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Supporting Information

for *Adv. Sci.*, DOI: 10.1002/advs.202105544

Tungsten Nanoparticles Accelerate Polysulfides Conversion: A Viable Route toward Stable Room-Temperature Sodium-Sulfur Batteries

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Yuping Liu,[1,2] Shuangying Ma,[3,4] Marina Rosebrock,[2,5] Pascal Rusch,[2,5] Yvo Barnscheidt,[6] Chuanqiang Wu,[7] Pengfei Nan,[7] Frederik Bettels,[1,2] Zhihua Lin,[1,2] Taoran Li,[1,2] Binghui Ge,[7] Nadja C. Bigall,[2,5,8] Herbert Pfnür,[1,2] Fei Ding,[1,2] Chaofeng Zhang,[7] and Lin Zhang[1,2]*

*Corresponding Authors: lin.zhang@fkp.uni-hannover.de

Experimental Section

Materials: Glucose and dicyandiamide were purchased from Sigma-Aldrich. Ammonium tungsten oxide hydrate ($(NH_4)_6W_{12}O_{39}•xH_2O$) was purchased from Alfa-Aesar. All the chemical reagents were used without further purification.

Preparation of W@N-G and W@N-G/S: 0.25 g glucose and 5 g dicyandiamide were dissolved into 250 mL deionized water, and then 2 mL $(NH_4)_6W_{12}O_{39}•xH_2O$ salt solution (0.025 M) was added dropwise into the above solution under the protection of N_2. The mixture was stirred and heated at 80 ℃ for 2 h. After cooling down and freeze-drying, the precursor was annealed at 600 ℃for 2 h and then rose to 900 ℃ for another 2 h (with a rate of 3 ℃/min). The S loading into/onto the W@N-G host is through a melt-diffusion process, firstly, mixing excess sulfur with W@N-G, and then heating at 155 °C under an Ar atmosphere for 12 h, finally, further heating at 200 °C for 2 h to obtain the W@N-G/S cathode. As a comparison, nitrogen-doped graphene (NG) was also prepared using the same method without the addition of $(NH_4)_6W_{12}O_{39}•xH_2O$ salt solution.

Materials Characterization: XRD patterns were collected on a Bruker D8 Advance Discovery X-ray Diffractometer. Raman spectroscopy was carried out on the inVia Raman spectrometer from Renishaw with a HeNe laser (632.8 nm excitation wavelength). The morphology, microstructure, and composition of samples were characterized by emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) and transmission electron microscopy (FEI Talos F200X equipped with One View camera operated at 200 kV). XPS analysis was performed with a hemispherical analyzer of 100 mm radius (Leybold Heraeus). For the *ex-situ* XPS, the electrodes were measured after three cycles and opened the batteries in the glove box, then the electrode surfaces were cleaned carefully use the

pure PC/EC, after dried, the electrodes were covered in the XPS holder and transferred to the XPS chamber. Thermogravimetric analysis (Mettler Toledo TGA/DSC 3+) was conducted under the N_2 atmosphere by heating from RT to 750 ℃ at 5 ℃ min^{-1}. Ultraviolet/visible absorbance spectroscopy was performed in the spectral range of 200-800 nm using a Cary 5000 UV–vis variable wavelength spectrophotometer to evaluate the sodium NaPSs absorption capability of W@N-G and NG composite (the Na_2S_6 solution was synthesized by mixing Na_2S and sulfur in a stoichiometric ratio of 2:6 in DME (dimethoxyethane)).

The W Nanoparticles Size Statistical Analysis: The W nanoparticles size distribution was calculated by the Photoshop soft, briefly, enlarge the STEM image 100 times (Figure 2c), select 50 W nanoparticles (random) and measure the largest length of each nanoparticle, and finally calculate the size distribution.

