Construction of highly ordered ZnO microrod@SnO$_2$ nanowire heterojunction hybrid with a test-tube brush-like structure for high performance lithium-ion batteries: experimental and theoretical study

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Abstract
ZnO@SnO$_2$ heterojunction hybrid with a novel test-tube brush-like structure is fabricated successfully through a facile hydrothermal approach. Sixfold symmetric epitaxial growth of SnO$_2$ nanowires on non-polarized planes of ZnO microrods is realized via the approach. The synthesized ZnO@SnO$_2$ with the unique structure as a lithium-ion battery anode material exhibits enhanced electrochemical properties when compared with the single-phase ZnO microrod and SnO$_2$ nanowire electrode. The existence of heterostructure on the influence of lithium storage performance is studied by using first-principles calculations through density functional theory method. Experimental and theoretical calculation results demonstrate that the excellent electrochemical performance of the heterojunction hybrid is ascribed to the synergistic effect of the respective components. The construction of ZnO@SnO$_2$ heterojunctions can not only provide facile Li$^+$ kinetics and enhanced ion diffusion, but also improve the mobility rate of electrons and holes by means of the presence of internal electric field.

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1. Introduction

Secondary lithium-ion batteries (LIBs) have been extensively explored and broadly utilized in energy storage systems such as electronics and electric vehicles with advantages of excellent reversible capacity and cyclability [1]. With the rapid progress of social modernization and industrialization, there are increasing demands for developing LIBs with high-performance to meet the requirements for practical applications. Anode is one of the important components for LIBs. The current used anode material of graphite was unable to fit the needs of high energy storage ability owing to of its low theoretical capacity (372 mAh g$^{-1}$) and poor rate performance [2]. Hence, exploring a new electrode material is of great significant to supply the increasing demand for high-performance LIBs. Recently, special attention is given to heterojunction hybrids owing to their advantages of providing low diffusion resistance and fast ion diffusion rate when applied as electrode materials for energy storage systems [3–9]. The energy storage performance of the hybrids can be enhanced generally by the synergistic behavior of the interfacial interaction of respective components.

ZnO and SnO$_2$ are typical semiconductors with wide applications in photocatalysis, photoelectronic devices, and chemical sensors [10–13]. They are also alternative candidates that can be applied as anodes for LIBs with high theoretical specific capacity (978 mAh g$^{-1}$ for ZnO, and 781 mAh g$^{-1}$ for SnO$_2$) together with their superior characteristics such as facile synthesis, morphological diversity, low cost, and environmental nontoxicity [14,15]. However, severe volume changes during the lithiation and
delithiation procedures and inferior electron conductivity of the two materials lead to rapid electrode degradation and poor lithium storage performance [16–18]. Modifying them with metal oxides M₂O₃ (M = Ni, Cu, Co, Ti, etc.) to construct hybrid structure (ZnO–NiO, ZnO–CuO, SnO₂–CoO, SnO₂–TiO₂, etc) has been confirmed as an effective approach to accommodate volume effect and further improve electron conductivity of ZnO or SnO₂ electrodes [19–23]. This is because the synergistic effect of lithium storage between two kinds of metal oxides usually can be occurred, resulting in the enhanced electrochemical kinetics and properties of the hybrids.

Besides the above synthesized hybrid architectures, ZnO and SnO₂ can also be constructed into hybrid structure with excellent energy storage properties. By using the electrospinning method with a subsequent calcination route, several researchers have reported the synthesis of ZnO–SnO₂ micro- or nano-fibers and have investigated the lithium storage performance of them for high performance LIBs [24–28]. Their experimental results indicated that the synthesis of heterojunction hybrids can be realized through the synthetic approach, and the hybrid could work effectively to complement the drawbacks of the individual materials, exhibited enhanced electrochemical performance. However, considering the used apparatus and the applied thermal treatment conditions, it should be noteworthy that the current synthetic approach to construct ZnO–SnO₂ heterostructures requires relatively complicated and harsh conditions. Additionally, although highly ordered fibers can be fabricated through the approach, a disordered distribution of ZnO and SnO₂ particles in each fiber were unavoidably generated. That means the construction of the multi-component heterostructure is randomness and uncertainty on those fibers. This is unfavorable for the precise controlled formation of the heterojunction hybrid. More importantly, the underlying reasons why the construction of the heterostructures could improve the lithium storage properties did not elucidate in detail in the works. Based on the research situations of ZnO–SnO₂ heterostructures used for LIBs, it is important to develop relatively facile method to synthesize highly ordered ZnO–SnO₂ hybrids and to investigate the existence of heterostructure on the influence of lithium storage performance in-depth.

