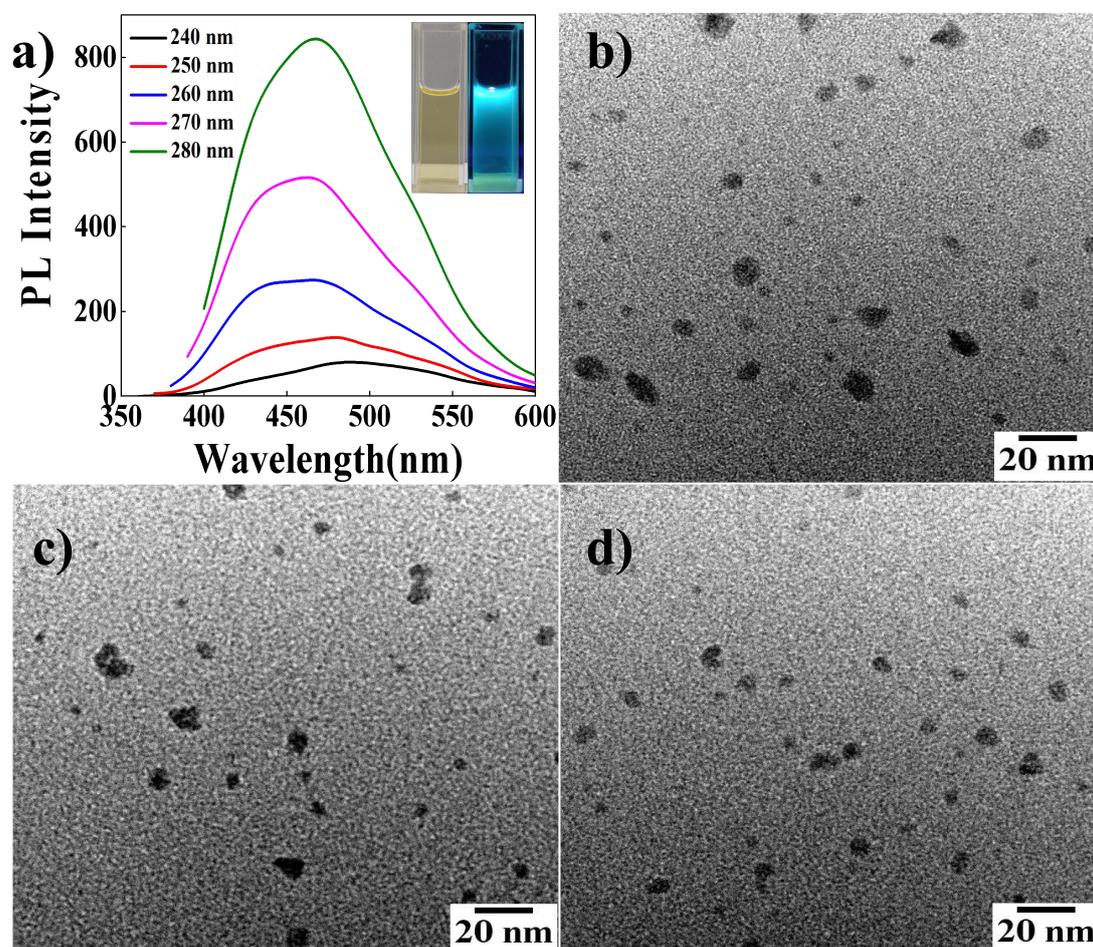


Figure S1. PL (a), photographs (inset) of sulfur quantum dots in daylight (left) and irradiated by UV light at 365 nm (right) and TEM images (b, c, d) of sulfur quantum dots