Electrochemical Measurements: The working electrodes for the Na-S cells were fabricated by mixing the as-synthesized composites (W@N-G/S or NG/S), carbon black, and polyvinylidene difluoride (PVDF) with a weight ratio of 8: 1: 1 in N-methyl-2-pyrrolidone (NMP) to form a slurry, then uniformly pasted on the aluminum foil followed by drying under vacuum oven at 60 °C overnight. The Na-S cells were assembled with metallic sodium as the anode and the W@N-G/S (or NG/S) as the cathode by the CR2032 coin cell, glass fiber (Whatman GF/F) as the separator, and 1 M $NaClO_4$ in 1:1 (volume ratio) ethylene carbonate/propylene carbonate (PC/EC) with 3 wt. % fluoroethylene carbonate (FEC) additive as the electrolyte, and 5 μL mg^{-1} and 10 μL mg^{-1} electrolyte was used in low and high (> 3 mg cm^{-2}) sulfur loading electrodes, respectively. The assembly of all the Na-S cells was carried out in the Ar-filled glovebox (MBraun) with water and oxygen

concentrations less than 0.1 ppm. The electrochemical properties of the W@N-G/S and NG/S cathodes were investigated by the LAND CT 2001A charge/discharge system with a cut-off voltage range from 0.8 to 2.6 V (vs. Na/Na^+). The cyclic voltammetry (CV, at a scan rate of 0.1 mV s^{-1}) and electrochemical impedance spectroscopy (EIS) of the cells were conducted using Metrohm Auto-lab.

Computational Methods: Based on density functional theory, the first-principles calculations were performed using LCAO calculator as implemented in QuantumATK package to investigate the equilibrium configurations and adsorption energies of NaPSs (Na_2S_n (n=1, 2, 4, 6, 8)) and S_8 on N-doped graphene film.[1] The valence electrons and core interactions were described with PseudoDojo pseudopotentials. A generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) was used to treat the exchange-correlation functional.[2] A density mesh cut-off of 120 Ha was used to ensure reliable accuracy. The van der Waals (vdW) correction was also considered by using a Grimme DFT-D3 dispersion term.[3] A 6 × 7 × 1 supercell of graphene was utilized to adsorb NaPSs. A vacuum layer of at least 20 Å perpendicular to the graphene film was applied to avoid the interaction between neighboring images. The first Brillouin zone was sampled using a 2 × 2 × 1 and 6 × 5 × 1 Monkhorst-Pack k-point scheme for structural optimization and adsorption energy calculations. All the structures were fully relaxed until the residual Hellmann-Feynman force on each atom is smaller than 0.01 eVÅ^{-1}. The total energy convergence criterion was 1×10^{-6} eV. The adsorption energy was defined as:

$$E_{adsorption} = E_{polysulfides/substate} - E_{polysulfides} - E_{substrate} \quad (1)$$

Where $E_{polysulfides/substate}$, $E_{polysulfides}$, and $E_{substrate}$ denote the total energies of the NaPSs molecule (Na_2S_n (n=1, 2, 4, 6, 8)) or S_8 adsorbed on the substrate (W@N-G or N-G), single PSs molecule and substrate, respectively.

Table S1. A list of the catalyst weight ratio in sulfur cathode and the electrochemical performances in the recently reported RT Na-S batteries.

Catalyst	Ratio	Initial capacity (2^{nd}, mAh g^{-1})	Capacity retention	Rate performance	Reference
Co@PCNFs/S	**50%**	600 (0.5 C)	398 (after 600 cycles)	240 (5 C)	[4]
CNF-L@Co/S	**55%**	745 (0.5 C)	538 (after 150 cycles)	442.7 (1.5 C)	[5]
S/TiN-TiO_2@MCCFs	**43.1%**	1150 (0.1 A g^{-1})	640.4 (after 100 cycles)	440.2 (5 A g^{-1})	[6]
CoS_2/NC/S	**49.3%**	700 (0.1 A g^{-1})	488 (after 100 cycles)	262 (5 A g^{-1})	[7]
ZnS/C@S	**38%**	1070 (0.1 A g^{-1})	1082 (after 100 cycles)	390 (3 A g^{-1})	[8]
FeS_2@NCMS/S	**34.5%**	760 (0.1 A g^{-1})	524 (after 300 cycles)	337 (5 C)	[9]
S/MoS_2/NCS	**56.2%**	970 (0.5 A g^{-1})	711.6 (after 200 cycles)	470.7 (5 A g^{-1})	[10]
S@BPCS	**30%**	755 (0.5 C)	701 (after 350 cycles)	349 (3 C)	[11]
W@N-G	**9.1%**	1160 (0.2 C,)	962 (after 100 cycles)	461 (5 C)	This work