In the present work, without the use of neither special apparatus nor high temperature thermal treatments, a highly ordered ZnO microrod@SnO₂ nanowire heterojunction hybrid (ZnO@SnO₂) with a novel test-tube brush-like structure was synthesized through a simple hydrothermal route. The synthesized ZnO@SnO₂ with the unique structure as a LIB’s anode material exhibited enhanced cycling capability and rate performance when compared with the single-phase ZnO microrod and SnO₂ nanowire electrode. To illuminate the role of heterojunction in improving electrochemical performance, the electronic structure, work function and charge transfer mechanism of ZnO@SnO₂ were studied by using first-principles calculations through density functional theory (DFT) method. Our experimental and theoretical calculation results indicated that the construction of ZnO@SnO₂ heterojunctions can not only provide facile Li⁺ kinetics and enhanced ion diffusion, but also improve the mobility rate of electrons and holes by means of the presence of internal electric field. To the best of our knowledge, this study is the first to utilize DFT theoretical calculation to explain the kinetic, lithium ion diffusion and electron mobility of the ZnO@SnO₂ hybrid electrode for LIBs.

2. Experimental

2.1. Materials

All chemicals and reagents were analytical grade and were used without further purification. Zn(CH₃COO)₂·2H₂O and SnCl₄·5H₂O were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., China. NaOH was purchased from Tianjin Fuchen Chemical Reagent Co., Ltd., China.

2.2. Synthesis of ZnO microrods

Typically, 1.552 g of Zn(CH₃COO)₂·2H₂O was solubilized into 40 ml of distilled water to form a luculent solution. Subsequently, 4.083 g of NaOH was introduced into the solution with constant magnetic stirring for 0.5 h. The obtained intermixture was then migrated into a Teflon-lined stainless steel autoclave with volume space of 50 ml and heated up to 100 °C for 12 h. After the hydrothermal route, the autoclave was cooled naturally to 25 °C. Finally, the sediment was acquired and washed with distilled water for 5 times, and then dried at 80 °C overnight in a vacuum oven.

2.3. Synthesis of test-tube brush-like ZnO@SnO₂ heterojunction hybrid

Typically, 1.240 g of SnCl₄·5H₂O was solubilized into 40 ml of distilled water to form a luculent solution. Subsequently, 1.560 g of NaOH was introduced into the solution with continue magnetic stirring for 0.5 h. After that, 0.048 g of the synthesized ZnO microrods was put into the intermixture with continue magnetic stirring for 1 h. The turbid solution was then treated through an ultrasonic approach for 10 min. The obtained suspension was migrated into a Teflon-lined stainless steel autoclave with volume space of 50 ml and heated up to 200 °C for 20 h. After the hydrothermal route, the autoclave was cooled naturally to 25 °C. Finally, the sediment was acquired and washed with distilled water for 5 times, and then dried at 80 °C overnight in a vacuum oven. The simulation morphology results of the ZnO microrods, ZnO@SnO₂ hybrid, and SnO₂ nanowires are shown in Fig. 1.

2.4. Characterization

The crystalline structure of the final product was investigated by using an X-ray diffractometer (XRD, Shimadzu 6100) with Cu Kα radiation. The surface chemical composition of the final product was explored by employing an X-ray photoelectron spectroscopy (XPS, AXIS ULTRA). The binding energy of each element was corrected by C 1s at 284.6 eV as a reference to reduce the relative surface charging effect. The specific surface areas of the samples were tested by using a TriStar II 3020 analyzer through the Brunauer-Emmett-Teller (BET) method. The morphologies of the ZnO and ZnO@SnO₂ specimens were explored by using a scanning electron microscopy (SEM, Zeiss SIGMA/VP). And elemental mapping images and atomic ratio of the final product were obtained by using the energy dispersive spectroscopy (EDS) equipped on the SEM instrument. The structures of the ZnO@SnO₂ and SnO₂ specimens were investigated by using a transmission electron microscopy (TEM, JEOL JEM-3010). Fast Fourier transform (FFT) pattern of SnO₂ was obtained during the TEM characterization.