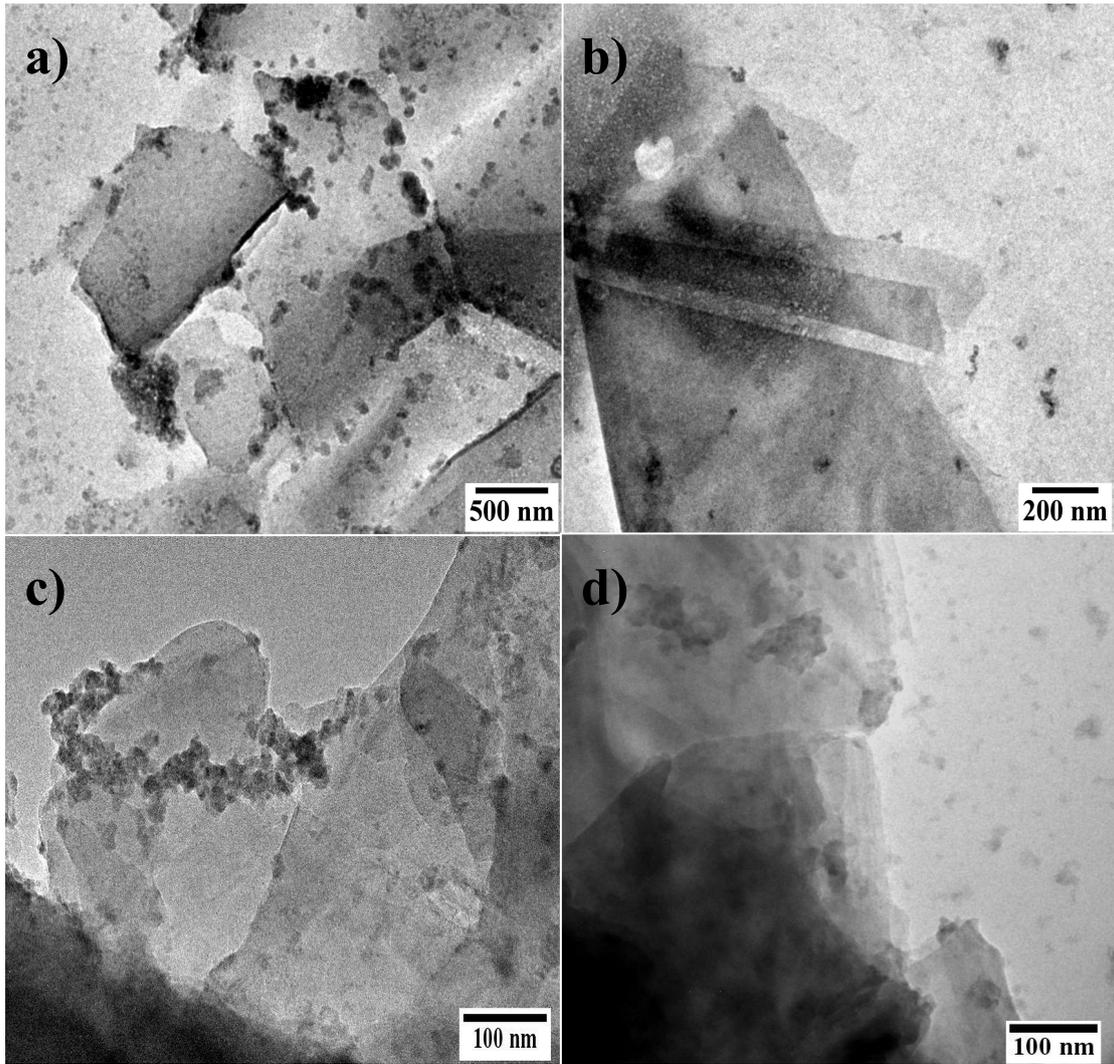


Figure S2. TEM images (a, b, c, d) of the prepared multilayer S-NSs without dialysis

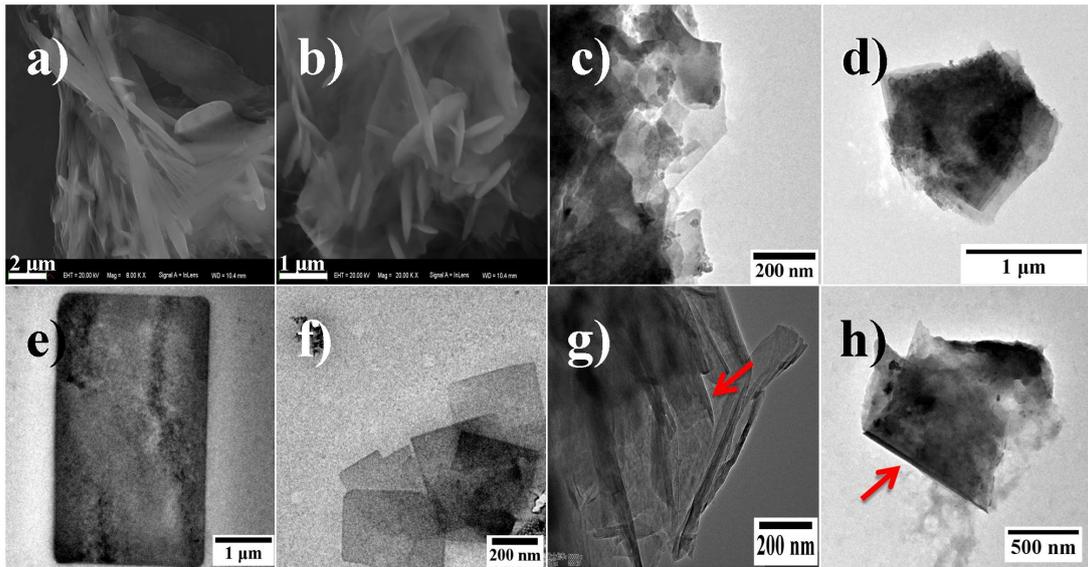


Figure S3. SEM (a, b) and TEM (c, d) images of the multilayer S-NSs after dialysis. TEM images of rectangle multilayer S-NSs (e, f) and curly multilayer S-NSs (g, h)

