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SnS₂ quantum dots-coated VO₂@carbon nanorods for secondary battery displaying high capacity and rate-performance

Tianli Han^{a,*}, Yan Wang^a, Kehao Tao^b, Xiangbin Zeng^{c,d}, Peng Zhan^c, Yajun Zhu^{a,e}, Jinjin Li^{b,*} and Jinyun Liu^{a,*}

Experimental

Preparation of lamellar VO2@C

First, lamellar VO₂@C nanorods were prepared through a hydrothermal method. All chemicals were purchased from Aladdin. 2 mmol VCl₃ and 2 mmol C₈H₆O₄ were added to 30 mL water, which was transferred to an autoclave and heated at 180 °C for 24 h. Green powders (V-MOF) were obtained after washing and drying. V-MOF precursor was put loosely in a ceramic boat and annealed for 3 h under argon in a tubular furnace heating at 500 °C under a rate of 2.5 °C min⁻¹. After cooling down, the VO₂@C was obtained.

Preparation of VO2@C@SnS2 composite

The as-prepared VO₂@C was dispersed in water, then $SnCl_2 \cdot 2H_2O$ was added under stirring for 1 h. *L*-semiluminine was dissolved at room temperature by stirring. Then, they were mixed, and transferred to an autoclave for heating at 180 °C for 6 h. Products were obtained after collecting, washing, and drying.

Characterization and tests

X-ray diffractometer (XRD, SMART APEX II Brook), scanning electron microscope (SEM, Hitachi S-8100), transmission electron microscope (TEM, HT-7700). X-ray photoelectron

spectroscopy (XPS, America ThermoFischer, ESCALAB Xi+), Al K α ray (hv=1486.6 eV) was used as excitation source. Raman spectroscopy (Renishaw in Via), and Brunauer-Emmtt-Teller (BET, Micromeritics) were used for charactering the samples. A high-resolution TEM (HRTEM) was used to observe the lattice fringes. In addition, the details for constructing coin cells were presented in our previous reports [1,2]. A slurry-based approach was used. *In-situ* reaction resistance was measured by galvanostatic intermittent titration technique (GITT). Charge-discharge was tested on a battery tester (NEWARE CT-4008). Electrochemical workstation (Chen Hua, CHI660e) was employed to measure cyclic voltammetry (CV) curves and electrochemical impedance spectra (EIS).

Theoretical calculation

The Vienna Ab initio Simulation Package (VASP) was employed in this work to implement first-principles calculations. And the structure optimization in this work was accomplished by the Perdew-Burke-Ernzarhof (PBE) exchange–correlation function under generalized gradient approximation (GGA) and project-augmented wave (PAW) atom potentials, where the Coulomb U and exchange J parameters were considered ($U_{eff} = U - J$). The primitive structures of VO₂ and SnS₂ was obtained from Material Project. During the optimization process, the cutoff energy of the plane-wave basis was set as 520 eV, and the structural optimization process stopped when an energy convergence was lower than 10^{-5} eV and the atomic force was less than 0.01 eV/Å. For the V element, the values of coulomb U and exchange J are 3.25 eV and 0 eV, respectively. For the O, Sn, and S elements, both coulomb U and exchange J have values of 0 eV. The initial VO₂ and SnS₂@VO₂ heterojunction structures were constructed in a supercell of a $1 \times 1 \times 3$ unit cell with a total of ~10 atoms. Brillouin zone integration was performed using a $3 \times 3 \times 1$ k-point mesh for the cubic phase.



Fig. S1 Adsorption-desorption isothermal and pore-size distribution of (a) $VO_2@C@SnS_2$ and (b) $VO_2@C$.





Fig. S2 (a-e) Elemental mapping and (f) EDS spectrum of VO₂@C@SnS₂. XPS spectra of VO₂@C@SnS₂: (g) C 1s, (h) S 2p, (i) Sn 3d, (j) O 1s, (k) V 2p and (l) survey spectrum.