2.5. Electrochemical measurements

The energy storage capabilities of the specimens were evaluated at 25 °C by using CR2025 button cells packed in a glovebox full of Ar. The working electrodes were made by casting slurries on Ni foam. The slurry was made by mixing an active material of ZnO@SnO₂, ZnO, or SnO₂ with Super P and polyvinylidene fluoride (8:1:1, weight percentage) in a certain amount of N-methyl-pyrrolidone solvent. The obtained slurry was coated and pressed on a Ni foam substrate in a diameter of 12 mm and dried at 100 °C.
overnight in a vacuum oven. The active material mass loading on each Ni foam was approximate 1 mg cm⁻². Polypropylene membrane and lithium tablet were utilized as separator and counter electrode, respectively. 1 M LiPF₆ in a mixture of dimethyl carbonate, diethyl carbonate, and ethylene carbonate (1:1:1, volume percentage) was utilized as electrolyte. The packed button cells were measured by a battery tester (LAND CT2001A) with a potential scope of 0–3.0 V (versus Li⁺/Li). The voltage of the cells at open voltage circuit is 2 V. Cyclic voltammetry (CV) measurement was implemented on an electrochemical workstation (CHI 660D) in a potential scope of 0–3.0 V. Measurements of electrochemical impedance spectroscopy (EIS) results were implemented on the same electrochemical workstation in the fully charged state with 10 mV amplitude over the frequency range between 10⁵ and 10⁻² Hz.

2.6. Computational methods

The electronic structure, work function and charge transfer mechanism of SnO₂, ZnO, and ZnO@SnO₂ heterojunction hybrid were studied by using first-principles calculations through DFT method [29]. The hybrid DFT of Heyd-Scuseria-Ernzerh of 06 (HSE06) was performed to improve the precision of density of states (DOS) and band structures due to the undervalued band gaps with the inexact characterization of the self-interaction between electrons in Perdew-Burke-Ernzerh (PBE) [30]. The plane-wave cut-off energy is set to be 420 eV. The Monkhorst Pack k-point grid of 9 × 9 × 6, 6 × 6 × 6 and 4 × 4 × 1 are used for ZnO, SnO₂ and ZnO@SnO₂ heterojunction for the Brillouin Zone sampling, respectively. The convergence criteria of energy are set to be 5.0 × 10⁻⁶ eV atom⁻¹. The largest force between atoms is 0.01 eV Å⁻¹ and the largest internal stress does not exceed 0.05 GPa.

3. Results and discussion

The crystal phase and structure information of the synthesized ZnO@SnO₂ hybrid were examined by XRD measurement (Fig. 2). As displayed in the XRD pattern, the diffraction peaks located at 2θ = 31.7°, 34.3°, 36.1°, 47.6°, 56.7°, 62.9°, 67.8°, and 69.0° can be attributed to the (100), (002), (101), (102), (110), (103), (112), and (201) crystallographic planes of hexagonal wurtzite structure ZnO (JCPDS No. 36–1451, Space group: P6₃mc), respectively. The diffraction peaks located at 2θ = 26.7°, 33.8°, 38.0°, 51.9°, 54.7°, 57.9°, 61.8°, 64.8°, and 65.9° can be attributed to the (110), (101), (200), (211), (220), (002), (311), (112), and (301) crystallographic planes of SnO₂ with tetragonal rutile structure (JCPDS No. 41–1445, Space group: P4₂mm). No other evident diffraction peak was found in the pattern, suggesting that the hybrid is a combination of ZnO and SnO₂ with high crystallization.

