Supplementary information

A three dimensional Sulfur/reduced Graphene Oxide with embedded Carbon Nanotubes Composite as Binder-Free, Free-standing Cathode for Lithium-Sulfur Batteries

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Fig. S1 Photographs of sulfur precipitate processes by adding different suspensions into S/ethanol solution: (a) DI water, (b) GO suspension (7 mg mL-1), (c) CNTs suspension (2 mg mL-1), (d) The final suspensions of (a) and (b) after 30 minutes' standing. (e) The mixture of 20 mL ethanol and 4 mL GO suspension after 30 minutes' standing.

Fig. S2 (a) TEM image of elemental sulfur, (b) Sulfur particles precipitated from the ethanol by mixing method, (c) S/rGO synthetized by mixing method, (d) S/CNTs synthetized by mixing method, (e) S/rGO synthetized by drop-wise method and (f) S/CNTs synthetized by drop-wise method.

Fig. S3 (a-d) Mechanical performance test of the cuboid shaped 3D S-CNTs@rGO.

Fig. S4 SEM image of morphology and microstructure of the rGO.

Fig. S5 XRD patterns of S, rGO, S/rGO and S-CNTs@rGO.

Fig. S6 Cycling performance of the 3D S-CNTs@rGO at 0.2 A g^{-1}.

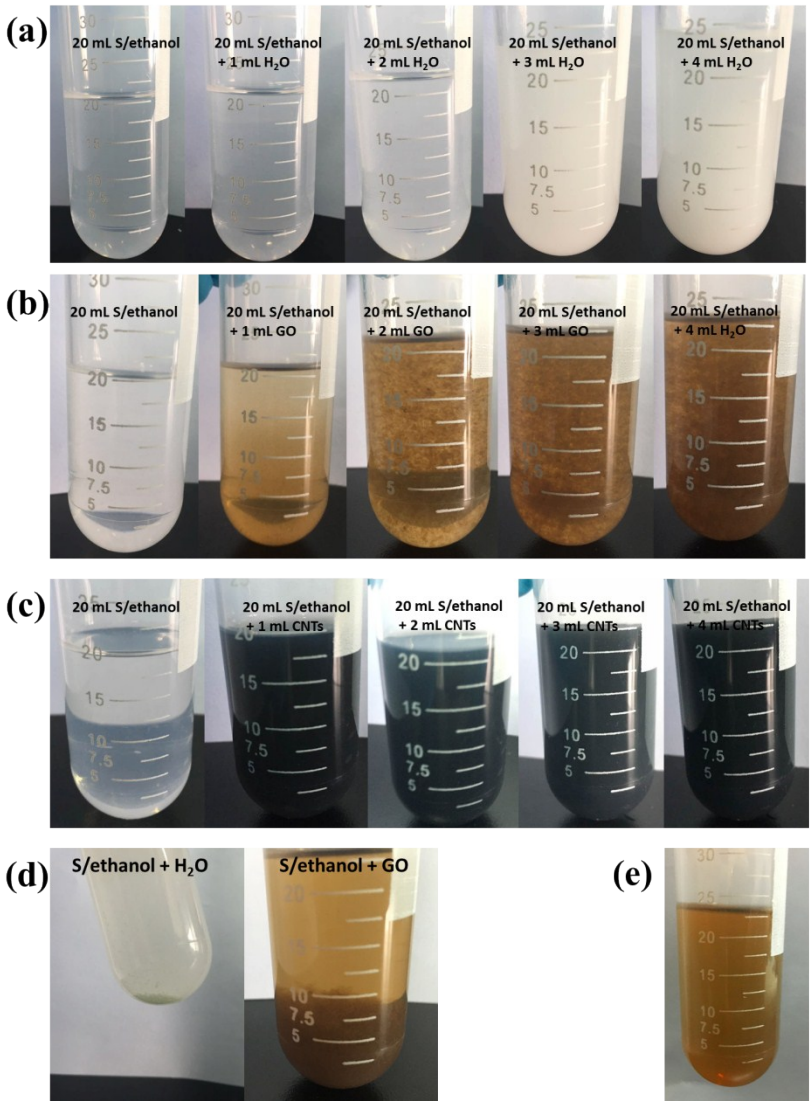

Fig. S1 Photographs of sulfur precipitate processes by adding different suspensions into S/ethanol solution: (a) DI water, (b) GO suspension (7 mg mL^{-1}), (c) CNTs suspension (2 mg mL^{-1}), (d) The final suspensions of (a) and (b) after 30 minutes' standing. (e) The mixture of 20 mL ethanol and 4 mL GO suspension after 30 minutes' standing.

