Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Highly Stable and Reversible Zn Anode Enabled by the Electrolyte Additive of Sucrose

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Experimental

Materials

Zinc sulfate heptahydrate ($ZnSO_4·7H_2O$, 99%), sucrose ($C_{12}H_{22}O_{11}$, 99.5%), N-Methyl-2-pyrrolidone (NMP, C_5H_9NO, 99%), Oxalic acid ($H_2C_2O_4$, 99%) and Vanadium pentoxide (V_2O_5, 99%) were purchased from Aladdin. Polyvinylidene fluoride (PVDF, Arkema) and conductive carbon black (Timical) were purchased from Saibo Electrochemical Materials Pte Ltd. Glass microfiber filter (Whatman GF/D, Diameter 47mm, 1823-047) was obtained from Huidi Pte Ltd. Zn foils (30 μm, 99.9%), Cu foam (1.2 mm, 99.9%), Titanium mesh and stainless steel were provided by Shengshida Metallic Materials Pte Ltd.

Electrolyte preparation

The 1 M $ZnSO_4$ aqueous electrolyte was prepared using $ZnSO_4·7H_2O$ and deionized water based on the molar ratio. Certain amount of sucrose was introduced into the $ZnSO_4$ electrolyte to obtain the electrolyte containing different amounts of sucrose. The electrolyte without sucrose was denoted as $ZnSO_4$, and the electrolyte with 10 mmol sucrose was signed as $ZnSO_4$-Sucrose. The electrolyte with 5 and 20 mM sucrose were denoted as 5 mmol sucrose and 20 mmol sucrose, respectively.

Fabrication of Zn||Zn and Zn||Cu cell

The Zn plating/stripping tests were performed on Zn symmetrical cells. Two pieces of Zn foil were used as electrodes for Zn||Zn cell. The GE-Whatman glass fiber was employed as the separator. Coulombic efficiency (CE) measurements were carried out on asymmetrical Zn||Cu cells. Zn foil and copper foam were used as electrodes. The electrolyte and glass fiber in Zn||Cu cell were the same as that in Zn||Zn cell.

Fabrication of Zn||VO_2 full Cell

VO_2 was synthesized by the hydrothermal method. Typically, 1.2 g of V_2O_5 was dispersed in 40 mL of deionized water under string, followed by adding 1.8 g of $H_2C_2O_4$. Then, the above suspension was heated at 80 °C for 1 h. After that, the solution was transformed into a hydrothermal reactor, and maintained at 180 °C for 4 h. When the reactor cooled down to room temperature, the product was washed with deionized water for several times to obtain the VO_2. The cathode was prepared by mixing VO_2 with conductive carbon black and PVDF at the weight ratio of 7:2:1 and dissolving the above mixture in an appropriate amount of NMP to form homogeneous slurry. The obtained slurry was then spread onto the titanium mesh, and dried in a vacuum oven at 60 °C overnight. The mass loading of the above cathode active materials was about 2.0~4.0 mg cm^{-2}. Zinc foil and glass fiber were used as the anode and separator, respectively.

Electrochemical Test

The performances of Zn||Zn symmetric cells, Zn||Cu asymmetric cells, and Zn||VO_2 full cells were carried out on a Neware CT-3008 battery test system. The Zn||Zn cells were tested at 5 mA cm^{-2} / 1 mAh cm^{-2}, 5 mA cm^{-2} / 5 mAh cm^{-2}, and 10 mA cm^{-2} / 5 mAh cm^{-2}, respectively. The Zn||Cu asymmetric cells were carried out at 1 mA cm^{-2} / 0.5 mAh cm^{-2}. For Zn||VO_2 cell, the rate performance was tested at various current densities (0.1, 0.2, 0.5, 1, and 2 A g^{-1}) and the cycling performance was evaluated with the voltage range of 0.3~1.5 V under 1 A g^{-1}. The specific capacities were evaluated according to the mass of active materials. The corrosion, diffusion, and hydrogen evolution behaviors of Zn foil anode were tested under an electrochemical workstation (CHI 660e) with a three-electrode system (Zn foil as work electrode, Pt as counter electrode, and Ag/AgCl as reference electrode). The Tafel plot was recorded with a potential range of ±0.3 V versus open-circle potential of the system at a scan rate of 1 mV s^{-1}. The hydrogen evolution performance was collected by linear sweep voltammetry (LSV) with a potential range of -1~-1.6 V at a scan rate of 1 mV s^{-1}. The diffusion curves were measured by chronoamperometry method under an overpotential of -150 mV. The cyclic voltammetry (CV) for the nucleation overpotential was tested with a voltage rage of -1.4~-0.2 at a scan rate of 1 mV s^{-1} (Zn foil as counter electrode, Ti as work electrode, and Ag/AgCl as reference electrode). The electrochemcial potential window was tested at 1 mV s^{-1} (steel-mesh as working electrode and counter electrode, and Ag/AgCl electrode as reference electrode). Electrochemical impedance spectroscopy (EIS) was implemented within a range of 10^5 to 10^{-2} Hz.