The surface element valence state of the synthesized ZnO@SnO₂ was investigated by XPS measurement (Fig. S1). The XPS spectrum survey scan (Fig. S1a) exhibits the existence of tin (Sn 3d), zinc (Zn 2p), oxygen (O 1s), and carbon (C 1s) elements. The enlarged range of the Zn 2p XPS spectrum in Fig. S1b presents two peaks located at the bond energies of 1021.3 and 1044.6 eV, assigned to the Zn 2p1/2 and Zn 2p3/2, respectively. The spin orbital splitting binding energy between the Zn 2p1/2 and Zn 2p3/2 is 23.1 eV, which agrees with the Zn²⁺ bonding in ZnO [31]. For the high-resolution Sn 3d spectrum (Fig. S1c), it indicates two main peaks situated at 486.7 and 495.4 eV, which can be ascribed respectively to Sn 3d₅/₂ and Sn 3d₃/₂ configuration [24]. The XPS spectrum for O 1s can be deconvoluted into two peaks (Fig. S1d). The peaks situated at binding energy 530.4 and 531.8 eV are characteristics of O lattices of ZnO and SnO₂, respectively [32]. The XPS result reveals the presence of SnO₂ and ZnO species in the sample, which is tally with the result obtained from the XRD measurement. The BET measurements reveal the change of specific surface area of the ZnO sample before and after SnO₂ coating. Fig. S2a and b shows the N₂ adsorption/desorption isotherms of ZnO and ZnO@SnO₂ hybrid, respectively. Accordingly, the specific surface area of the ZnO@SnO₂ is measured to be 15.9 m² g⁻¹, almost 3.8 times higher than that of ZnO (4.1 m² g⁻¹). The higher surface area of the hybrid will provide more reaction sites for lithium storage, which is favorable to enhance the hybrid’s electrochemical performance.

The morphological and structural features of the hybrid were characterized using SEM and TEM. Fig. 3a and b shows the morphological features of ZnO sample. The synthesized ZnO exhibited a rod-like morphology with a relatively smooth surface without obvious defects such as breakages or branches. These rods have a typical length of 10–15 μm with diameter range of approximately 0.5–1 μm. Fig. 3c–f shows the gradually enlarged SEM images of the ZnO@SnO₂ hybrid. After the growth of SnO₂...
nanowires, the initial smooth ZnO microrods branched out, formed a hierarchical structure resembling the brushes with densely and uniformly distributed SnO2 nanowires as the bristles and ZnO microrods as the backbones. According to the high magnification SEM image in Fig. 3e, it is observed that the secondary nanowires self-organized into very regular arrays. A cross-section view of the ZnO@SnO2 hybrid displayed in Fig. 3f demonstrates that sixfold symmetric epitaxial growth of SnO2 nanowires with a length of ~500 nm on non-polarized planes of ZnO microrods can be realized. The reason for nanowire arrays to grow into six-fold symmetry should be arise from the hexagonal symmetry of the major core [33]. Fig. 4a shows a single ZnO@SnO2 brush used for EDS element mapping and spot scanning analyze. As revealed in element mapping images, the bright spots represent the positions of each element where red (Fig. 4b), blue (Fig. 4c), and yellow (Fig. 4d) indicate O, Sn, and Zn, respectively. These images clearly verify the homogenous distribution of the elements in the whole sample. And according to the EDS analyses, the Zn/Sn atomic ratio is 0.46.

The brush-like morphology of the ZnO@SnO2 heterojunction hybrid was further characterized by TEM. As displayed in Fig. 5a, the ZnO microrods can be densely coated by SnO2 nanowires. A single SnO2 nanowire shown in Fig. 5b demonstrates that the nanowire diameter is approximately 50 nm. Fig. 5c exhibits the HRTEM image of the SnO2 nanowire. The visible lattice fringe with an interplanar crystal spacing of 0.33 nm is assigned to the (110) plane of the SnO2. The inset FFT pattern in Fig. 5c shows diffraction spots, which is characteristic of monocristalline SnO2. According to the above characterization results, it is obvious that the brush-like ZnO@SnO2 heterojunction hybrid which integrated the wurtzite structure ZnO microrods with the rutile structure SnO2 nanowires has been constructed successfully during the hydrothermal routes.