Fig. S2a-e shows the elemental mapping images of the composite, which presents the uniform distribution of elements C, O, Sn, V and S. Fig. S3a,b displays the line sweep diagram to determine the proportion of each element on the surface, and the high content of O element is caused by surface adsorption. Fig. S2f shows the EDS spectrum, which verifies a high purity. Fig. S4a-c shows the elemental mapping images of VO₂@C with elements C, O and V uniformly distributed on the surface. Fig. S4d shows its corresponding SEM image. Fig. S4e shows the proportion of each element, while Fig. S4f proves the existence of them. The surface components of $VO_2(a)C(a)SnS_2$ and the chemical states were further analyzed by X-ray photoelectron spectroscopy (XPS). C 1s spectrum is shown in Fig. S2g. Peaks at 284.8, 285.6, and 289.4 eV correspond to C-C/C=C, C-O, and C=O, respectively. In Fig. S2h, S 2p spectrum displays 163.9 and 165.1 eV from S 2p_{3/2} and S 2p_{1/2} of S²⁻, respectively, confirming the formation of SnS₂. The latter two lower intensity peaks, 161.9 eV, belong to the C–S–C bond, indicating the presence of S doping in the carbon-containing nanosheets. The peak appearing at 168.6 eV is a S–O formed on the surface due to unavoidable contact with air. The XPS spectrum of Sn 3d (Fig. S2i) can be directly fitted to the two peaks of typical Sn $3d_{5/2}$ and Sn $3d_{3/2}$ located at 486.6 and 495.0 eV, confirming the presence of Sn⁴⁺. In Fig. S2i, the 530.5, 531.8, and 532.9 eV correspond to V–O, C–O, and C=O, respectively. V 2p spectrum is shown in Fig. S2k. The two positions of 523.5 and 516.1 eV are assigned to V $2p_{1/2}$ and V $2p_{3/2}$ orbital splitting of V³⁺, while the peaks of 517.1 and 524.8 eV belong to V^{4+} . Fig. S2l proves the existence of C, O, V, Sn and S.



Fig. S3 (a) SEM images and (b) line scanning profiles of VO₂@C@SnS₂.



Fig. S4 (a-c) Elemental mapping images and (d) SEM of VO₂@C. (e) Line-scanning curves and (f) EDS spectrum of VO₂@C.



Fig. S5 The first-five CV curves at 0.1 mV s^{-1} of VO₂@C.



Fig. S6 GITT time-potential distribution of (a) $VO_2@C$ and (b) $VO_2@C@SnS_2$ at room temperature, (c) $VO_2@C$ at -10 °C.



Fig. S7 (a) CV profiles, log(i) vs. log(v) of (b) oxidization and (c) reduction peaks of $VO_2@C@SnS_2$.



Fig. S8 Differential specific capacity versus voltage plots of (a) $VO_2@C@SnS_2$ and (b) $VO_2@C$ at various rates.



Fig. S9 (a) CV curves at 0.1 to 1.0 mV s⁻¹. The log(i) vs. log(v) of (b) oxidization and reduction peaks. (c) Contribution ratio of capacitance control and diffusion control of VO₂@C. EIS spectra of (d) VO₂@C and VO₂@C@SnS₂ before and after cycling at 25 °C.



Fig. S10 Structural models of (a) VO_2 and (b) SnS_2 . (c) Band gap structure of VO_2 .



Fig. S11 SEM images of $VO_2@C@SnS_2$ after 100 cycles at 0.5 A g⁻¹.



Fig. S12 XRD pattern of VO₂@C@SnS₂ after 100 cycles at 0.5 A g⁻¹.

Cathode	Cycling	Cycle	Capacity	Ref.
	rate	number	$(mAh g^{-1})$	
Graphitic carbon nitride	0.2 C	500	75	[3]
$(g-C_3N_4)$	0.2 0	200	10	[3]
MnFe-PBA	$0.2 \mathrm{A g^{-1}}$	50	106.3	[4]
VOC1	$0.05 \mathrm{~A~g^{-1}}$	100	41.5	[5]
the hexagonal NiS	$0.2 \mathrm{A g^{-1}}$	100	100	[6]
nanobelts	e			
$Cu_{0.31}Ti_2S_4$	$0.005 \mathrm{~A~g^{-1}}$	50	70	[7]
Cu ₂ -xSe	0.2 Ag^{-1}	100	100	[8]
Co-P	0.2 Ag^{-1}	400	85.1	[9]
MoS_2	0 04 A σ ⁻¹	100	77 7	[10]
microsphere	0.07715	100	//•/	
VO2@C@SnS2	$0.5 \mathrm{A g}^{-1}$	200	157.6	This
	$1.0 \mathrm{A g^{-1}}$	1000	97.2	work

Table S1. Comparison of the electrochemical performance with some other cathodes.

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