Supporting Information for

# Atomic layer deposited TiO<sub>2</sub> on nitrogen-doped graphene/sulfur electrode for high performance lithium-sulfur battery

Mingpeng Yu,<sup>\*a, b</sup> Junsheng Ma,<sup>a</sup> Hongquan Song,<sup>c</sup> Aiji Wang,<sup>d</sup> Fuyang Tian,<sup>c</sup> Yinshu Wang,<sup>d</sup> Hong Qiu<sup>a</sup> and Rongming Wang<sup>a</sup>

<sup>a</sup>Department of Physics, University of Science and Technology Beijing, Beijing 100083, People's Republic of China. E-mail: <u>yum@ustb.edu.cn</u> <sup>b</sup>Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China.

<sup>c</sup>Institute for Applied Physics, University of Science and Technology Beijing, Beijing 100083, People's Republic of China.

<sup>d</sup>Department of Physics, Beijing Normal University, Beijing 100875, People's Republic of China.

## 1. ALD of TiO<sub>2</sub> onto NG-S composite electrode

 $TiO_2$  nanolaminates were deposited onto NG-S composite electrode by using an ALD system of SUNALE R200 (Picosun). A series of pneumatic and needle valves are applied to control the introduction of the precursor and purge gases.

A piece of NG-S composite electrode was placed in the ALD chamber where titanium tetraisopropoxide ( $Ti\{OCH(CH_3)_2\}_4$ , 99.99999%, Jiangsu Nata Opto-electronic Material Co. Ltd) reacted with H<sub>2</sub>O to form TiO<sub>2</sub> for 0, 5, 20, 40 ALD cycles. The operational pressure of the ALD system was maintained at about 1800-2000 Pa and the temperature was kept at 150°C throughout the deposition.

# 2. Theoretical calculations

#### 2.1 Calculation methods

All calculations were carried out in this study with the CASTEP program package.<sup>1</sup> The exchange and correlation potential was calculated by using the generalized gradient approximation (GGA) of Wu and Cohen (WC).<sup>2</sup> Moreover, interactions between core electrons and valence electrons can be described by ultrasoft pseudopotentials. The convergence criterion of optimal geometry which were based on the energy, force and displacement convergence, are  $1*10^{-5}$  eV/atom, 0.3 eV/nm and  $1*10^{-4}$  nm, respectively. All of

the computations were performed with spin-polarization.

## 2.2 Structure model

Considering the calculated accuracy and efficiency, we modelled the anatase-TiO<sub>2</sub> (101) surface by a periodic eight-layer slab with a p(1\*3) unit cell and the rutile-TiO<sub>2</sub> (110) surface by a periodic six-layer slab with a p(4\*2) unit cell. Only one Li<sub>2</sub>S (LiS•) molecule was adsorbed on one side of these slabs. The vacuum region thickness between the repeat slabs was 1.2 nm, which is large enough to avoid interactions between different slabs. During the simulating process, the Li<sub>2</sub>S (or LiS•) molecule and the top two layers of the slab surface were allowed to relax freely, and the bottom layer were kept fixed.

The binding energy (E<sub>b</sub>) is computed to measure the binding strength between TiO<sub>2</sub> and the Li-S• radical/Li<sub>2</sub>S species. It is defined as the energy difference between the adsorbed system ( $E_{TiO2+Li-S}$ • radical/Li<sub>2</sub>S) and the summation of pure TiO<sub>2</sub> and pure Li-S• radical/Li<sub>2</sub>S and can be expressed as  $E_b=E_{Li-S}$ • radical/Li<sub>2</sub>S+ $E_{TiO2}-E_{Li-S}$ • radical/Li<sub>2</sub>S+ $E_{TiO2}-E$ 

#### 3. Supplementary figures



Fig. S1 SEM image of as-prepared GO sheets (left) and the size distribution (right).



Fig. S2 Thermal gravity analysis (TGA) curve of NG-S composites.

The cathode for Li–S batteries was prepared by mixing 80 wt% composite materials, 10 wt% carbon black and 10 wt% polyvinyldenedifluoride (PVDF) binder in N–methyl–2–pyrrolidinone (NMP) to obtain a viscous slurry, followed by uniformly coating onto Al foils and dried at 60 °C overnight to form the S cathodes.

Based on the TGA analysis, 73.8% sulfur content was obtained from nitrogen-doped graphene/sulfur composite. Thus, it should be 73.8%\*80%=59% sulfur in the electrode.



Fig. S3 SEM image of as-prepared NG sheets.



Fig. S4 TEM image of as-prepared N doped graphene.



Fig. S5 Elemental mapping images of carbon. Scale bar=100 nm.



Fig. S6 XRD patterns of NG, NG-20 TiO<sub>2</sub>, and NG-40 TiO<sub>2</sub>.

The absence of TiO<sub>2</sub> diffraction peaks in NG-20 TiO<sub>2</sub> can be explained as that TiO<sub>2</sub> particles are

so tiny (less than 3 nm) and the ordering regions were beyond the detection limit of XRD. In addition, a weak signal appeared for NG-40  $TiO_2$ , which belongs to the anatase phase of  $TiO_2$ .



Fig. S7 Raman spectra of NG-20 TiO<sub>2</sub> and NG-40 TiO<sub>2</sub>. The raman spectra of anatase and rutile TiO<sub>2</sub> were also shown.

