Synthesis of Polyvinylpyrrolidone-Stabilized Nonstoichiometric SnO₂ Nanosheets with Exposed {101} Facets and Sn(II) Self-Doping as Anode Materials for Li-Ion Batteries

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Abstract. Engineering of facet exposure, nonstoichiometric defects and morphology are the key parameters affecting the SnO₂ performance. Development of synthetic procedures enabling to control all these variables in one pot towards enhanced storage performance is a big challenge. Herein we report such a facile microwave hydrothermal preparation of 3D hierarchical architecture assembled from single-crystalline nonstoichiometric SnO₂ (denote as SnO_{2-δ}) nanosheets with self-doped Sn²⁺ and controllably exposed {101} facets. Polyvinylpyrrolidone (PVP) is used as capping agent allowing to stabilize the ultrathin and ultra-large SnO_{2-δ} nanosheets and avoid their dissolution in the highly alkaline environment due to the introduction of highly concentrated NaOH, which together with PVP contribute to the formation of nanosheet morphology with preferential growth plane (121) and dominant reactive {101} surfaces. The detailed structural characteristics are examined by XRD, SEM, TEM, FTIR, XPS and Mössbauer spectroscopy, revealing that SnO_{2-δ} contains 17 at.% of Sn²⁺ dopant. These nonstoichiometric SnO_{2-δ} hierarchical architectures capped with carbonized PVP manifest superior lithium storage properties compared with the stoichiometric SnO₂, owing to the novel open hierarchical structure composed of flexible and ultrathin nanosheets with large surface area (82 m²/g) and carbon-coating, which avoid the aggregation and provide porous channels facilitating the diffusion of electrolyte and lithium ions.

Keywords: hierarchical architecture, PVP-stabilizing, exposed {101} facets, Sn(II) self-doping, electrochemical properties

Introduction

Tin dioxide (SnO_2) is an important n-type semiconducting metal oxide with coexistence of conductivity and transparency owing to its natural nonstoichiometry such as tin interstitial and oxygen vacancies,[1] which has been widely used in transparent conducting films,[2, 3] gas sensors,[4-6] lithium ion batteries,[7-10] and solar cells.[11-13] Thus, synthesis of SnO_2 nanostructures with well-defined morphologies, highly reactive surfaces and tunable nonstoichiometric defects have attracted intense research interests due to their shape, size, surface and composition dependent properties.[14-16] Until now, a number of SnO_2 nanostructures have been fabricated such as 0D nanoparticles,[17] 1D nanorods,[18] nanowires[19] and nanotubes,[20] 2D nanosheets,[21] and their high-dimensional hierarchical architectures with hollow or mesoporous structures.[5, 22, 23] Among these different morphologies, 3D hierarchical nanostructures normally assembled from low-dimensional nanosized building blocks offer additional novel physical and chemical properties, especially those constructed by 2D SnO_2 nanosheets with a large percentage of reactive facets exposed. Hierarchical SnO_2 architectures assembled from 2D nanosheets have been widely reported by treating $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in basic solutions (ex. NaOH , $\text{NH}_3 \cdot \text{H}_2\text{O}$, NaF , NH_4F , etc.) via solvo/hydrothermal method.[4, 21-26] However, nonstoichiometric defects and facet control were rarely investigated. On one hand, the use of divalent tin source could unavoidably result in the formation of SnO or self-doping of Sn^{2+} , which greatly affects the electrical and optical properties, and this phenomenon has not been thoroughly investigated. On the other hand, the as-prepared SnO_2 nanosheets were usually polycrystalline. Therefore, synthesis of single-crystalline SnO_2 nanosheets with certain facet exposed, pure phase and defect control is still a challenge.

