Supplementary Figures

Supplementary Figure 1 SEM and EDX mapping characterizations of materials. (a) SEM image of the VN/G composite, and EDX elemental maps of (b) carbon, (c) vanadium, (d) nitrogen and (e) oxygen in the red solid line area, respectively. Scale bars, 5μm (a), 1 μm (b-e).
Supplementary Figure 2 Characterization of the VOx/G composite. (a) SEM image and (b) TEM image of the VOx/G composite before annealing in NH3. Scale bars, 2μm (a), 500nm (b).
Supplementary Figure 3. Nitrogen adsorption-desorption isotherm of the VN/G composite. Inset: the pore size distribution obtained using the BJH method.
Supplementary Figure 4. Nitrogen adsorption-desorption isotherm of the RGO. Inset: the pore size distribution obtained using the BJH method.
Supplementary Figure 5 Electrochemical performances of the VN/G composite without Li$_2$S$_6$ catholyte. (a) Charge-discharge profiles and (b) Cycling performance of the VN/G composite without Li$_2$S$_6$ catholyte at a current density of 335 mA g$^{-1}$ in the voltage range 2.8-1.7 V. The pure VN/G composite shows a capacity of < 10 mAh g$^{-1}$ at a current density of 335 mA g$^{-1}$ in the voltage range 2.8-1.7 V.
Supplementary Figure 6. Comparison of the electrochemical impedance spectra of the VN/G and RGO cathodes before cycling. The data was recorded from 10 kHz to 100 MHz at open circuit voltage at room temperature.
Supplementary Figure 7 XPS spectra of the RGO. (a) High-resolution C1s and (b) N1s XPS spectra acquired from the RGO.
Supplementary Figure 8. Galvanostatic charge-discharge profiles of the VN/G cathode at different rates.
Supplementary Figure 9 Electrochemical performances of the VO$_x$/G cathode. (a) Cycling stability at 1C and (b) rate performance of the VO$_x$/G cathode.
Supplementary Figure 10 XPS spectra of the VN/G composite. (a) High-resolution V2p3/2 and (b) N1s XPS spectra acquired from the VN/G composite.
**Supplementary Table 1** Electrical conductivity of different metal nitrides at room temperature\(^1\).

<table>
<thead>
<tr>
<th>Materials</th>
<th>VN</th>
<th>TiN</th>
<th>Mo(_2)N</th>
<th>WN</th>
<th>Ni(_3)N</th>
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<td>Conductivity ((\times 10^6) S m(^{-1}))</td>
<td>1.17</td>
<td>4.0</td>
<td>5.05</td>
<td>11.1</td>
<td>0.36</td>
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Supplementary Note

Supplementary Note 1. Theoretical calculation Methods

DFT calculations were performed using the projector augmented wave method\textsuperscript{2,3} and a plane-wave (PW) basis set as implemented in the Vienna \textit{ab-initio} simulation package\textsuperscript{4}. The Perdew-Burke-Ernzerhof functional\textsuperscript{5} for the exchange-correlation term was used for all calculations. The energy cutoff for the PW basis set was set to be 400 eV. For the structural relaxations and energy calculations, vdW interactions were incorporated by the optB88 exchange functional\textsuperscript{6,7}, and this proved to be very important to accurately evaluate the interactions between the S-containing clusters and pristine graphene\textsuperscript{8}. In order to calculate the binding energy between Li$_2$S$_6$ and VN, a slab model of a 3×3×1 supercell with four atomic layers was constructed to simulate the (200) surface of VN substrate based on HRTEM observations. One edge C atom was substituted by the N atom in a large poly-aromatic hydrocarbon (PAH) molecule of C$_{96}$H$_{24}$, resulting in a N-doped PAH molecule (C$_{95}$N$_1$H$_{23}$) to represent N-doped graphene (N-G) with a pyridinic N atom in a 30×30×20 Å$^3$ supercell, the size of this PAH molecule was confirmed to be large enough to accurately evaluate the interactions between S-containing clusters lithium polysulfides and graphene\textsuperscript{9}. A Γ-centered k-mesh (3×3×1) and only the Γ point was used to sample the first Brillouin zone of the VN slab model and the PAH supercell, respectively, for the structural relaxation and energy calculations. Except for the bottom two atomic layers of the VN slab, all atoms were allowed to be fully relaxed while keeping the supercell boxes unchanged until the residual force per atom decreases to less than 0.01 eV Å$^{-1}$. The binding energies between Li$_2$S$_6$ and VN (N-G) are defined by equation (1):

$$E_b = E_T - E_S - E_{Li_2S_6}$$

(1)

where $E_{Li_2S_6}$, $E_S$, and $E_T$ are, respectively, the total energies of an isolated Li$_2$S$_6$ cluster, substrate (N-doped graphene or VN), and a composite system of the substrate with Li$_2$S$_6$.\textsuperscript{7}
Supplementary References