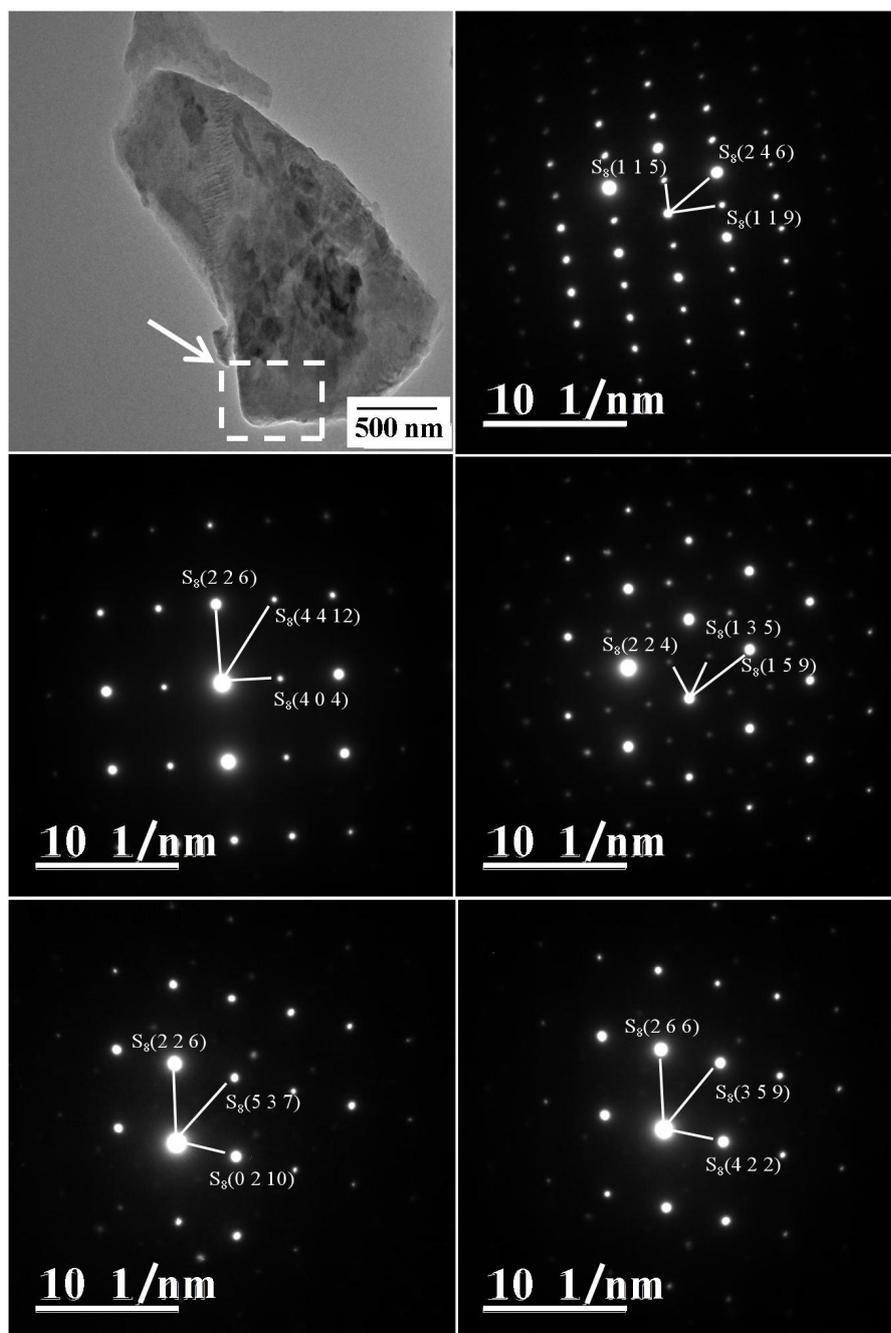


Figure S4. Electron diffraction pattern of the multilayer S-NSSs

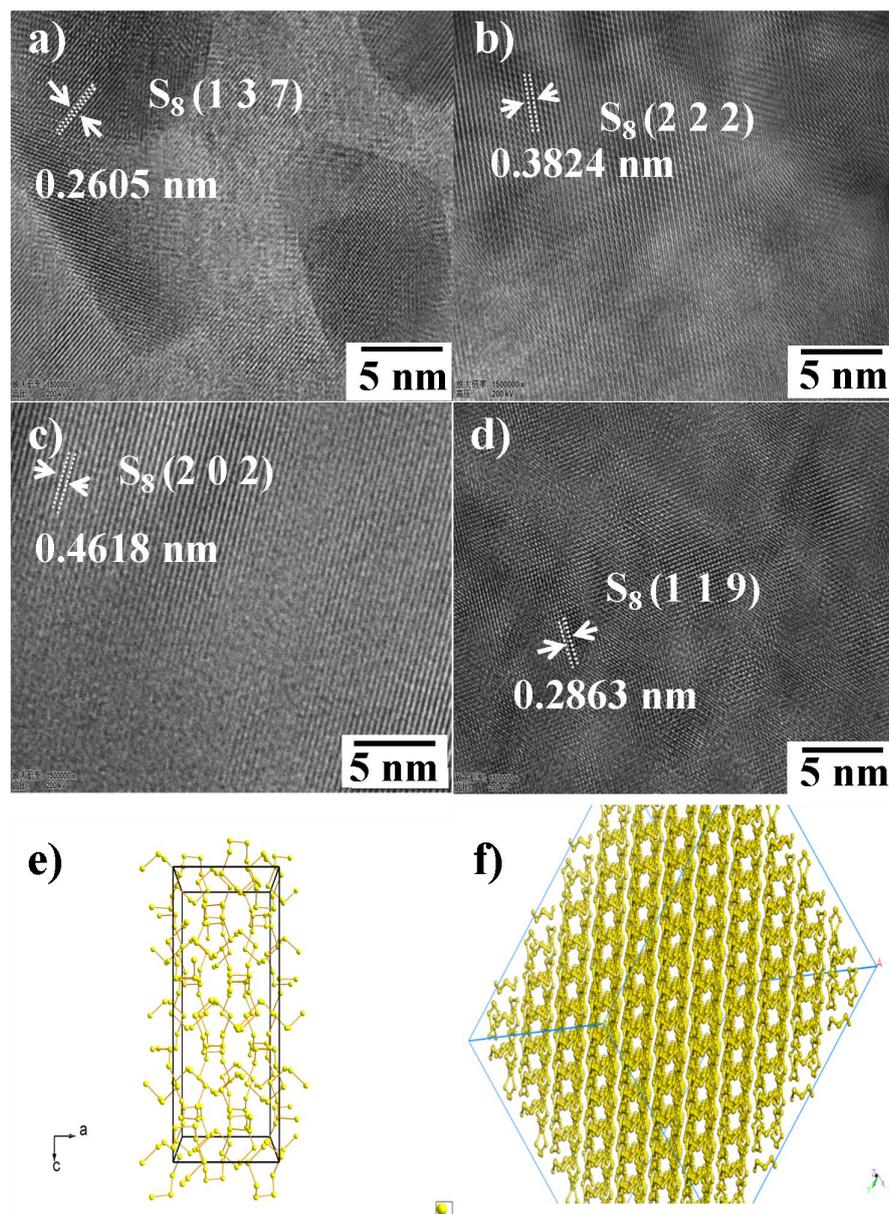


Figure S5. HRTEM image of the multilayer S-NSs (a, b, c, d) and the proposed unit cell structure(e) and its huge cell (f)

The selected area electron diffraction (SEAD) pattern and the HRTEM of the prepared S-NSs showed that the prepared S-NSs had the similar unit cell structure with the sublimed sulfur. The proposed structure of the S-NSs ($a=10.44 \text{ \AA}$ $b=12.84 \text{ \AA}$ $c=24.37 \text{ \AA}$ $\alpha=90.00^\circ$ $\beta=90.00^\circ$ $\gamma=90.00^\circ$) was also described by Cheng, et.al.(*J. Am. Chem. Soc.* 2012, 134, 9070–9073). According to the proposed cell structure, the thickness for monolayer was about $\sim 1.0 \text{ nm}$, it was also near the value of the 0.84 nm in AFM observation.