Characterization

The properties of electrolyte were studied by the Raman (Thermo, DRX-2), FT-IR (Bruker Alfar) and contact angle meter (Jinhe, JY-PHB). The Zn foil (pristine, soaked and cycled) and VO_2 were characterized by the X-ray diffraction with Cu Kα (λ=1.54060 Å) (XRD, Rigaku, Ultima IV) and field-emission scanning electron microscopy (SEM, Hitachi SU8600). The images of Zn deposition process were obtained on an industrial optical microscope (Aoweisi, AW33T-4K).

Calculations

All density functional theory (DFT) calculations were implemented by the Vienna Ab initio Simulation Package (VASP). The electron exchange and correlation energies were handled using the Perdew-Burke-Ernzerhof (PBE) functionals. The projector augmented wave (PAW) potentials was used to describe the interactions between the cores and valence electrons. The expansion of the Kohn-Sham valence states were carried out with a 400 eV plane-wave cutoff energy. For Brillouin zone integration, 1×1×1 Γ-centered Monkhorst-Pack grids were performed. The cell parameters for complex structure are set as a = 10 Å, b = 10 Å, c = 27 Å. A vacuum space 20 Å was employed to eliminate the interaction between the neighboring layers. The Zn (002) surface unit cells were four layers thick, and the bottom two layers were fixed to the bulk position of Zn. The convergence criterion of structure optimization for energy and force were set as 10^{-4} eV and 0.05 eV $Å^{-1}$, respectively.

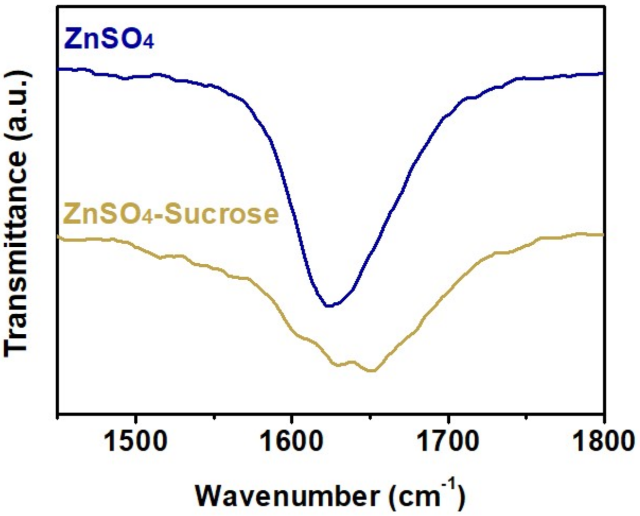

Fig. S1 FT-IR profiles of different electrolytes.

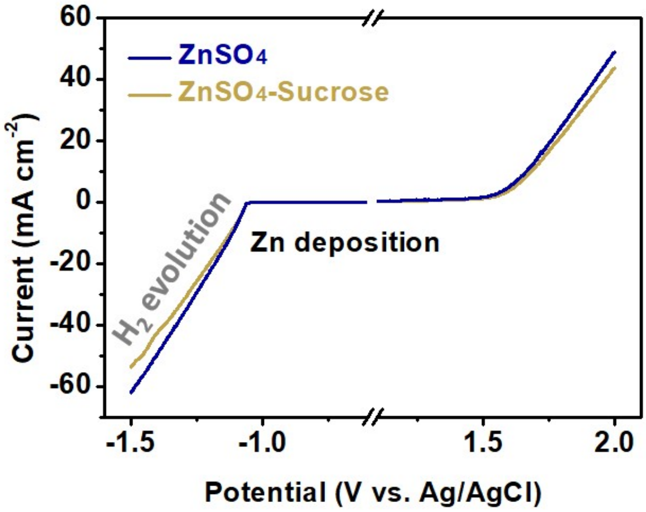

Fig. S2 The overall electrochemical stability window.