As can be seen in **Fig. S7**, the bending and stretching modes of  $TiO_2$  were appeared below 750 cm<sup>-1</sup>. However, since the thickness of the  $TiO_2$  nanolaminates were such small (less than 10 nm), these peaks were not detectable alone in the NG-TiO<sub>2</sub> composite due to the superposition with the signal from the carbonaceous matrix (the analysis depth of Raman test was about 1 µm).



Fig. S8 High-resolution TEM images of NG-20 TiO<sub>2</sub>.



Fig. S9 High-resolution TEM images of NG-40 TiO<sub>2</sub>.

Due to the low deposition temperature (150 °C), most of the  $TiO_2$  materials were in amorphous state.



Fig. S10 TEM images of the NG/S–20 TiO<sub>2</sub> composite.



Fig. S11 A planar view SEM image of NG/S-20 TiO<sub>2</sub> electrode and corresponding EDS results of S and Ti elements are shown in (b) and (c), respectively.

As a chemical microanalysis technique, it needs to mention that the analysis depth for Energy dispersive X-ray spectroscopy (EDS) used in conjunction with SEM was over 1  $\mu$ m. It is quite fast and theoretically enables the observation of all elements simultaneously with a lower precision, so the accuracy is not that good. For the NG/S-20 TiO<sub>2</sub> electrode, the information depth for Ti

element is only a few nm. Although the signal was weak, EDS spectra can still demonstrated the Ti particles are well-dispersed in the electrode without aggregation (**Fig. S11c**).



**Fig. S12** (a) The charge–discharge voltage profiles of NG/S electrode at current densities varying from 0.1 to 4 C. (b) Galvanostatic charge–discharge tests of NG/S electrode at a current density of 1 C.



Fig. S13 Cyclic voltammograms of (a) NG/S (b) NG/S–5 and (c) NG/S–40 TiO<sub>2</sub> composite electrodes at a scan rate of 0.1 mV s<sup>-1</sup>.



**Fig. S14** Coulombic efficiency for the NG/S electrode during the process of charging/discharging at 1 C for 500 cycles. The average value is about 98.2%.



Fig. S15 EIS profiles of NG/S composite cathodes with different TiO<sub>2</sub> cycles.



Fig. S16 The rate performances of the NG/S/TiO<sub>2</sub> electrodes with different ALD cycles at various current densities.





Fig. S17 Cyclic voltammograms of (a) NG/S/TiO<sub>2</sub>-5 (b) NG/S/TiO<sub>2</sub>-20 and (c) NG/S/TiO<sub>2</sub>-40 composite electrodes at a scan rate of 0.1 mV s<sup>-1</sup>.

The first, second and fifth cyclic voltammograms (CV) curves of the NG/S/TiO<sub>2</sub>–20 electrode were illustrated in **Fig. S17**, and two pairs of peaks were exhibited, demonstrating the typical S cathode redox behavior. Compared with **Fig. S13**, the CV curves were not overlapped with each other, confirming worse electrochemical behavior.



**Fig. S18 SEM images of the NG/S–20 TiO<sub>2</sub> cathode (a) before and (b) after 100 cycling tests.** The SEM image (**Fig. S18a**) revealed that NG/S–20 TiO<sub>2</sub> particles tend to aggregate and form large porous structures in the pristine electrode. After cycling, the electrode demonstrated a more dense structure. Since sulfur electrode experienced morphological change (from solid to liquid and finally, to solid) during electrochemical cycling, the porosities in the pristine electrode could be gradually filled with the active sulfur materials.

SEM image (**Fig. S18b**) revealed that no glassy discharge products ( $Li_2S_2$  and  $Li_2S$  phases) on the surface of the electrode after 100 cycles, indicating polysulfides absorption ability of NG and TiO<sub>2</sub> due to the porous architecture or *via* physical/chemical adsorption. Dissolved polysulfides were effectively trapped within the cathode region. Thus, the utilization of the active sulfur materials was enhanced.



Fig. S19 Typical SEM images of the cross-sections of NG/S-20 TiO<sub>2</sub> electrode, (a) the pristine electrode and (b) the electrode after 100 charge/discharge cycles.

**Fig. S19** demonstrated the thickness for the cross-sections of the pristine electrode and the electrode after cycling, no signs of serious volume expansion could be observed.



Fig. S20 TEM image of the NG/S–20 TiO<sub>2</sub> cathode after 100 cycling test. EDS spectrum was used to map the distributions of elements in the material structure. Scale bars, 100 nm.

The sulfur element was homogenously distributed over the graphene framework and no large aggregates were observed (**Fig. S20c**). Meanwhile, the backbone structure of NG was well maintained after the cycling test. The flexible and conductive NG can accommodate the mechanical stress induced by the active sulfur materials as well as inhibit the aggregation of lithium sulfide aggregation. Combined with ALD-TiO<sub>2</sub> coating, the soluble polysulfide intermediates were effectively entrapped and reutilized, which is beneficial for high reversible capacity and excellent rate performance.

S1 Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M I J, Refson K and Payne M C
2005 Zeitschrift fur Kristallographie 220 567
S2 Wu Z G and Cohen R E 2006 Physical Review B 73 6