The influences of dosage of H_2O and supporting medium on turning the sulfur particle with larger size to smaller one were studied. Fig. S1 showed the photographs of sulfur precipitate processes by adding different suspensions into S/ethanol solution. And S/ethanol solution and suspensions or water were mixed directly and shacked before photographing. Fig. S1a showed the process of mixing S/ethanol solution and different dosage of DI water. It can be seen that the solution was gradually becoming gray with more DI water added, and the color change could be owe to the S precipitated from ethanol. And there was no difference between adding 3 mL and 4 mL DI water. The final deposition was 17.3 mg after vacuum filtering, which was close to the total sulfur amount in ethanol (20 mg). Therefore, the preferable ratio of water to S/ethanol solution was approximately 1:5 by volume. Fig. S1b showed the process of mixing S/ethanol solution and different dosage of GO suspension. And it

was clearly shown in the Fig. S1b that there was floccule precipitate from the solution. Comparing to Fig. S1e, the GO suspension in Fig. S1b was very unstable when it added to the S/ethanol solution. And this phenomenon could be caused by sulfur deposited on the sheets of GO, which obviously added the weight of the sheets and turned the sheets into floccule in the solution. Regretfully, as for the process of mixing S/ethanol solution and CNTs suspension, there was nothing could be observed for it was completely dark. Therefore, TEM was taken in the Fig. S2. Fig. S1d showed the suspension of Fig. S1a and b after 30 minutes' standing. As for the S/ethanol and DI water suspension, bulk sulfur could be observed and deposited on the bottom of the tube. For the S/ethanol and GO suspension, floccule also deposited on the bottom of the tube, but no obvious bulk sulfur could be observed. This phenomenon could be a very important evidence for the opinion that graphene oxide provided abundant adhesion location for sulfur deposition, which was a very important influencing factor for turning sulfur particle with larger size to nano size.