It is known that surfaces with high reactivity usually diminish rapidly during crystal growth to minimize the total surface energy. The surface energies of SnO_2 facets follow the trend of $(110) < (100) < (101) < (001)$, promoting the growth in the $[001]$ direction faster, which leads to the formation of surfaces enclosed by the thermodynamically most-stable $\{110\}$ planes in order to maintain the lowest surface energy.[27] However, surface energy can be strongly affected by the foreign ions adsorbed on the crystal faces.[28] Considerable efforts have been devoted to their kinetic and thermodynamic control by using foreign adsorbate atoms to attach on specific facets of metal oxides, in order to prevent their growth along that particular direction, and a few achievements have been made on the aspect of facet engineering of SnO_2 . [4, 29, 30] Wang *et al.*[4]

demonstrated that the relative stability of SnO₂ facets can be changed by coupling with F ions using NaF as fluorine source and fabricated SnO₂ nanosheets with exposed high-index {102} or {113} facets, which can be selectively regulated by controlling the fluorine concentration when using SnCl₂·2H₂O as tin source. Moreover, the effect of Sn²⁺ self-doping and the resultant oxygen vacancies on the electronic structure of SnO₂ was investigated via the density functional theory (DFT) calculations, which demonstrated the influence on the optical and gas sensing properties. Sun *et al.*[30] prepared atomic-layer-thick SnO₂ sheets with exposed {001} facets by the chemical reaction between SnCl₂·2H₂O and ethylenediamine in sealed autoclave, suggesting that ethylenediamine prefers to adsorb on the most reactive {001} facet and makes {001} the most stable. Han *et al.*[29] prepared octahedron shaped SnO₂ nanoparticles with exposed high-index {221} facets by hydrothermally treating SnCl₄·5H₂O with the help of the coordinative/adsorption effect of HCl and polyvinyl pyrrolidone (PVP).

Herein, we report the successful synthesis of hierarchical architectures composed of ultrathin, ultra-large, single-crystalline and nonstoichiometric SnO_{2-δ} nanosheets by microwave hydrothermal route using SnCl₂·2H₂O as tin source and Sn²⁺ dopant, NaOH and PVP as controlling and stabilizing agents. The nonstoichiometric defect of SnO_{2-δ} was investigated by Mössbauer spectroscopy, and the surface characteristics were investigated by HRTEM, XPS and FTIR analysis, revealing that SnO_{2-δ} nanosheets with large amount of Sn²⁺ doping (~17 at.%) were exposed dominantly with reactive {101} facets owing to the crystal growth directing effect of NaOH and facet stabilization effect of PVP. When used as anode materials for lithium ion batteries, the nonstoichiometric SnO_{2-δ} demonstrated enhanced lithium storage properties with improved cycle performance as compared with its stoichiometric SnO₂ counterpart.

Experimental Section

Materials Preparation. All chemicals including tin(II) chloride dehydrate (SnCl₂·2H₂O, Sigma-Aldrich), sodium hydroxide (NaOH, Sigma-Aldrich), and polyvinylpyrrolidone (*Abbr.*: PVP; *Formula*: (C₆H₉NO)_n; *M_w*~10000 g/mol, Sigma-Aldrich) were used as received. A microwave-hydrothermal reactor (XH-800S-10, Beijing Xiang-Hu Reagent Co., Ltd.) was used for the materials preparation. In a typical synthesis, 0.677g of SnCl₂·2H₂O, 0.57g of NaOH and 3.5g of PVP were mixed in 30 mL distilled water forming a translucent precursor solution, which was then transferred to a 100 mL reaction tank and hydrothermally treated at 160°C for 90 min under microwave radiation. After cooling to room temperature, the brown precipitate was collected and washed with distilled water and ethanol for several times until the pH value was close to 7. Dilute HCl aqueous solution (0.1M) was also used to neutralize the excessive NaOH in

the solution. Finally, the product was dried at 90°C overnight. In this work, the as-prepared product was denoted as nonstoichiometric $\text{SnO}_{2-\delta}$. As comparison, stoichiometric SnO_2 was prepared by annealing nonstoichiometric $\text{SnO}_{2-\delta}$ in air at 600°C for 2h, in order to demonstrate the effect of Sn^{2+} and carbonized-PVP-capping on the lithium storage properties. Besides, parallel experiments were also carried out in order to understand the formation mechanism of nonstoichiometric $\text{SnO}_{2-\delta}$ nanosheets with {101} facets, and detailed reaction parameters were given in the main text where they were mentioned.