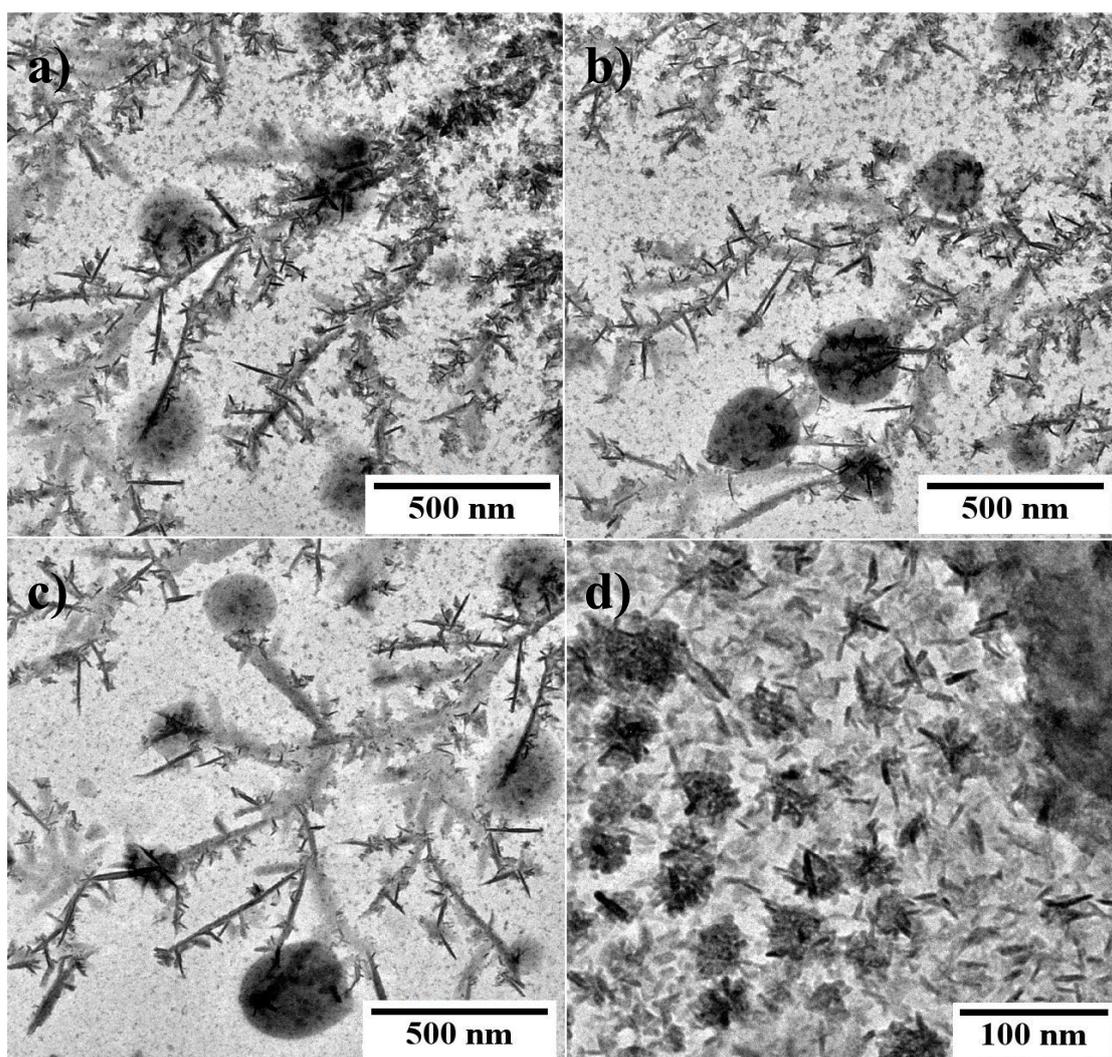


Figure S6. TEM images (a, b, c, d) of the prepared sulfur nanorods

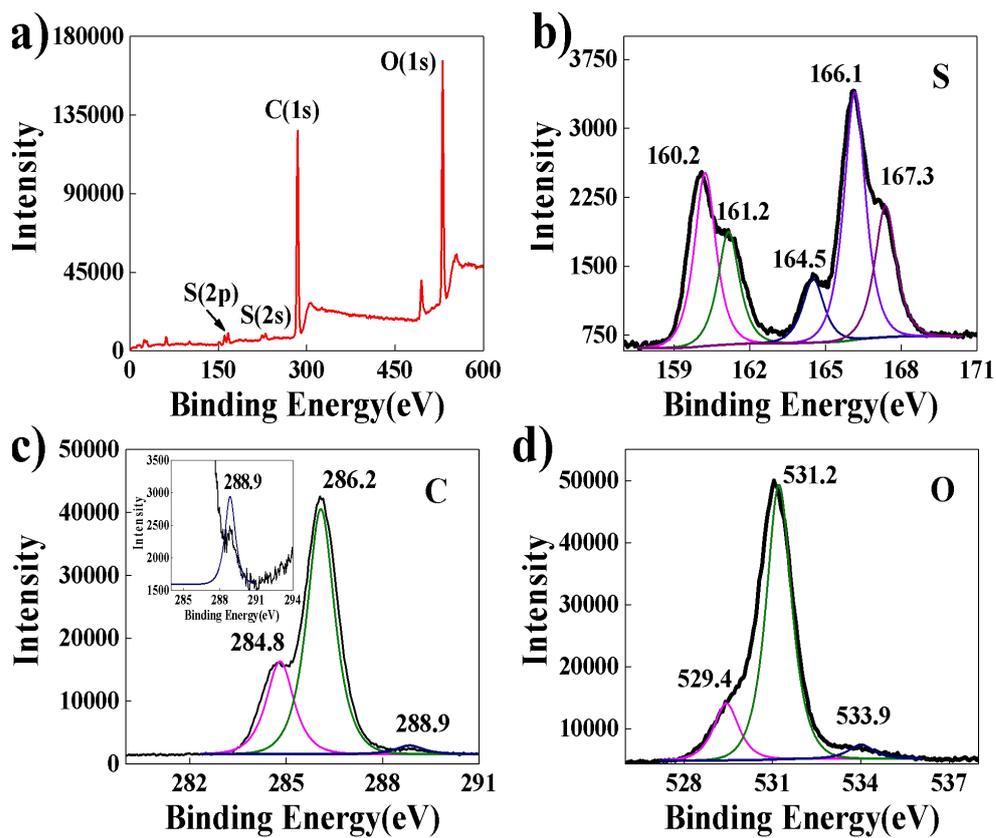


Figure S7. XPS survey (a), XPS S 2p spectra (b), XPS C 1s spectra (c) and XPS