The electrochemical reactions of the ZnO, SnO2, and ZnO@SnO2 hybrid electrodes were investigated by CV measurements. Fig. S3a presents the CV curves of ZnO electrode in the initial three cycles. In the first cathodic sweep, an obvious peak located at ~0.2 V was observed, which can be ascribed to the generation of a solid electrolyte interphase (SEI) membrane and the reduction of ZnO to Zn and the subsequent generation of LixZn alloys [34]. Due to the stabilization of the electrode, the cathodic peak shifts to a higher potential of ~0.6 V at the second and the third cycle. In the anodic sweeps, broad slightly peaks located at the potential range of 0.3-0.7 V were observed, which can be ascribed to the multistep delithiation process of LixZn alloys. The other obvious peak at ~1.4 V should be assigned to the regeneration of ZnO with the reaction between Zn and Li2O[35]. The CV result on the ZnO electrode implies that the electrochemical reactions are reversible (Eq. (1) and (2)). Fig. S3b presents the CV curves of SnO2 electrode in the initial three cycles. In the first cathodic sweep, a broad peak located at ~0.85 V was observed, which can be ascribed to the generation of a SEI membrane and the reduction of SnO2 to Sn. This cathodic peak
shifts to higher potential of ~1.0 V in the following sweeps. Except for the peak, a wide peak located between 0.1 and 0.5 V can also be found, which is assigned to the lithium alloying reactions with Sn to form Li$_y$Sn \[36\]. In the anodic sweeps, a large peak situated at ~0.7 V represents the dealloying reactions of the Li$_y$Sn. And a broad peak at the potential range of 1.0–1.5 V represents the regeneration of SnO$_2$ with the reaction between Sn and Li$_2$O \[37\]. The CV result on the SnO$_2$ electrode implies that the electrochemical reactions are reversible (Eq. (3) and (4)).

\[
\begin{align*}
\text{ZnO} + 2\text{Li}^+ + 2e^- & \rightarrow \text{Zn} + \text{Li}_2\text{O} \quad (1) \\
\text{Zn} + x\text{Li}^+ + xe^- & \rightarrow \text{Li}_x\text{Zn} \quad (0 < x \leq 1) \quad (2) \\
\text{SnO}_2 + 4\text{Li}^+ + 4e^- & \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \quad (3) \\
\text{Sn} + y\text{Li}^+ + ye^- & \rightarrow \text{Li}_y\text{Sn} \quad (0 < y \leq 4.4) \quad (4)
\end{align*}
\]

Fig. 6a shows the representative initial three CV curves of the ZnO@SnO$_2$ hybrid electrode at 0.1 mV s$^{-1}$ between a potential scope of 0 and 3.0 V (versus Li$^+$/Li$^-$). It appears like that the CV curves of the hybrid electrode were a superposition of the ZnO and SnO$_2$ CV curves. During the initial cathodic sweep, an intense peak situated at 0.85 V can be observed, which is related to the electrochemical lithium reactions with a multi-step procedure containing the reduction of SnO$_2$ to Sn (Eq.(3)), the decomposition reactions of the electrolyte as well as the formation of a SEI membrane \[28\]. Except for the strong peak, a wide peak located between 0.1 and 0.5 V can be observed, which should be assigned to the reduction of ZnO to Zn and the subsequent generation of Li$_x$Zn and Li$_y$Sn alloys, as described in Eqs.(1), (2) and (4) \[25\]. Owing to the developed reaction dynamics after the first cycle, the locations of the cathodic peaks move to ~1.0 V and ~0.6 V in the subsequent cycles. Throughout the first anodic sweep, two major peaks situated at ~0.7 and ~1.4 V were appeared. The former peak is attributed to the delithiation reactions of Li$_x$Zn and Li$_y$Sn, while the latter peak can be assigned to the regeneration of ZnO and SnO$_2$. There is a decrease in peak area between the first and the second cycle, implying a reduction in the discharge and charge capacities. However, the CV curves are overlapping with each other for the second and the third cycle, implying the electrode possesses a good reversibility. The charge/discharge profiles of the ZnO@SnO$_2$ electrode at a current density of 0.1 A g$^{-1}$ for the initial three cycles are shown in Fig. 6b. The recognizable plateaus in the discharge and charge curves are in accordance with the CV result, matching well with the reduction and alloying procedures to form Sn, Zn, Li$_x$Zn, and Li$_y$Sn, and the oxidation procedure to regenerate SnO$_2$ and ZnO, respectively.