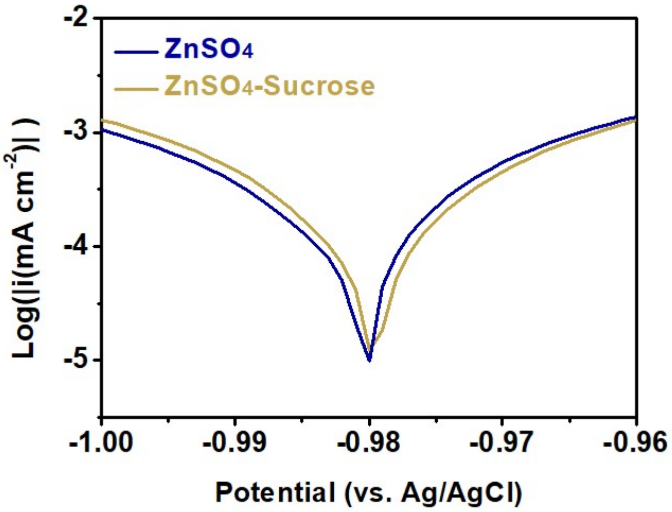

Fig. S3 Tafel plots of Zn plating tested in different electrolytes at a scan rate of 1 mV s^{-1} using a three-electrode system.

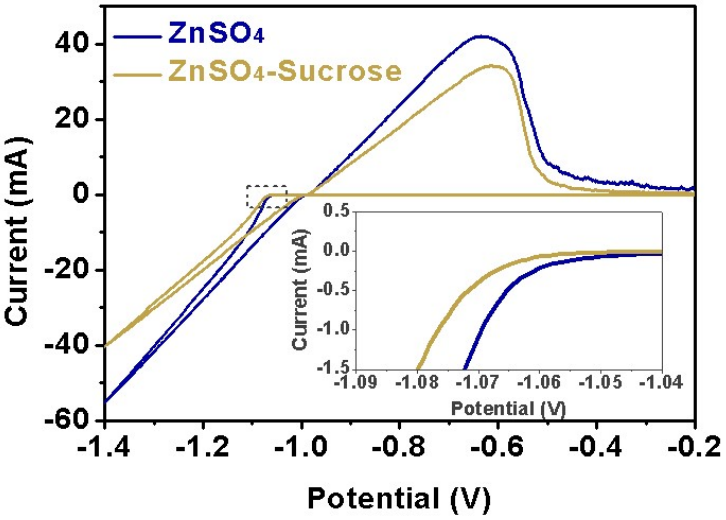

Fig. S4 The cyclic voltammetry curves of different electrolytes at a scan rate of 1 mV s^{-1}.

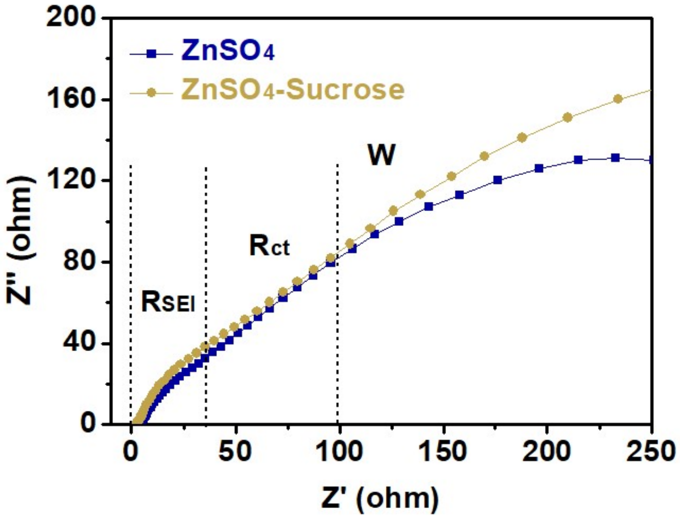

Fig. S5 The electrochemical impedance spectroscopy profiles of Zn||Zn cells with different electrolytes after 10 cycles.