O1s spectra (d) of the prepared S-NSs

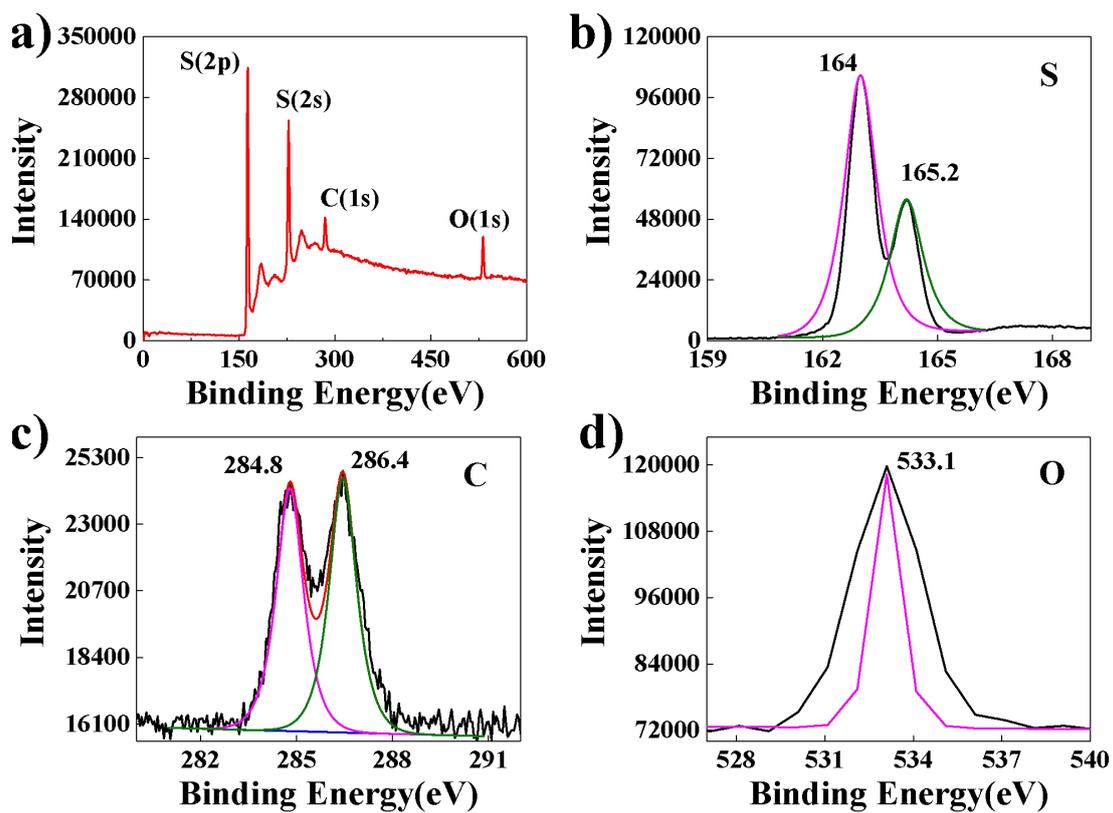


Figure S8. XPS survey (a), XPS S2p spectra (b), XPS C1s spectra (c) and XPS O1s spectra (d) of sublimed sulfur powder act as a contrast experiment