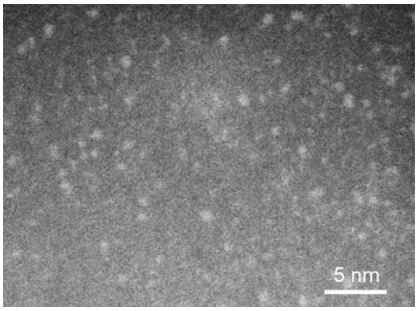

Figure S1. STEM of the W@N-G.

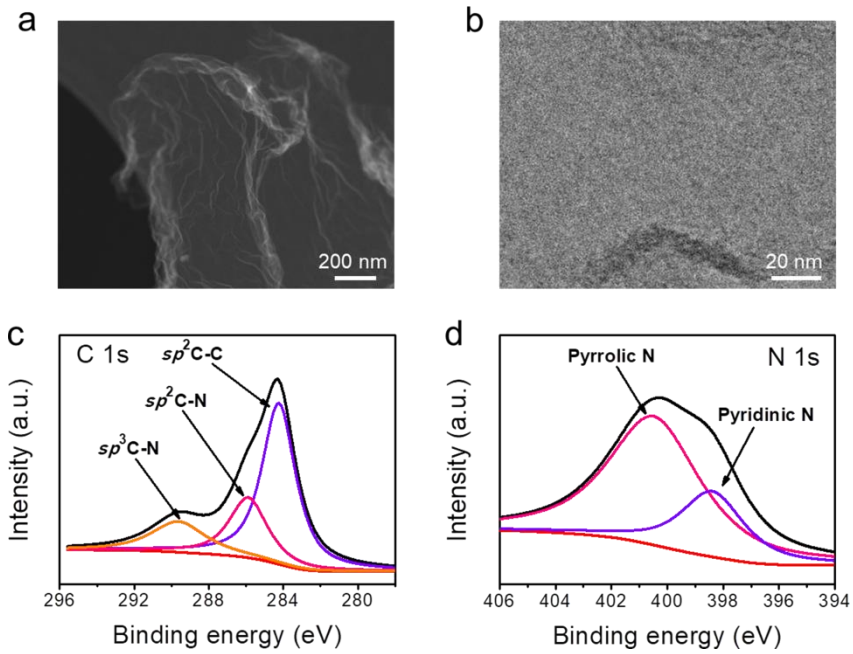

Figure S2. Morphological and structural characterizations of the N-G nanosheets. (a) STEM, and (b) HRTEM. XPS analysis of the (c) C 1s, and (d) N 1s spectrum.

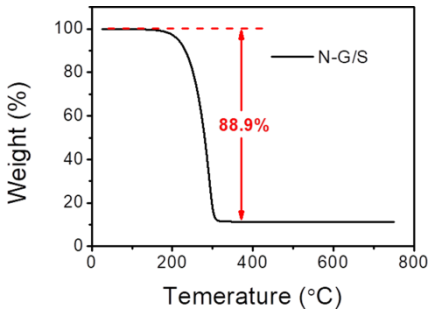

Figure S3. TGA curve of N-G/S cathode under N_2 atmosphere.