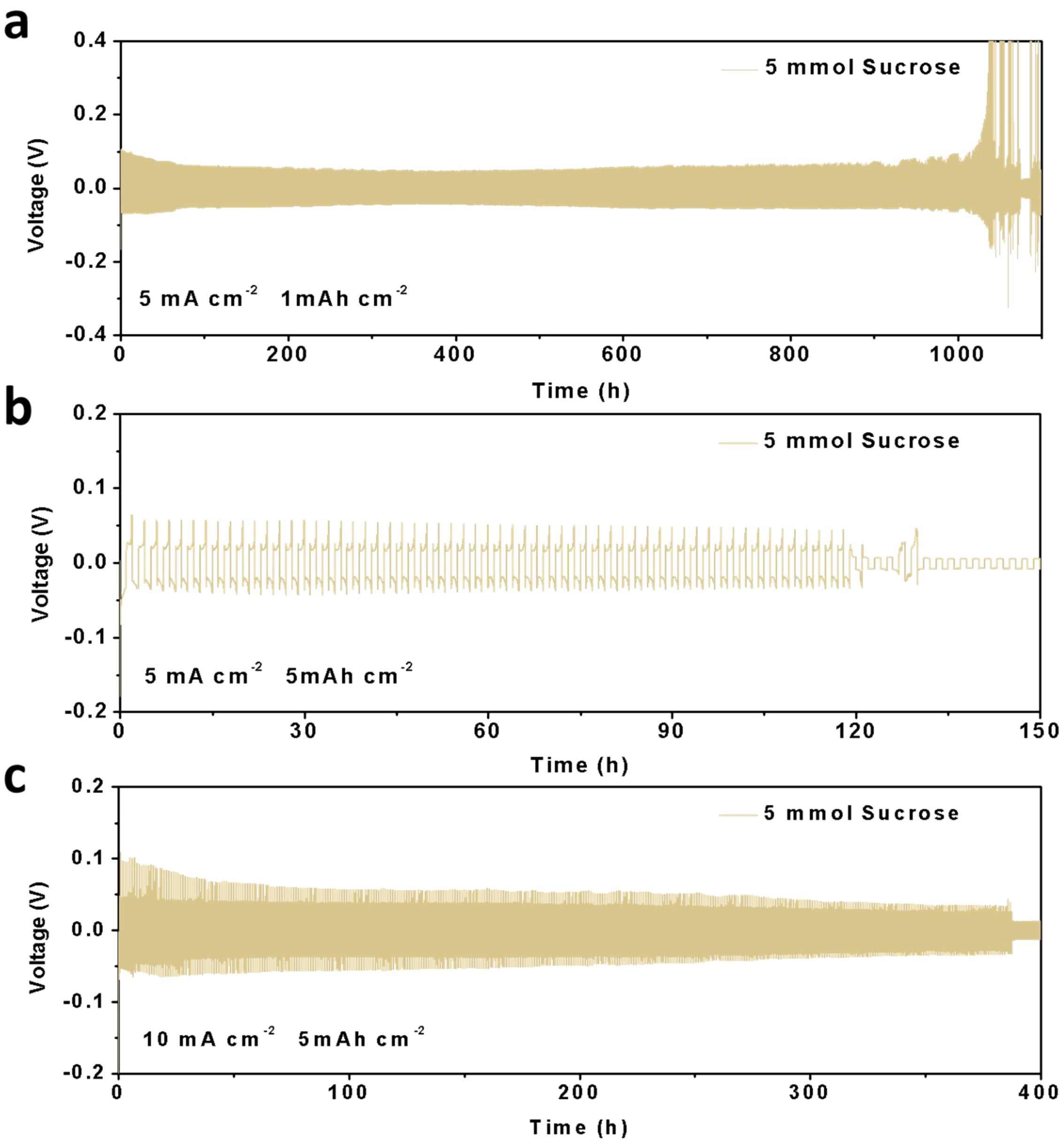

Fig. S6 The cycling performance of the Zn||Zn cells using the electrolyte containing 5 mM sucrose at (a) 5 mA cm^{-2} /1 mAh cm^{-2}; (b) 5 mA cm^{-2}/ 5 mAh cm^{-2}; (c) 10 mA cm^{-2}/ 5 mAh cm^{-2}.