The charge/discharge cycling properties of the ZnO, SnO$_2$, ZnO@SnO$_2$ electrodes are exhibited in Fig. 6c. The first cycle of ZnO@SnO$_2$ reveals discharge and charge capacities of 1193 and
1005 mAh g\(^{-1}\), respectively. And the initial discharge and charge capacities of ZnO (SnO\(_2\)) are found to be 767 (1138) and 614 (933) mAh g\(^{-1}\), respectively. Obviously, very high capacity losses were obtained among the three electrodes at the first cycle. The large irreversible capacities for the electrodes should be attributed to the nonreversible electrochemical reactions and the generation of SEI membrane on the electrode surface, which has been commonly observed for metal oxide electrode materials [38–40]. After the first cycle, The ZnO@SnO\(_2\) electrode delivers a slightly capacity decay within the initial several cycles. However, the electrode exhibits a high reversible capacity of 686 mAh g\(^{-1}\) after 150 cycles, with a capacity conservation rate of 68%. This value is in sharp contrast to those of the bare ZnO and SnO\(_2\), which show fast and continuous capacity decline during the cycling procedure. With the increase of the cycle number, the ZnO and SnO\(_2\) electrodes can exhibit a high irreversible capacity of 686 mAh g\(^{-1}\) after 150 cycles, with a capacity conservation rate of 68%. This value is in sharp contrast to those of the bare ZnO and SnO\(_2\), which show fast and continuous capacity decline during the cycling procedure. With the increase of the cycle number, the ZnO and SnO\(_2\) electrodes can exhibit poor reversible capacities of 223 and 315 mAh g\(^{-1}\), respectively. Obviously, the ZnO@SnO\(_2\) delivers a superior reversible capacity and a greater stability which outperform the bare ZnO and SnO\(_2\) electrodes. Additionally, as far as we know, the delivered cycling property of the brush-like ZnO@SnO\(_2\) hybrid is much higher than those of previously synthesized ZnO–SnO\(_2\) based electrode materials by electrospinning method [24–28]. A detailed comparison of the ZnO–SnO\(_2\) based anodes is summarized in Table 1.

In addition to the excellent capacity and stable cycling properties, the ZnO@SnO\(_2\) also exhibited a better rate performance than the single-phase ZnO microrod and SnO\(_2\) nanowire electrodes. Fig. 6d displays the comparative rate performance for the three electrodes at various test ampere densities from 100 to 1600 mAh g\(^{-1}\). It is found that the ZnO@SnO\(_2\) delivers the greatest reversible capacities at each current density. As the current rates enlarged inchmeal to 100, 200, 400, 800, and 1600 mAh g\(^{-1}\), the relevant average reversible capacities of the electrode achieve 917, 714, 608, 517, and 413 mAh g\(^{-1}\), respectively. In contrast, rate properties of ZnO (SnO\(_2\)) electrodes declined rapidly with average reversible capacities of 822 (465), 606 (266), 474 (194), 331 (121), 180 (66) mAh g\(^{-1}\), respectively. This may be attributed to the improved cycling capacity and rate capability of ZnO@SnO\(_2\) hybrid versus with the single-phase ones should be attributed to the impactful synergistic effect between both constituents.

EIS was performed on the electrodes of ZnO@SnO\(_2\) and ZnO to ascertain the relation between electrode kinetics and electrochemical properties. Fig. S4a records the Nyquist plots after the first cycle in the fully charged state over a frequency scope from 10\(^5\) to 10\(^{-2}\) Hz at voltage amplitude of 10 mV. Both two electrodes reveal similar EIS curve shapes comprising a depressed semicircle in the high frequency zone with a straight sloping line in the low frequency zone. A simplified equivalent circuit model was used to fit the EIS curves (inset in Fig. S4a). And the dynamics parameters were acquired from the model. In the circuit, R\(_f\) is the total resistance of electrolyte, electrode, separator, and current collector. R\(_t\) is the SEI membrane resistance, R\(_d\) is related to the charge-transfer resistance, and Z\(_w\) refers to the Warburg diffusion process of lithium ions [41]. The R\(_t\) values (~2 \(\Omega\)) of the two electrodes are roughly equal, implying that there is little difference derived from the contact and the electrolyte resistances at the interfaces between the electrode materials and the current collectors [42]. The R\(_d\) values are 98 and 183 \(\Omega\) for ZnO@SnO\(_2\) and ZnO electrodes,