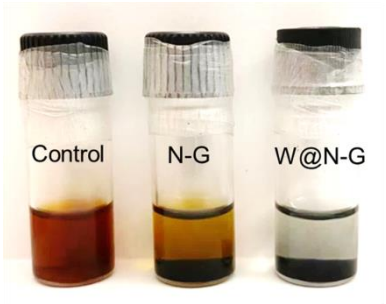

Figure S4. Photos showing the colour changes of Na_2S_6 solution after the exposure to N-G or W@N-G.

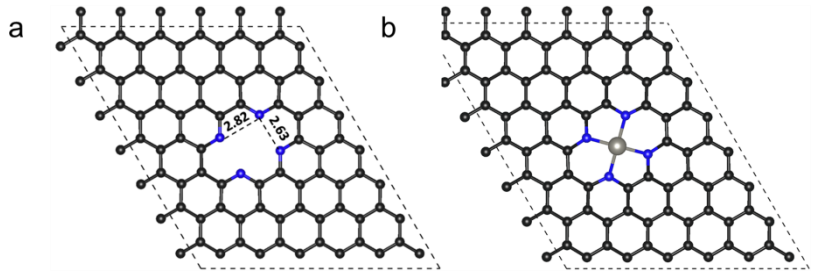

Figure S5. Structures of (a) N-G and (b)W@N-G hosts used in first-principles calculations.

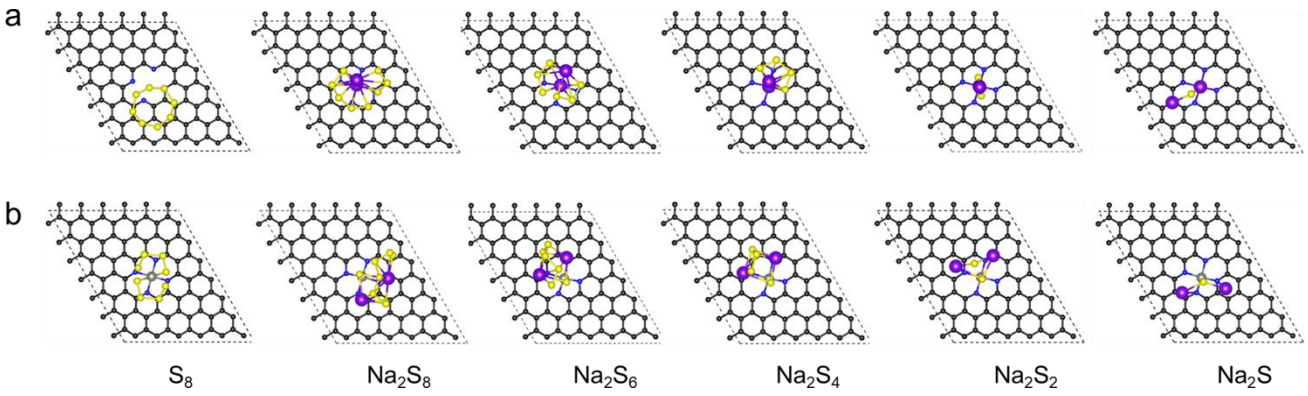

Figure S6. Top view of the optimized adsorption conformations of intermediate species on (a) N-G, and (b) W@N-G.

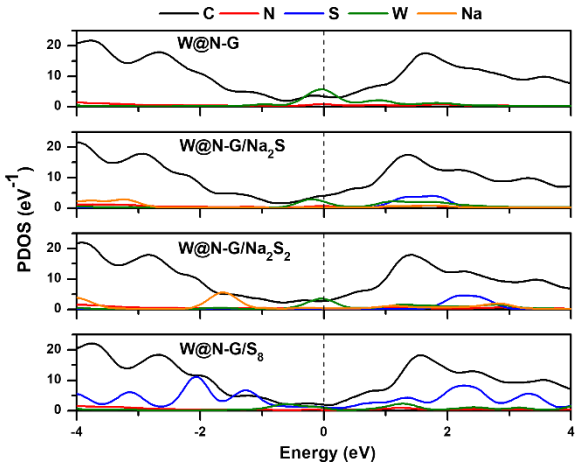

Figure S7. The electronic properties of W@N-G with and without the adsorption of NaPSs.