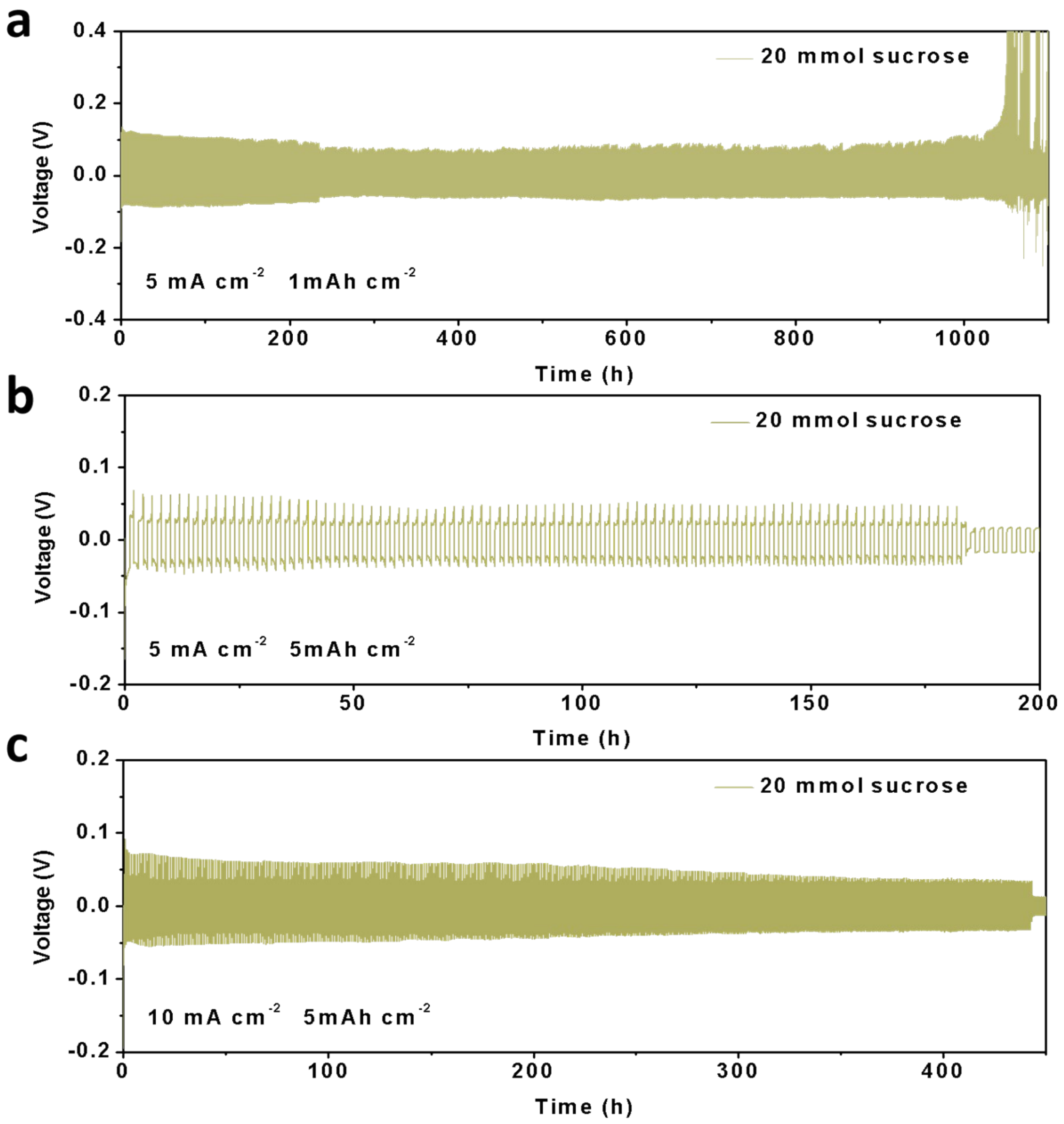

Fig. S7 The cycling performance of the Zn||Zn cells using the electrolyte containing 20 mM sucrose at (a) 5 mA cm^{-2} / 1 mAh cm^{-2}; (b) 5 mA cm^{-2} /5 mAh cm^{-2}; (c) 10 mA cm^{-2}/5 mAh cm^{-2}.