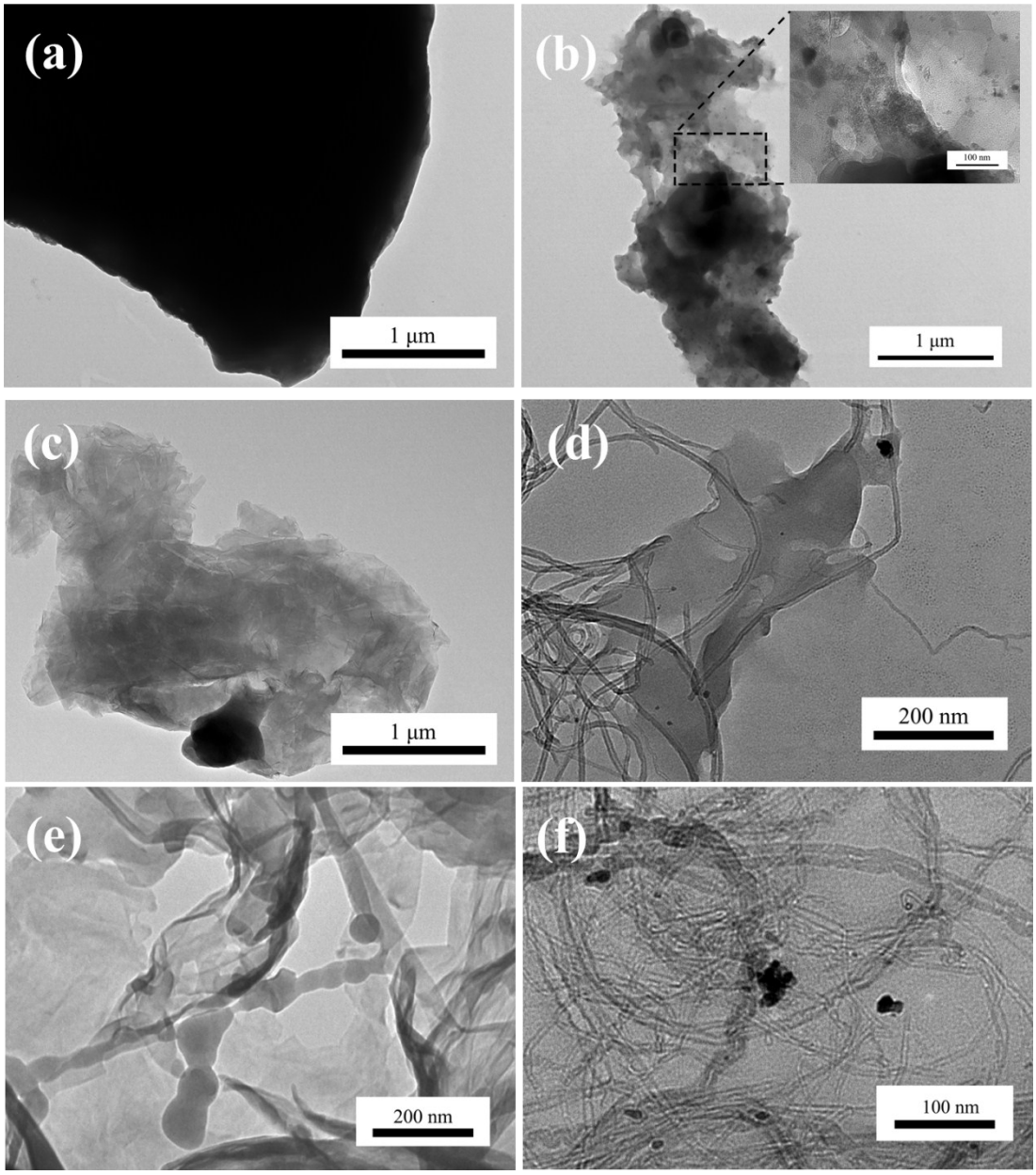

Fig. S2 (a) TEM image of elemental sulfur, (b) Sulfur particles precipitated from the ethanol by mixing method, (c) S/rGO synthetized by mixing method, (d) S/CNTs synthetized by mixing method, (e) S/rGO synthetized by drop-wise method and (f) S/CNTs synthetized by drop-wise method.

The microstructure of sulfur particles, S/rGO and S/CNTs, which were synthetized by different methods, were shown in Fig. S2. The Fig. S2a displayed the size of elemental sulfur, purchased from Sinopharm Chemical Reagent Co .,Ltd., which was more than 3 μm. Comparing to sulfur particle displayed in Fig. S2a, the sulfur particles (Fig. S2b) precipitated from the ethanol by mixing DI water and S/ethanol directly was relatively smaller, which indicated the method of preparing sulfur by precipitated from the ethanol could reduce the sulfur particle size. Besides, the size of the whole particle was large, while there were lots of sulfur particles in nano size anchored on the bulk sulfur. These nano S particles were probably precipitated from the ethanol in the water diffusion process. And this interesting

phenomenon also suggested the importance of the supporting medium. As it could be seen from Fig. S2c and d, with the help of rGO and CNTs, S particles would have a smaller size, which suggested the opinion that supporting medium provided abundant adhesion location for sulfur deposition and was very helpful for reducing the sulfur particle size. However, by directly mixing the water and S/ethanol solution, S particle precipitated from the ethanol was in a relatively large size. S/rGO and S/CNTs shown in Fig. S2e and f, were synthesized by dropping the GO and CNTs suspension into S/ethanol solution at the rate of 1 mL/min with stirring. The reduction process of S/rGO was similar to the S-CNTs@rGO. As it could be appreciated in Fig. S2e, S particles with nano size could be prepared but the nanoparticles were easily agglomerated together. As the images of the S/CNTs shown in Fig. S2f with the assistance of CNTs, nano S particles could be prepared without severe agglomeration. These phenomenon implied dropping rate of water was an important influencing factor for turning sulfur particle with larger size to nano size. By low dropping rate, nano S particle rather than large S particle would be slowly precipitated from the ethanol and anchor on the supporting medium. Therefore, low dropping rate would be beneficial for preparing nano size S particle. Besides, for the supporting medium, CNTs could relieve the S agglomeration problem. Therefore, it would be a good choice to take CNTs and rGO as the supporting mediums to prepar the electrode of Li-S batteries.