![Fig. 6. (a) CV curves and (b) charge/discharge profiles of ZnO@SnO\(_2\) electrode, (c) cycling and (d) rate performance comparison for ZnO@SnO\(_2\), ZnO, and SnO\(_2\) electrodes.](image-url)
respectively. The much smaller \( R_{ct} \) value of ZnO@SnO2 suggests the improved conductivity of the electrode, which can facilitate a faster ion-transfer kinetics and higher electrochemical activity, and thus promote an enhanced lithium storage property. Fig. S4b describes the fitted straight line between \( Z' \) and \( \omega^{-1/2} \) (\( \omega = 2\pi f \)) in the low-frequency region. The ZnO@SnO2 electrode (40.2) exhibits much lower slope than that of ZnO electrode (78.5), implying facile Li\(^+\) kinetics and enhanced ion diffusion of the former. The better Li\(^+\) diffusivity of ZnO@SnO2 electrode could lead to an improved lithium storage capability. Fig. S4c records the Nyquist plots of ZnO and ZnO@SnO2 electrodes after the 100th cycle in the fully charged state. Fitting by the equivalent electrical circuit, the \( R_{ct} \) values of the two electrodes after 100 cycles slightly increase (110 \( \Omega \) for ZnO, and 206 \( \Omega \) for ZnO@SnO2) when compared with the values obtained in Fig. S4a. Such a result implies that the two materials maintains a stable electrode structure after the multiple discharge and charge procedures [43].

The electronic structure, work function and charge transfer mechanism of ZnO/SnO2 heterojunction hybrid were studied by using first-principles calculations through DFT method to understand the excellent lithium storage performance of ZnO@SnO2 hybrid. The band structures of SnO2 and ZnO are shown in Fig. 7. SnO2 and ZnO have theoretical direct band gaps (3.03 eV for SnO2 and 2.76 eV for ZnO) where the bottom of conduction band (CB) and the top of valence band (VB) are both located at \( \Gamma \) point. The contributions of different atoms for the VBs and CBs were evaluated by calculating the partial density of states (PDOS) and the total density of states (TDOS) (Fig. 8). As displayed in Fig. 8a, c, and e, the top of VBs (−5 to 0 eV) for ZnO are mostly originating from the Zn 3d and O 2p states, the lower VBs (−6.8 to −5 eV) are mostly originating from the Zn 3d and O 2p states, and the bottom of CBs are dominantly constructed by the Zn 4s states. Accordingly, the upper VBs electrons of ZnO are easily to be excited due to low hybridization between Zn 3d and O 2p states (−5.0 to 0 eV), Fig. 8b, d, and f shows the TDOS and PDOS of SnO2. The top of VBs (−1.5 to 0 eV) for SnO2 are mainly comprised of O 2p states with partial donation of Sn 4d states. The middle VBs (−5.5 to −1.5 eV) are mainly comprised of Sn 4d and O 2p states. The lower VBs are dominantly constructed by the Sn 5s and O 2p states. The bottom of CBs is formed by Sn 5s and O 2p states. Whereas there are powerful hybridization effects between O 2p states and Sn 4d (in the range of −1.5 to 0 eV) and 5p states in VBs (in the range of −5.5 to −1.5 eV). Therefore, the electrons of VBs are difficult to be excited. The above results indicated that the charge carriers are easy to leak from ZnO to SnO2.

The work functions of ZnO, SnO2, and ZnO@SnO2 heterojunction hybrid as well as their charge density difference are shown in Fig. 9. The work functions of them are calculated to be 5.17 (ZnO), 4.86 (SnO2), and 4.96 (ZnO@SnO2) eV. Obviously, the work function value of ZnO is higher than that of SnO2, the electrons thus will flow from ZnO to SnO2 through ZnO@SnO2 heterojunction, and the holes will flow from SnO2 to ZnO till the Fermi energy of ZnO@SnO2 are equivalent. The ZnO accumulates more positively charges, while the SnO2 accumulates more negatively charges close to the interface of the SnO2@ZnO hybrid. This result is illustrated by the diverse charge density as depicted in Fig. 9d. In this case, the pale green and pale yellow areas demonstrate electron accumulation and depletion, respectively. Charge redistribution are founded near the interface of ZnO@SnO2 heterostructures. It is indicated that the covalent interaction was occurred between the interface of SnO2 and ZnO to generate the stabilized heterojunction. And the results indicate that the electrons migrate from ZnO to SnO2, while the holes migrate from SnO2 to ZnO during the heterojunction generated over the interface of ZnO and SnO2. This leads to the positive space charge zone on the ZnO side, and the negative space charge zone on the SnO2 side (Fig. S5). The amassing of net charge results

