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Supporting Information

Forming Bubble-Encapsulated Double-Shelled Hollow Spheres towards Fast Kinetics and Superior High Rate Performance for Aqueous Rechargeable Zn-ion Batteries

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Part I: Experimental details, Calculations & Discussions

S-1: Sample synthesis

S-1-1: Synthesis of bubble-encapsulated double-shelled hollow sphere (BDHS) sample

All the chemical reagents were purchased from Macklin Chemical Reagent Co. Ltd and used without further purification. Firstly, a solvothermal synthesis is used to construct the BDHS structured precursor. The starting materials of ammonium metavanadate and zinc nitrate were dissolved in distilled water and ethylene glycol to form two transport solutions. Then the solutions are mixed with the cetyltrimethylammoniumbromide (CTAB) and citric acid aqueous solutions. The mixture was vigorous stirring for two hours, then it was transferred into an auto-controlled Teflon-lined stainless steel autoclave (Figure S7). The hydrothermal treatment was reacted at 180 ^oC under carefully controlled temperature, pressure and stirring. After cooling to the room temperature, the resultant intermediate product was filtrated and washed with distilled water and alcohol several times and dried in an over at 70 ^oC. Finally, the obtained precursor was annealed at 400 ^oC for 5 hours in the air with a slow heating rate of 1 ^oC min^{-1} to achieve the final product.

S-1-2: Synthesis of reference samples

Two kinds of references samples were prepared by solid-state and sol-gel synthesis.

i) For the preparation of the LB reference sample, the solid-state method was employed. The starting materials of ammonium metavanadate and zinc nitrate were finely grounded using a mortar. Then the mixture was calcinated at 400 ^oC for 5 hours in air atmosphere with a slow heating rate of 1 ^oC min^{-1} to achieve the LB reference sample.

ii) For the preparation of the PR reference sample, the sol-gel method was employed. The starting materials of ammonium metavanadate and zinc nitrate were separately dissolved in distilled water to form two transport solutions. Then both solutions are mixed followed by the addition of citric acid. Then the mixture was kept stirred at 80 ^oC until it turns into a gel. After drying the gel in an oven, the precursor was grounded in a motor. The resultant precursor was annealed at 400 °C for 5 hours in air atmosphere with a slow heating rate of 1 °C min^{-1} to achieve the PR reference sample.

S-1-3: Synthesis of IP reference sample

The IP reference sample was prepared by the same process of BDHS sample. The only difference between two samples is the different reaction time of hydrothermal process. For the BDHS sample, the reaction time of hydrothermal process is 10 hours; as for the IP sample, the reaction time of the hydrothermal process is only 4 hours.

S-1-4 Synthesis of the BDHS/C samples

Single wall carbon nanotubes (SWNT) and graphene (GA) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. The powder of the BDHS sample, the single-walled carbon nanotubes/graphene and the PVDF binder were mixed in the NMP solution, which was then put into ultrasonicating bath for one hour. The resultant uniform ink was casting onto the surface of a piece of glass, which was then dried at room temperature to achieve the BDHS/C samples.

S-2: Materials characterizations

Powder X-ray diffraction (XRD, Bruker D8/Germany) using Cu Kα radiation was employed to identify the crystalline phase of the material. The experiment was performed by using step mode with a fixed time of 3 *s* and a step size of 0.02°. The XRD pattern was refined by using the Rietveld method. The morphology was observed with a scanning electron microscope (SEM, HITACHIS-4700) and a transmission electron microscope (TEM, JEOS-2010 PHILIPS). The element distribution of the sample was confirmed by energy dispersive X-ray detector (EDX). Thermogravimetric analysis (TGA, NETZSCH STA 449C) in flowing nitrogen was used to monitor the combustion process of the gel precursor. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP 2010. Sample preparation included degassing at 523 K for 12 h in a vacuum of 10^{-6} Torr. Specific surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. Element analysis was carried out by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500CX). Inductively coupled plasma mass spectrometry

(ICP-MS, Agilent 7500CX) was employed to analyze the vanadium concentration of the solution.