Materials Characterization. Powder X-ray diffraction (XRD) patterns of the products were recorded on a Rigaku SmartLab diffractometer using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) with an operating voltage of 40 kV and a current of 30 mA. Scanning electron microscopy (SEM) was performed in a FEI Quanta 250F SEM. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out by JEOL JEM2100 TEM operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was employed to determine the surface composition and chemical states of the products, using a Physical Electronics PHI-5802 equipped with a monochromatic Al K α X-ray source in an ultra-high vacuum environment. All the binding energies were calibrated with the reference C 1s peak at 284.6 eV from the surface adventitious carbon. The room-temperature ^{119}Sn Mössbauer spectra were collected in a constant acceleration mode with an $^{119\text{m}}\text{Sn}$ γ -ray source (185 MBq) in a CaSnO_3 matrix. The calibration of the velocity axis was performed at room temperature employing α -Fe foil as an absorber and $^{57}\text{Co(Rh)}$ as a γ -ray source (1.85 GBq). The isomer shift values are reported with respect to BaSnO_3 at room temperature. Mössbauer spectra were fitted by the Lorentz functions using the MossWinn computer program. Fourier transform infrared spectroscopy (FTIR) was employed to determine PVP using a Perkin-Elmer Spectrum One FTIR Spectrometer using KBr discs in the range of 4000-500 cm^{-1} . The specific surface area of the products was measured by nitrogen adsorption-desorption isotherms at 77 K according to the Brunauer-Emmett-Teller (BET) method by using an Autosorb iQ-MP Surface Area and Pore Size Analyzer (Quantachrome Instruments).

Electrochemical Characterization. Electrochemical measurements were performed using CR2025 coin-type cells assembled in an Ar-filled glove-box with both H_2O and O_2 content less than 1.0 ppm. The working electrode was prepared by spreading a mixture of 70 wt% $\text{SnO}_{2-\delta}$ powder, 20wt% acetylene black and 10 wt% polyacrylic acid (PAA, Mw=100000, Sigma-Aldrich) on a copper foil current collector. Lithium foil was used as the counter electrode and a Celgard 2400 microporous membrane as a separator. An electrolyte composed of 1 M LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate (1 : 1 in volume) was used. Galvanostatic cycling tests of the cells were carried out on a battery test system (Neware BTS, Neware Technology Co., Ltd., China) in the range of 0.01-2.0 V (vs. Li/Li^+) at 25°C. Cyclic voltammetry (CV) was carried out using

electrochemical station (Autolab PGSTAT 302N) in the range of 0.01-2.5V at a scan rate of 0.2 mV/s. Specific capacity was reported based on the mass of SnO₂ active materials.

Results and Discussion

Nonstoichiometric SnO_{2-δ} hierarchical architectures composed of ultrathin nanosheets with dominant {101} facets have been successfully synthesized through a microwave-assisted hydrothermal reaction between SnCl₂·2H₂O and NaOH in the presence of PVP as stabilizing agent (Fig. 1, 2). Fig. 1a shows the typical XRD pattern of the as-prepared product, which can be indexed to the tetragonal phase of SnO₂ (JCPDS No. 41-1445).[25, 30] In order to reveal the nonstoichiometry of the product, Mössbauer spectroscopy was performed to determine the presence and the relative content of Sn²⁺ and Sn⁴⁺. Fig. 1b displays the room-temperature ¹¹⁹Sn Mössbauer spectrum, revealing the nonstoichiometric nature of the as-prepared product. The atomic ratio between Sn⁴⁺ and Sn²⁺ is calculated to be 83:17. The values of the Mössbauer hyperfine parameters of the Sn²⁺ component (i.e., the isomer shift, $\delta = 2.53$ mm/s, quadrupole splitting, $\Delta E_Q = 1.96$ mm/s, and linewidth, $\Gamma = 1.21$ mm/s) are typically observed for Sn²⁺ ions occupying low coordination sites in the surface layers. If the recoil-free fraction for Sn²⁺ and Sn⁴⁺ is assumed to be identical in the SnO_{2-δ} structure, the level of non-stoichiometry can be assessed, giving a chemical formula of SnO_{1.83}.