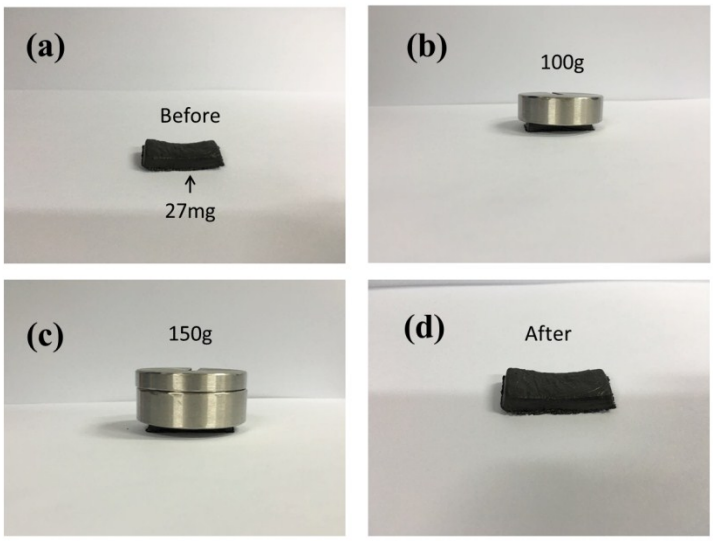

Fig. S3 (a-d) Mechanical performance test of the cuboid shaped 3D S-CNTs@rGO.