S-3: Electrochemical measurements of single electrode

The electrodes are made by mixing the active material, the carbon black and the binder (PTFE) in a weight ratio of 7:2:1. The mixture was casting on the stainless steel and vacuum drying at 100 ^{o}C overnight to for the working electrode. The mass loading of the active materials is controlled to be ~3 mg cm^{-2}. Zn foil was used as the counter electrode and the 1M $ZnSO_4$ aqueous solution was used as the electrolyte. The cyclic voltammetry (CV) were measured in a CHI electrochemical workstation, and the galvanostatic charge/discharge tests were conducted on a LAND battery testing system (Wuhan, China).

S-4: Fabrication of flexible solid-state-battery

S-4-1: Synthesis of the Zn nanosheet/SWNT anode

Firstly, the SWNT based film was prepared in the same process as described above. The CNT-ink was prepared by dispersing the single-walled carbon nanotubes and the PVDF in the NMP solution, and then it is put into ultrasonicating bath for one hour. The resultant uniform ink was casting onto the surface of a piece of glass, which was then dried at room temperature. After it is separated from the substrate, the flexible SWNT film was obtained.

Next, Zn nanosheets were grown on the SWNT film by electrodeposition at room temperature employing the CHI 760 electrochemical work station. The electrodeposition was carried out in a three-electrode configuration with the textile as working electrode, a Pt plate as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The mixed solution of $ZnSO_4 \cdot 7H_2O$, Na_2SO_4 and H_3BO_3 was used as electrolyte. The electrodeposition was conduct at -40 mA cm^{-2} at room temperature. Then the resultant electrode was washed with DI water and dried in a vacuum oven at 60 ^{o}C for 12 hours.

S-4-2: Fabrication of sandwich-type solid-state-battery

The sandwich-type battery was assembled by the BDHS/SWNT cathode, Zn nanosheet/SWNT anode and the polymer gel electrolyte. Firstly, the commercial gelatine and potassium persulfate were dissolved in the mixed solution of $ZnSO_4$ under stirring at 80 ^{o}C. Then the acryamide and N, N'-methylenebisacrylamide were added to the mixture for another three hours stirring. Afterwards, the mixture was injected into the flexible electrodes and assembled the sandwich type cell. Then the cell was soaked again in the mixture solution of $ZnSO_4$ for another two hours to achieve the equilibrated state. The galvanostatic charge/discharge tests were conducted on a LAND battery testing system (Wuhan, China).

S-4-3: Fabrication of thin-film micro-battery

i) Synthesis of interdigitated microelectrodes

The films were laser-ascribed using a commercial laser marking machine with the maximum power of 5 W. The digital computerized control system is used to control the structure of the electrode. The interdigitated structure is built to prevent short circuit between two adjacent microelectrodes.

ii) Fabrication of thin-film micro-battery

The thin-film microbattery was fabricated based on the interdigitated electrodes. The microelectrodes were soaked in the aqueous electrolyte for one day, and then they were encapsulated by the polymer gel electrolyte as described above. After that, the microbattery was soaked again in the aqueous electrolyte for another two hours to achieve the equilibrated state. The galvanostatic charge/discharge tests were conducted on a LAND battery testing system (Wuhan, China).

S-5: Calculation methods

(1) specific capacity (Q)

The specific capacity is calculated based on the galvanostatic charge/discharge curves,

$$Q = \frac{I \times \Delta t}{m} \qquad (1)$$

Where Q is the specific capacity, Δt is the discharge time, I is the discharge current, m is the mass of the active material in the single electrode.

(2) Relative capacity (Q_r)

The relative capacity of the single electrode is calculated based on the following equation,

$$Q_r = \frac{Q_i}{Q_s} \qquad (2)$$

Where Q_r is the relative capacity, Q_i is the specific capacity at a certain current density, Q_s is the specific capacity at 0.05 A g^{-1}.

(3) Cycling retention

The cycling retention is calculated based on the following equation,

$$CR = \frac{Q(after)}{Q(before)} \qquad (3)$$

Where *CR* is the capacity retentions after cycling, Q (after) is the capacity of the electrode after cycling, Q (before) is the capacity of the electrode before cycling,

(4) Energy density (E)

$$E = \int \frac{IUdt}{M} \qquad (4)$$

Where E is the energy density, I is the current density, Δt is the discharge time, M is the total mass of the cathode electrode.

(5) Power density (P)

$$P = \frac{E}{\Delta t} \qquad (5)$$

Where P is the power density, E is the energy density, Δt is the discharge time.