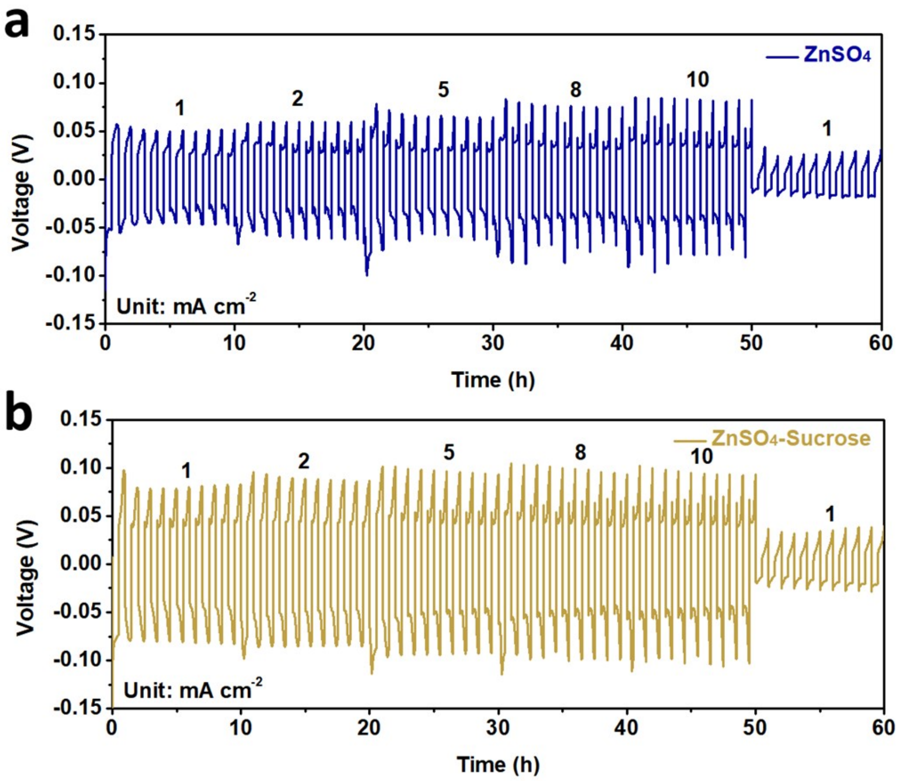

Fig. S8 The rate performance of Zn||Zn cell in (a) $ZnSO_4$ electrolyte; (b) $ZnSO_4$-Sucrose electrolyte.

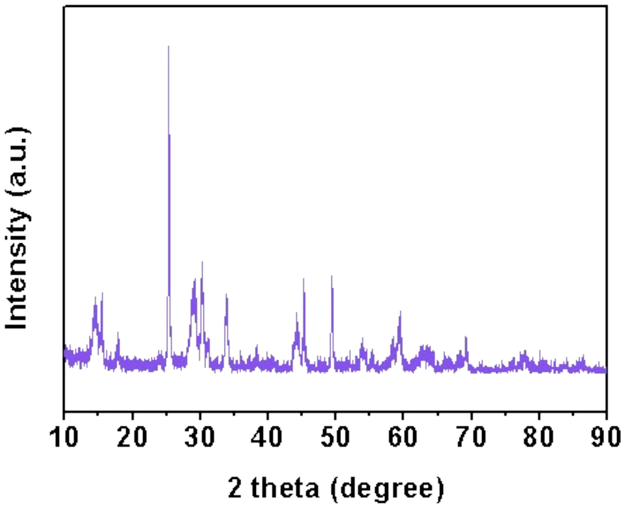

Fig. S9 The XRD pattern of prepared VO_2.

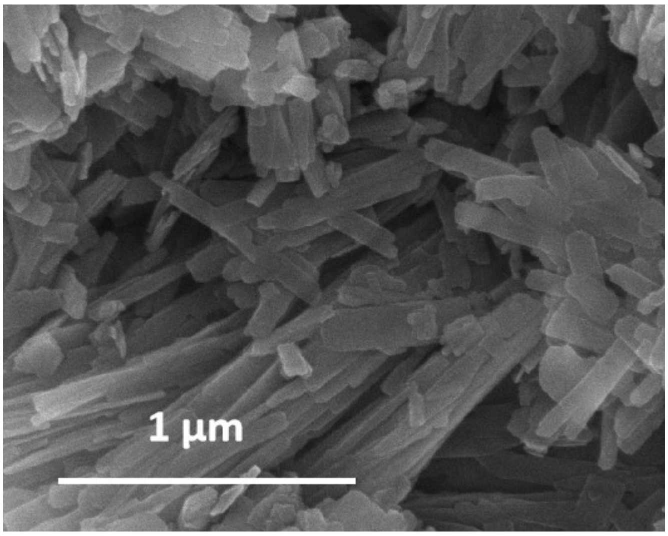

Fig. S10 The SEM image of prepared VO_2.