Rational Engineering VS$_4$ nanorod array on rose-shaped VS$_2$ nanosheets for high-performance aluminum-ion batteries

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Experimental section

Preparation of rose-shaped VS$_2$ microspheres: All chemicals were used directly without further treatment. The VS$_2$ microspheres were prepared by using a simple hydrothermal method. In a water bath, 4 mmol ammonium metavanadate (NH$_4$VO$_3$) was dispersed in 30 mL ultrapure water, 25 mmol thioacetamide (TAA) and 4 mL concentrated ammonia (NH$_3$·H$_2$O) were successively added. The mixed solution was stirred vigorously for 1 h, then transferred into a reaction kettle. After reaction at 180 °C for 8 h, the sample was washed three times with pure water and alcohol, then dried in an oven.

Preparation of VS$_2$@VS$_4$ composite: Under the condition of water bath at 80 °C, 3 mmol NH$_4$VO$_3$ and 0.5 g polyether F127 were dispersed in 30 mL ultrapure water to obtain solution A. Under the same conditions, 50 mmol TAA and 0.2 g VS$_2$ were dispersed in 30 mL ethylene glycol (EG) to obtain solution B, which was added into A drop by drop and stirred for 0.5 h.
The mixed solution was transferred to a reaction kettle and reacted at 160 °C for 12 h. After that, the sample was collected and washed.

**Characterization:** The phrase of the sample was determined by using an X-ray diffractometer (XRD, SMART APEX II Brook, copper target, Kα X-ray wavelength=1.5418 Å). The morphology was observed by field emission scanning electron microscope (SEM), Hitachi S-8100, and transmission electron microscope (TEM, HT-7700, TecnaiG220S-Twin). A high-resolution TEM (HRTEM) was used to observe the lattice fringes. Energy dispersive X-ray spectroscopy (EDX) was employed for elemental mapping and studying the elemental distribution. X-ray photoelectron spectroscopy (XPS, EscalAB250) and Raman spectroscopy (Renishaw in Via) were used for characterization. Before measuring the specific surface area, the sample was degassed in a vacuum at 120 °C for 6 h to remove the adsorbed water and surface impurities. The physical adsorption isotherms were measured in nitrogen at 77 K using an ASAP Micromeritics Tristar 2460 instrument.

**First-principle computation:** During DFT modeling, a plane wave basis set with an energy cutoff of 500 eV was adopted and the Brillouin zone integration was conducted on a $2\times2\times2$ Monkhorst–Pack k-point mesh. The cell parameter was $16.04\times16.04\times12.93$ Å for VS$_2$@VS$_4$ heterostructures; and all atoms were fully relaxed during the geometry optimization.

**Electrochemical tests:** The VS$_2$@VS$_4$ composite (70 wt%) and conductive carbon black (20 wt%) were mixed, grounded for 30 min, then polyvinylidene fluoride (PVDF, 10 wt%) and N-
methylpyrrolidone (NMP, 6.54 wt%) were added. It is noted that we used the PVDF on the basis of some reports [1,2]; however, the compatibility of PVDF in some electrolyte systems would be not good enough, which inspired a potential research direction in future. The slurry was coated on a carbon paper, dried in a vacuum oven at 80 °C for 24 h, and cut into 12 mm-diameter discs. The water and oxygen values were less than 0.01 ppm in a glove box (MIKROUNA, Super1220/750/900), which was filled with argon gas. In the 2032-typed coin cell system, a molybdenum disc with a diameter of 20 mm and a thickness of 0.02 mm was added to prevent the corrosion of the electrolyte on the cell shell before dropping the electrolyte. The counter electrode was aluminum foil; and the diaphragm was glass fiber. The electrolyte was AlCl₃:[EMIm]Cl=1.3:1 with an electrolyte volume/mass of 60 μL mg⁻¹. In the voltage range of 0.01-2.0 V, the cycling and rate-performance were explored by using a galvanostatic method charge-discharge mode. In-situ reaction resistance was measured by constant-current intermittent titration (GITT). Cyclic voltammetry (CV) was measured on an electrochemical workstation (CHI660e). For the tests at different temperatures, the batteries were put in a temperature-controlled chamber with a determined temperature. Prolonged lines were used to connect the tester (NEWARE, CT-4008) and batteries. Before starting each test, the batteries were putting in the low temperature chamber overnight.
Fig. S1 (a) SEM and (b) TEM images of VS₄. (c) SEM images and (d) SAED pattern of VS₂@VS₄. (e) Adsorption-desorption isothermal and pore-size distribution of VS₂@VS₄. XPS spectra: (f) survey spectrum, (g) V 2p and (h) S 2p of VS₂@VS₄.
**Fig. S2** (a) SEM images, (b,c) S and V elemental mapping, (d) EDS spectrum, and (e) line-scanning curves of VS$_2$@VS$_4$.