S-6: Investigation of the yields at each step during synthesis

The yield of the preparation at each step is investigated. Firstly, the yield of the hydrothermal process is studied. The obtained precursor prepared by hydrothermal treatment was dissolved in the nitrate acid at 60°C under continuously stirring. After the transport solution was obtained, it was naturally cooled to the room temperature and diluted for element analysis. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500CX) was employed to analyze the vanadium concentration of the solution. The yield of the preparation at the hydrothermal treatment is obtained by the following equation.

$$Y_{hydrothermal} = \frac{C_v \times V_v}{m_v} \times 100\% \qquad (6)$$

Where $Y_{hydrothermal}$ is the yield of hydrothermal process; C_v is the measured vanadium concentration in the solution with dissolved precursor; V_v is the volume of the solution; m_v is the mass of vanadium element in the mixed solution before the hydrothermal treatment.

Next, the yield of the calcination process is investigated. Two samples before and after calcination, *i.e.* the precursor and final product, were both dissolved in the nitrate acid as described above. Then both resultant solutions were diluted and analyzed by ICP-MS measurement. Based on the vanadium concentration of both solutions, the yield of the calcination treatment can be obtained by the following equation.

$$Y_{calcination} = \frac{C_f \times V_f}{C_p \times V_p} \times 100\% \qquad (7)$$

Where $Y_{calcination}$ is the yield of calcination process; C_f is the vanadium concentration of the solution for the final product; V_f is the volume of the solution for the final product; C_p is the vanadium concentration of the solution for the precursor; V_p is the volume of the solution for the solution of the precursor.

Part II: Supporting Figures

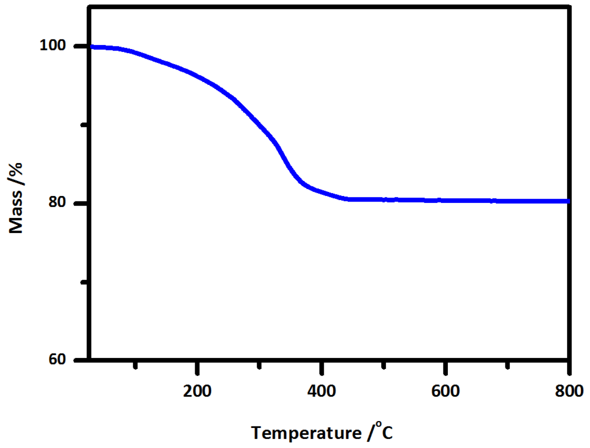

Figure S1 TG result of the prepared precursor.

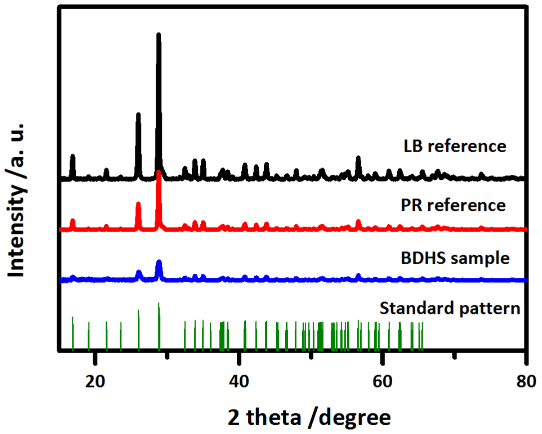

Figure S2 XRD patterns of the BDHS sample, PR reference and LB reference samples. The standard pattern of the $Zn_2V_2O_7$ is inserted to identify the single phase nature of the samples.

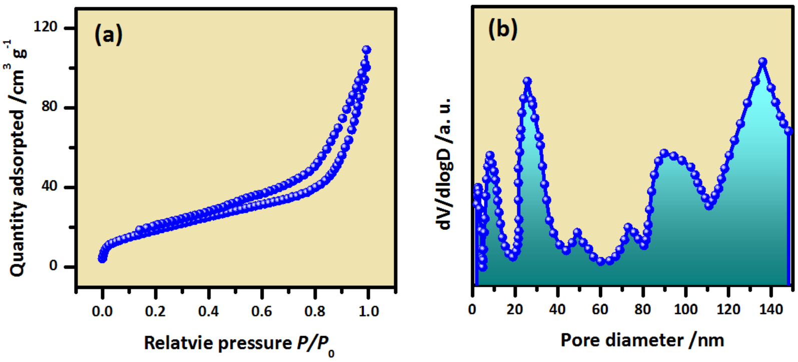

Figure S3 (a) N_2 adsorption/desorption results and (b) Pore size distribution of the BDHS sample.