Fig. 1. (a) XRD pattern and (b) room-temperature ¹¹⁹Sn Mössbauer spectrum of nonstoichiometric SnO_{2-δ} hierarchical architectures.

Fig. 2. (a, b) SEM images of nonstoichiometric $\text{SnO}_{2-\delta}$ hierarchical architectures. (c) TEM image of the nanosheet building blocks and corresponding (d) selected area electron diffraction (SAED) pattern. (e) Top-view and (f) cross-section view HRTEM images from single nanosheets.

SEM images show that the $\text{SnO}_{2-\delta}$ product consists of spherical particles with uniform sizes of 3-5 μm , which are hierarchically assembled from the flexible nanosheets (Fig. 2a, b). Moreover, the powder shows yellow color (inset of Fig. 2a, denote as *yellow $\text{SnO}_{2-\delta}$*), indicating the self-doping of Sn^{2+} and thus resultant narrowing of the bandgap, which has been investigated in detail in the previous work.[4] TEM image reveals that the leaf-like nanosheets have length of several hundreds of nanometers and apparent tips with angle of about 80° (Fig. 2c). Fig. 2d shows the SAED pattern of a typical nanosheet which lies flat on the ultrathin carbon film as displayed in Fig. 2c. There is only one set of diffraction spots in the pattern, indicating the single crystalline nature of the nanosheet. The pattern is indexed with tetragonal rutile SnO_2 , and the direction of the electron beam is along the $[101]$ zone axis. Because the normal of (101) plane is only a few degrees away from the $[101]$ direction and the nanosheet is very thin, we may conclude that the dominant surfaces of the nanosheets are parallel to (101) . The growth fronts of the nanosheet as indicated by dark lines in Fig. 2c are parallel to $(12\bar{1})$ and $(\bar{1}21)$, as the TEM image (Fig. 2c) and diffraction pattern (Fig. 2d) are correlated. It also should be noted that the crystal structure is not perfect tetragonal rutile SnO_2 . There are additional spots (or superstructure reflections) in Fig. 2d and the observed lattice spacings are relatively larger than those of stoichiometric rutile SnO_2 , indicating the nonstoichiometric nature of the as-prepared product due to the presence of large amount of Sn^{2+} and the resultant oxygen vacancies.[4] The superstructure reflections at the $\frac{1}{2}$ positions of $(12\bar{1})$ and $(\bar{1}21)$ correspond to the lattice spacing of 0.36 nm which is two times as

much as that of (121) plane. These larger lattice spacings can be readily observed in HRTEM images. Fig. 2e is the typical plan-view HRTEM image of a nanosheet and clearly shows two sets of lattice fringes with the same lattice spacing of 0.36 nm, indicating that the image zone axis [101] is approximately parallel to the normal of nanosheet surface (101). In addition, the angle between the two sets of lattice fringes with the lattice spacing of 0.36 nm is measured as about 80°, which further support the conclusion of SAED pattern analysis, that is, the growth fronts of the nanosheet are parallel to (12 $\bar{1}$) and (1 $\bar{2}$ 1). It is difficult to measure the thickness of the nanosheets because the sheets normally lie flat on the carbon film of TEM grid, but occasionally the sheets may be folded over at the edge, which enables us to observe the cross-section of the nanosheet. The HRTEM image Fig. 2f shows the cross-section of a single nanosheet, where the lattice fringes have an interplanar spacing of 0.27 nm which corresponds to the (101) plane of rutile SnO₂. The thickness measured from Fig. 2f is about 4 nm.