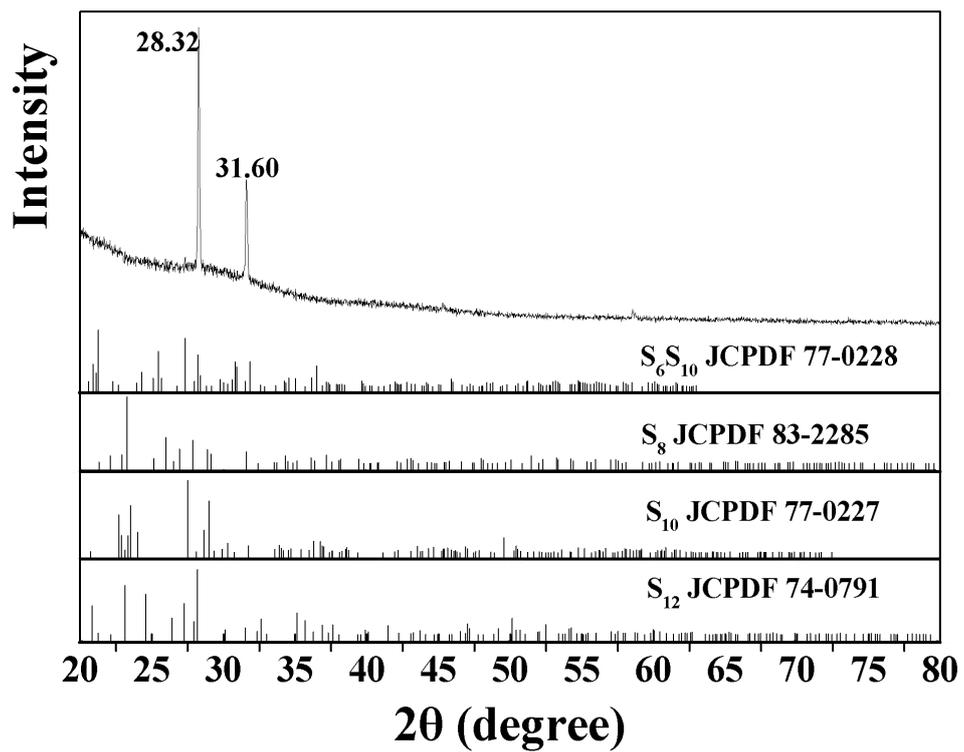


Figure S9. Comparison of XRD patterns of multilayer S-Ns with the standard JCPDS card of S₆S₁₀, S₈, S₁₀ and S₁₂