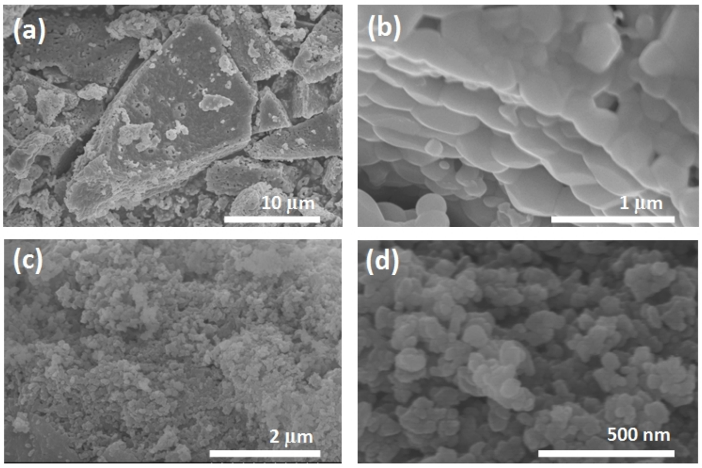

Figure S4 SEM images of the LB reference (a, b) and PR reference (c, d) samples.

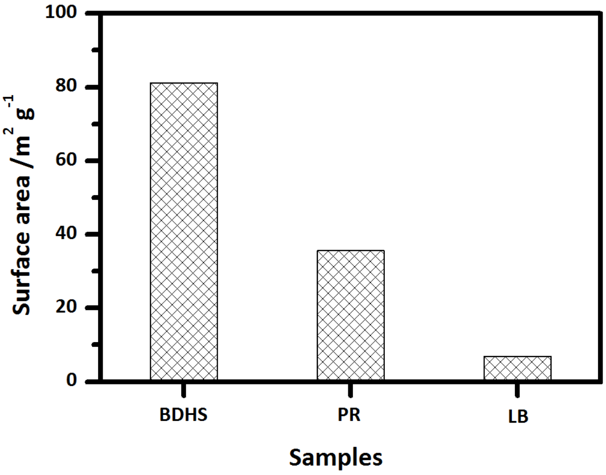

Figure S5 Comparison of the BET areas of the BDHS, LB reference and PR reference samples.

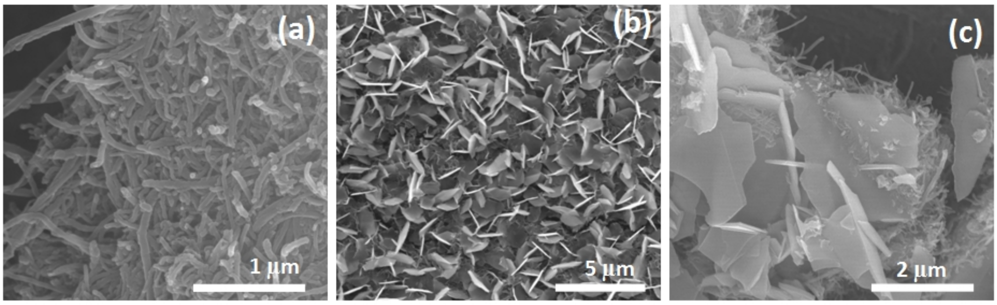

Figure S6 SEM image of the Zn nanosheet/SWNT electrode. (a) the SWNT substrate; (b) the Zn nanosheet on the SWNT substrate and its enlarged image (c).

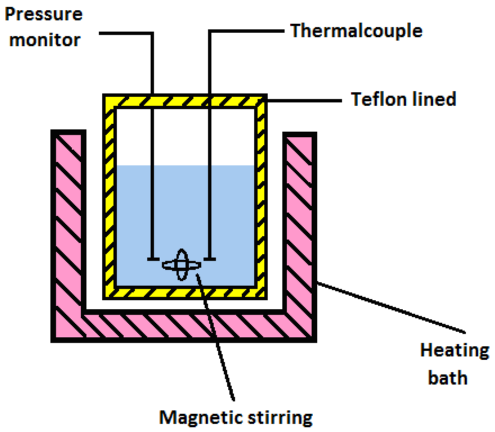

Figure S7 Scheme of the system for the preparation of the BDHS sample.