Fig. 3. FTIR spectra of (a) pure PVP, (b) nonstoichiometric SnO_{2- δ} hierarchical architectures and (c) the stoichiometric SnO₂ counterpart after annealing in air at 600°C.

Fourier transform infrared spectroscopy (FTIR) was used to detect the interaction between PVP and the as-prepared SnO_{2- δ} product. As shown in Fig. 3, the prominent peaks at around 3450 cm⁻¹ and 1650 cm⁻¹ are present in all the three samples, which can be ascribed to the OH stretching vibration modes and the bending vibrations of absorbed molecular water on the sample surfaces,

respectively.[31, 32] The broad peak at around 2900 cm^{-1} and a series of peaks in the range of $1000\text{--}1500\text{ cm}^{-1}$ can be ascribed to PVP, and these peaks can still be observed but become much less prominent in the $\text{SnO}_{2-\delta}$ product (Fig. 3b), indicating the coupling effect of PVP on the $\text{SnO}_{2-\delta}$ product. After annealing at $600\text{ }^{\circ}\text{C}$ in air, the nonstoichiometric $\text{SnO}_{2-\delta}$ becomes stoichiometric SnO_2 (denote as *white SnO₂*) with color changing from yellow to white (Fig. S1) and Sn^{2+} species oxidized into Sn^{4+} (Fig. S2). Consequently, an apparent peak at 640 cm^{-1} appears in the annealed sample, which relates to the Sn–O stretching modes of Sn–O–Sn in the crystalline SnO_2 . [26] The XRD pattern further reveals that the annealed sample is highly crystalline and can be indexed to the tetragonal rutile of SnO_2 (JCPDS No. 41-1445) (Fig. S3). However, this typical peak at 640 cm^{-1} does not appear in the $\text{SnO}_{2-\delta}$ product but shifts to around 500 cm^{-1} , owing to the terminal oxygen vibration of Sn–OH.[33]

Fig. 4. Comparison of XPS spectra of nonstoichiometric $\text{SnO}_{2-\delta}$ (black lines) and the stoichiometric SnO_2 counterpart (red lines). (a) C1s, (b) N1s, (c) Sn3d and (d) O1s. All the binding energies were calibrated with the reference C 1s peak at 284.6 eV from the surface adventitious carbon.

To further reveal the surface characteristics of the $\text{SnO}_{2-\delta}$ and its SnO_2 counterpart, XPS analysis was performed (Fig. 4). In Fig. 4a, the main peak at 284.6 eV relates to the sp^2 hybridized C from the surface adventitious carbon. Besides, an additional broad peak centered at around 287.1 eV in

$\text{SnO}_{2-\delta}$ is assigned to the sp^3 C atoms bonded to N atoms,[34] and the XPS spectrum clearly shows a peak at around 399.0 eV (Fig. 4b), confirming the presence of N elements. However, both peaks disappear after annealing the $\text{SnO}_{2-\delta}$ product, indicating that they come from the adsorbed PVP molecules ($(\text{C}_6\text{H}_9\text{NO})_n$) or their C/N/O-based derivate which is due to the carbonization of PVP during the microwave hydrothermal reaction. Fig. 4c and d compare the Sn3d and O1s XPS spectra of the nonstoichiometric $\text{SnO}_{2-\delta}$ and its stoichiometric SnO_2 counterpart. Due to the overlapping of Sn^{2+} and Sn^{4+} peaks, the Sn3d peak at 486.6 eV and O1s peak at 530.5 eV in the SnO_2 sample are assigned to the $\text{Sn}3d_{5/2}$ with dominated Sn^{4+} oxidation state and the typical metal-oxygen bonds (Fig. 4c, d), respectively. In contrast, the $\text{Sn}3d_{5/2}$ peak in the $\text{SnO}_{2-\delta}$ product shows apparent shift to lower binding energy of 485.9 eV (Fig. 4c), indicating the major contribution of Sn^{2+} on the shift. In addition, the O1s peak shifting to 529.8 eV indicates the oxygen ions are in low coordination at the surface (Fig. 4d), leading to the nonstoichiometric defects in the $\text{SnO}_{2-\delta}$ nanosheets.[4, 24] Moreover, the binding energy shift of around 0.7 eV between Sn^{4+} and Sn^{2+} is quite close to that in the previous report.[24]