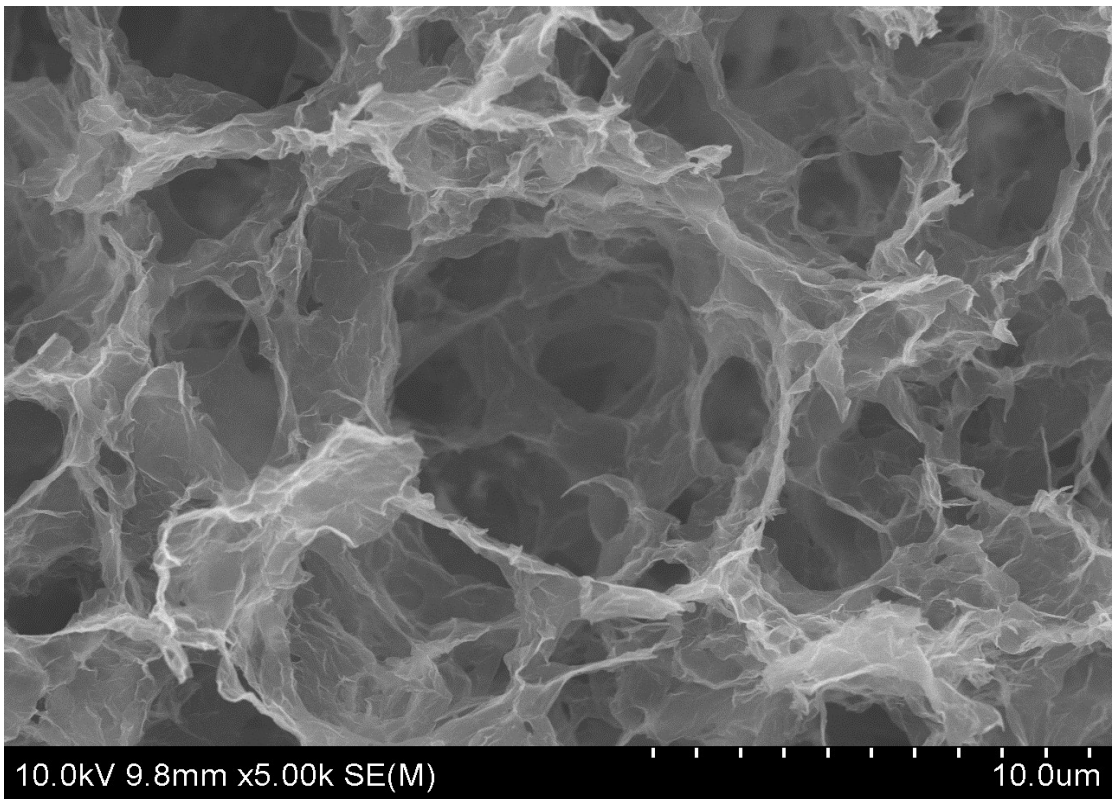

Fig. S4 SEM image of morphology and microstructure of the rGO.

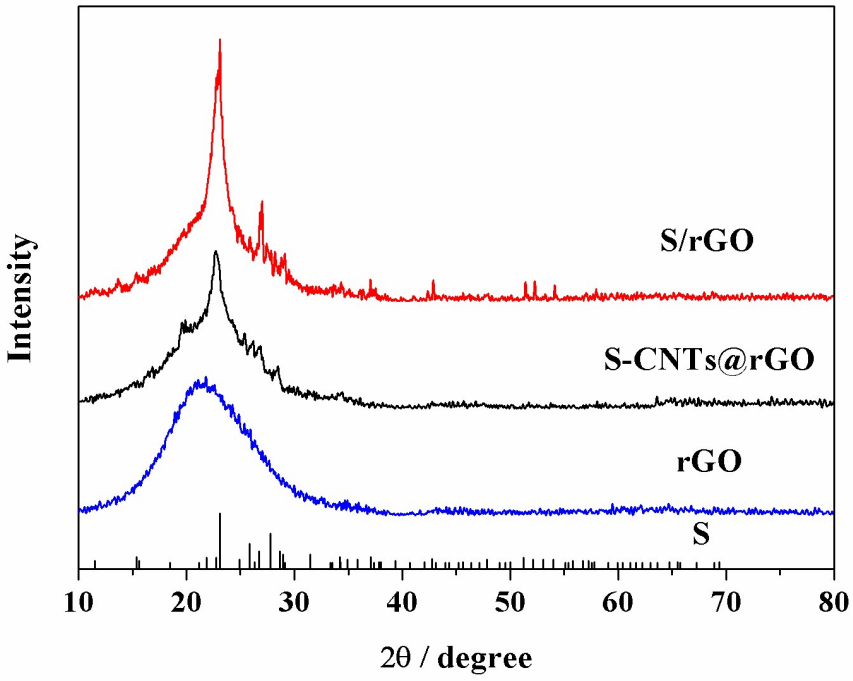

Fig. S5 XRD patterns of S, rGO, S/rGO and S-CNTs@rGO.

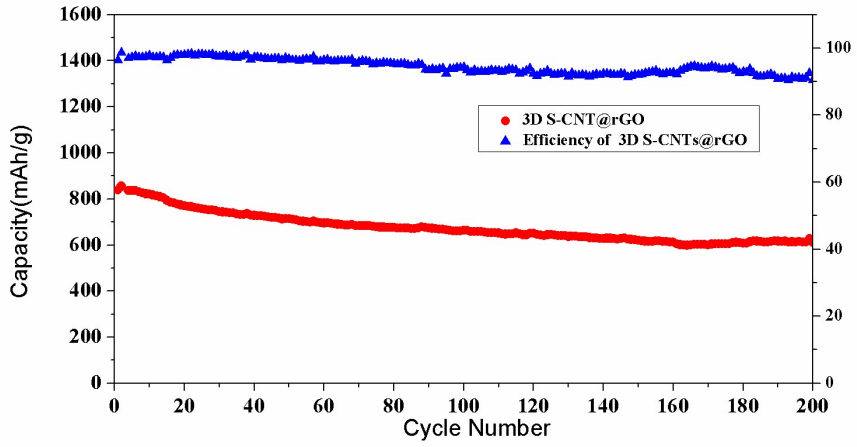

Fig. S6 Cycling performance of the 3D S-CNTs@rGO at 0.2 A g^{-1}.