Figure S8. Photos showing the glass fiber separators after three cycles.

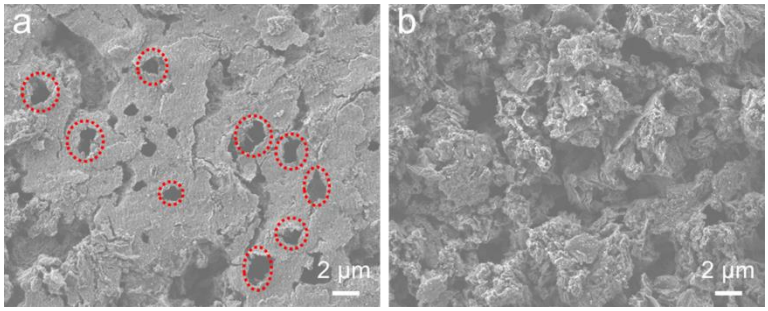

Figure S9. SEM of (b) N-G/S and (b) W@N-G/S cathodes after three cycles.

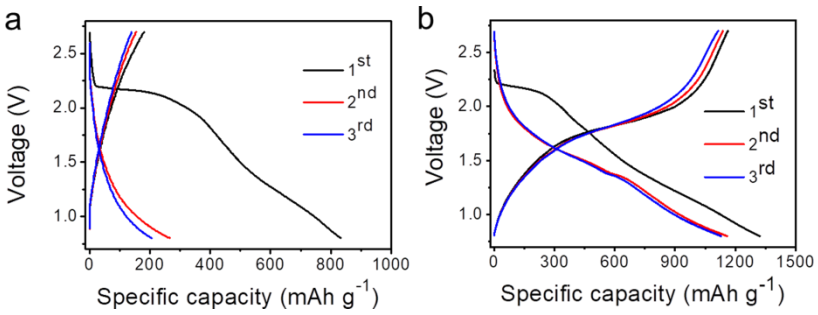

Figure S10. First three charge/discharge curves of (a) N-G/S and (b) W@N-G/S cathodes.

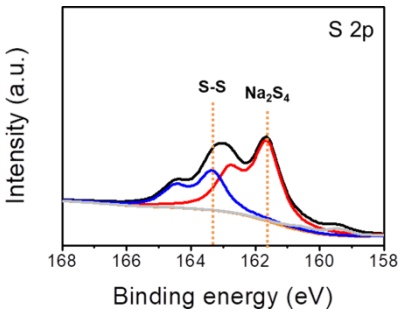

Figure S11. *Ex-situ* XPS spectra of N-G/S cathode after discharged to 0.8 V (after three cycles).

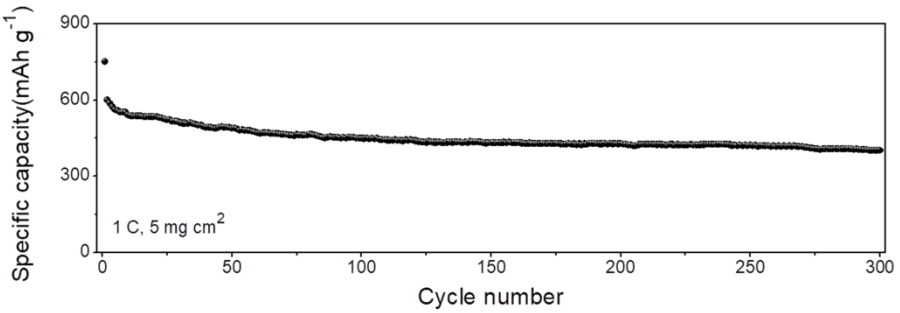

Figure S12. Cycling performance of W@N-G/S cathode with high S mass loading under large current.

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