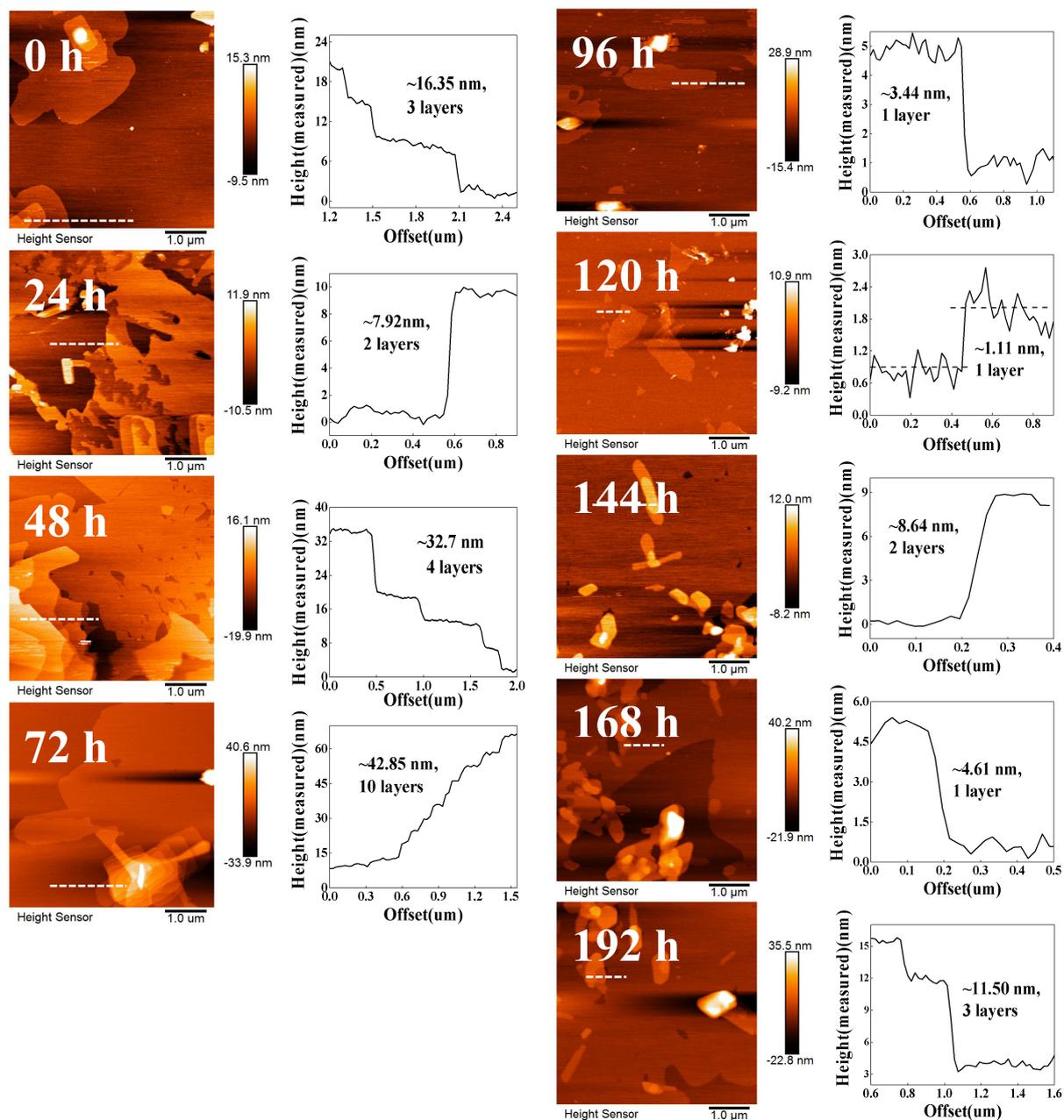


Figure S10. AFM images of the S-NSs after sonication exfoliation for different time

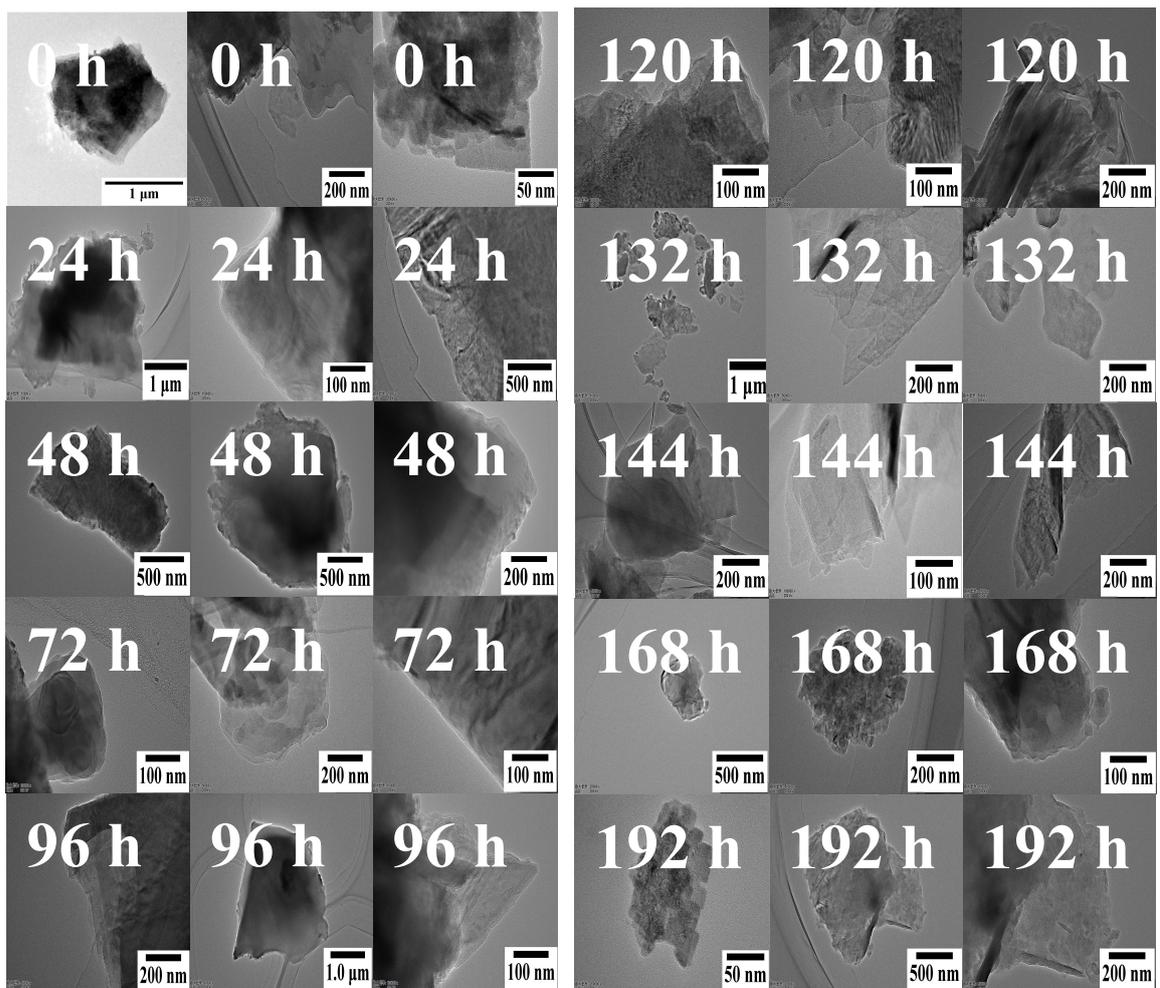


Figure S11. TEM images of the S-NSs after sonication exfoliation for different time