### Table 1
Comparison of electrochemical performance of the ZnO–SnO2 based anodes.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Synthetic method</th>
<th>Current density (A g(^{-1}))</th>
<th>Specific capacity (mAh g(^{-1}))</th>
<th>Cycle number</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO@SnO2</td>
<td>Hydrothermal method of 200 °C</td>
<td>0.1</td>
<td>686</td>
<td>150</td>
<td>This work</td>
</tr>
<tr>
<td>ZnO–SnO2 fibers</td>
<td>Electrosprining method with subsequent 500 °C calcination</td>
<td>0.08</td>
<td>521</td>
<td>120</td>
<td>[24]</td>
</tr>
<tr>
<td>ZnO–SnO2 fibers</td>
<td>Electrosprining method with subsequent 700 °C calcination</td>
<td>0.1</td>
<td>560</td>
<td>100</td>
<td>[25]</td>
</tr>
<tr>
<td>ZnO–SnO2 fibers</td>
<td>Electrosprining method with subsequent 700 °C calcination</td>
<td>0.1</td>
<td>430</td>
<td>20</td>
<td>[26]</td>
</tr>
<tr>
<td>ZnO–SnO2 fibers</td>
<td>Electrosprining method with subsequent 600 °C calcination</td>
<td>0.05</td>
<td>588</td>
<td>100</td>
<td>[27]</td>
</tr>
<tr>
<td>ZnO–SnO2 films</td>
<td>Electron beam evaporation with subsequent 500 °C calcination</td>
<td>0.05</td>
<td>450</td>
<td>42</td>
<td>[28]</td>
</tr>
</tbody>
</table>

Fig. 7. Electronic band structures of (a) ZnO and (b) SnO2.
in the generation of an internal electric field over the interface. It facilitates the disjunction of electron/hole pairs, decreases the odds of carrier recombination. The electron potential in the space charge zone changes due to the generation of the internal electric field, which conducts to the energy band bending and promotes the electrons migrate from the CB of ZnO to the CB of SnO$_2$ easily. Simultaneously, the facile migration of holes from the VB of SnO$_2$ to the VB of ZnO can be realized. The mobility rate of electrons and holes thus can be improved, which is favorable for achieving large current charge/discharge capability to amend the cycling and rate capabilities of the hybrid.

4. Conclusions

ZnO@SnO$_2$ hybrid with a unique test-tube brush-like structure has been produced successfully by using a simple hydrothermal technique. The characterization results indicated that sixfold symmetric epitaxial growth of SnO$_2$ nanowires on non-polarized
planes of ZnO microrods can be grown through the approach. When utilized as a LIB anode, the ZnO@SnO2 electrode delivered a superior reversible capacity (686 mAh g\(^{-1}\) after 150 cycles) and a greater stability together with high rate capability which outperform the bare ZnO and SnO\(_2\) electrodes. Experimental and theoretical calculation results demonstrated that the excellent electrochemical properties of the heterojunction hybrid were ascribed to the synergistic effect of the respective components. The construction of ZnO@SnO\(_2\) heterojunctions can not only provide facile Li\(^+\) kinetics and enhanced ion diffusion, but also improve the mobility rates of holes and electrons with the formation of the internal electric field.

**Author contribution statement**

Gang wang and Fuchun Zhang supervised the research. Panpan Xu designed the synthesis method and constructed the ZnO@SnO\(_2\) hybrid. Junfeng Yan performed the first-principle calculations. Sifan Chen, Wu Zhao, and Zhiyong Zhang measured the electrochemical cycling performance. Zhouhu Deng, Manzhang Xu, Jiangni Yun, and Yunyao Zhang conducted sample characterizations. All authors participated in analysis of the experimental data and discussions of the results, as well as editing the manuscript. Junfeng Yan and Panpan Xu contributed equally to this work.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.135312.

**References**


Fig. 9. Electrostatic potential graphs of (a) SnO\(_2\), (b) ZnO and (c) ZnO@SnO\(_2\). The grey, blue, and red spheres represent Zn, Sn, and O atoms, respectively. (d) The difference charge density of ZnO@SnO\(_2\). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)