**Fig. S3** (a) SEM image, (b,c) S and V elemental mapping, (d) EDS spectrum, and (e) line-scanning curves of VS$_2$. 
**Fig. S4** (a) SEM image, (b,c) S and V elemental mapping, (d) EDS spectrum, and (e) line-scanning curves of VS$_4$.

**Fig. S5** XRD patterns of VS$_2$@VS$_4$ after 100 cycles at 0.3 A g$^{-1}$. 
Fig. S6 (a) Cycling performance and (b) charge-discharge curves of pure carbon paper cycling at 0.013 A g\(^{-1}\).

Fig. S7 (a) Cycling performance and (b) charge-discharge profiles of VS\(_2@VS_4\) with a loading of 2.61 mg cm\(^{-2}\) at 0.3 A g\(^{-1}\). (c) Cycling performance and (b) charge-discharge curves of VS\(_2\) with a loading of 2.2 mg cm\(^{-2}\) at 0.2 A g\(^{-1}\).
**Fig. S8** (a) Charge-discharge profiles and (b) cycling performance of VS$_4$ at 0.3 A g$^{-1}$.

**Fig. S9** Charge-discharge profiles of (a)VS$_2$, (b)VS$_4$, (c)VS$_2$@VS$_4$ at $-10 \, ^\circ$C.
**Fig. S10** (a) Rate-performance of VS$_2$, VS$_4$ and VS$_2$@VS$_4$ at room temperature. Charge-discharge profiles of (b) VS$_2$@VS$_4$, (c) VS$_2$ and (d) VS$_4$. Charge-discharge profiles of (e) VS$_2$@VS$_4$, (f) VS$_2$ and (g) VS$_4$ at 10 °C.

**Fig. S11** (a) Differential specific capacity versus voltage plots at various rates. (b) Contribution ratio of capacitive and diffusion-control processes.

**Fig. S12** GITT time-potential distributions of (a) VS$_2$, and (b) VS$_4$. 
**Fig. S13** EIS spectrum of VS$_2$@VS$_4$ before and after cycling under 25 ºC and –10 ºC.

**Fig. S14** (a-d) Elemental mapping of S, V, Al and Cl, (e) SEM image, (f) EDS spectrum, (g) line-scanning curves, and (h) TEM image of VS$_2$@VS$_4$ after 100 cycles at 0.3 A g$^{-1}$.
Table S1. Comparison on the cycling performance of some cathodes.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Current density (A g(^{-1}))</th>
<th>Cycle number</th>
<th>Capacity (mAh g(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta)-MnO(_2) nanofibers</td>
<td>0.1</td>
<td>100</td>
<td>37</td>
<td>3</td>
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<td>Nanosphere-rod-like Co(_3)O(_4)</td>
<td>0.2</td>
<td>100</td>
<td>122.1</td>
<td>4</td>
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<td>VOCl</td>
<td>0.05</td>
<td>100</td>
<td>41.5</td>
<td>5</td>
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<tr>
<td>Graphitized soft carbon</td>
<td>0.5</td>
<td>1000</td>
<td>77.7</td>
<td>6</td>
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<tr>
<td>Hexagonal NiS nanobelts</td>
<td>0.2</td>
<td>100</td>
<td>100</td>
<td>7</td>
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<tr>
<td>SnSe</td>
<td>0.3</td>
<td>100</td>
<td>107</td>
<td>8</td>
</tr>
<tr>
<td>MoS(_2)</td>
<td>0.04</td>
<td>100</td>
<td>66.7</td>
<td>9</td>
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<tr>
<td>MoO(_2)@Ni</td>
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<td>100</td>
<td>90</td>
<td>10</td>
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<td>Cu-Al</td>
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<td>1000</td>
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<tr>
<td>Cu(_{2-x})Se</td>
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<td>100</td>
<td>12</td>
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<td>Co-P</td>
<td>0.2</td>
<td>400</td>
<td>85.1</td>
<td>13</td>
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<td>Hierarchical VS(_2@VS_4)</td>
<td>0.3</td>
<td>500</td>
<td>116.5</td>
<td>This work</td>
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</tbody>
</table>

Reference