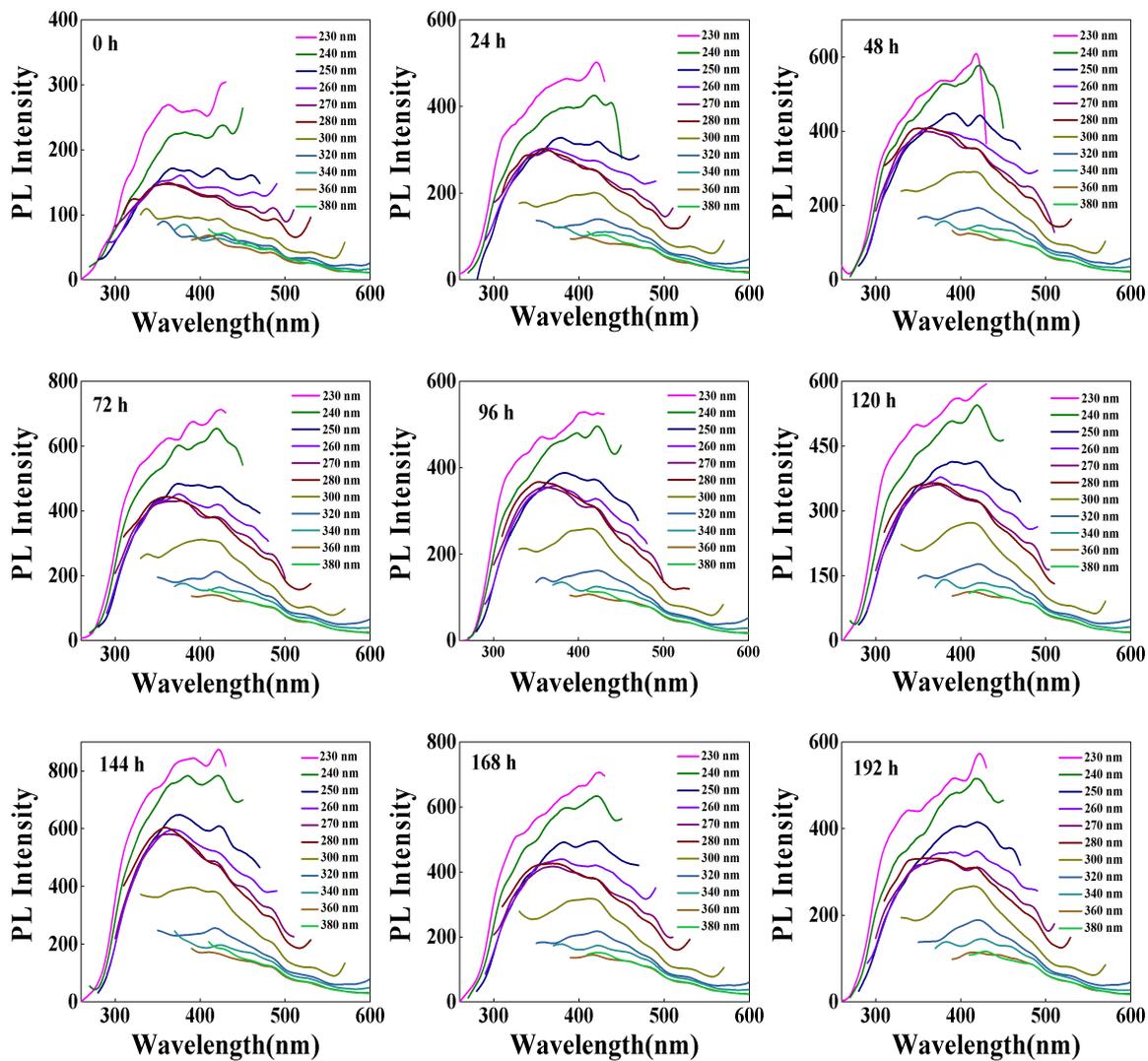


Figure S12. PL spectra of the S-NSs after sonication exfoliation for different time

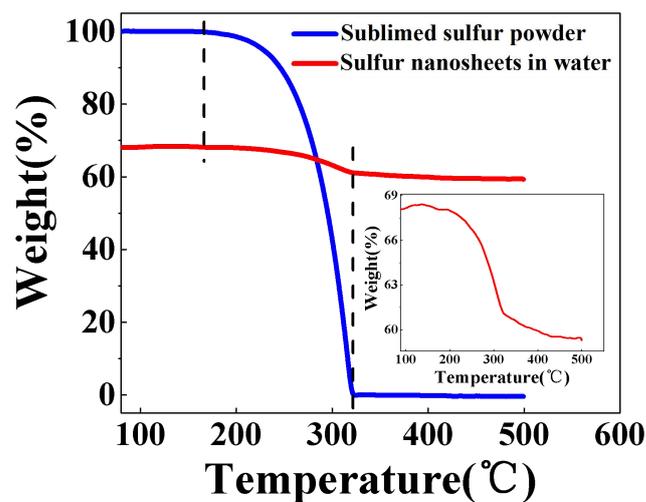


Figure S13. Thermogravimetric analysis of sublimed sulfur powder (blue line) and the multilayer S-NSs (red line) dispersed in water

It is found that sublimed sulfur powder starts to evaporate at about 166 °C and losses the weight completely above 318 °C. The S-NSs dispersed in water sample have observed to exhibit two distinct weight loss profiles. The first one starts at 30 °C which is due to the solvent of water, and the second major weight loss starts at about 166 °C, and also has a distinct transition temperature at 318 °C which means the decomposition of the S-NSs completely. This indicated that the S-NSs complex solution has the similar thermal degradation characteristics as sublimed sulfur, and also suggested that the composition of the S-NSs contains sulfur.