Due to the large amount of Sn^{2+} (~17 at.%) in $\text{SnO}_{2-\delta}$ product, the structural stability has become a major concern. On one hand, oxygen vacancies will be produced to maintain the charge balance, which is due to the limited oxygen content in the sealed hydrothermal reaction system. On the other hand, the coupling effect of PVP or its derivate (most properly the C/N/O-based compound) might play the important role on stabilizing the nonstoichiometric $\text{SnO}_{2-\delta}$ nanosheets. As a clear evidence, the amorphous carbon spheres was produced in the solution after hydrothermal reaction, and Fig. 5a shows the amorphous spheres with size ranging from several to tens of nanometers, which evolve into porous spheres composed of crystallized SnO_2 nanoparticles under successive electron-beam irradiation in the TEM mode, and the lattice spacing can be indexed to the (110) plane of rutile SnO_2 (Fig. 5b). This result indicates the mutual interaction between PVP and Sn ions and the formation Sn-C-O-based compound via carbonization under microwave irradiation, indirectly verifying the stabilization and capping effect of carbonized PVP in the $\text{SnO}_{2-\delta}$ product. Moreover, it is noted that these amorphous carbonized spheres only appear in the solution, which cannot be collected by centrifugation even at a higher speed (up to 50000 r/min). As a result, the nonstoichiometric $\text{SnO}_{2-\delta}$ nanosheets can be easily separated from these carbon-based spheres by repeated washing with water through centrifugation.

Fig. 5. (a) TEM image of C-O-Sn-contained nanospheres and (b) HRTEM image of a crystallized SnO_2 nanosphere obtained by successive irradiation on the sphere in (a) using electron-beam in the TEM mode. Insets of (a) and (b) illustrate the morphology change upon successive irradiation. Upper inset of (a) shows the color change of PVP aqueous solution before and after hydrothermal reaction under irradiation, indicating the carbonization of PVP.

Additional experiments were carried out to investigate the formation mechanism of the ultrathin, ultra-large nonstoichiometric $\text{SnO}_{2-\delta}$ nanosheets with exposed $\{101\}$ facets and their hierarchical assembly into spherical architectures. As comparison, mesoporous SnO_2 nanospheres composed of randomly oriented nanoparticles were obtained by hydrothermally treating 0.1M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in distilled water at 160°C for 90min under microwave irradiation (Fig. S4). After introduction of excessive NaOH (the molar ratio of NaOH to $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is 5/1), irregular SnO_2 aggregates composed of nanosheets were produced (Fig. S5a, b), but the yield is very low (<10 wt.% of the theoretical yield) owing to the corrosion effect of the highly alkaline solution by forming $\text{Sn}(\text{OH})_6^{2-}$ ions.[11, 35] Room-temperature ^{119}Sn Mössbauer spectrum reveals the presence of 11 at.% of Sn^{2+} (Fig. S5c), and the XRD pattern can be indexed to the tetragonal rutile of SnO_2 (JCPDS No. 41-1445) (Fig. S5d). The HRTEM image taken from the cross-section of a single nanosheet reveals the lattice spacing of 0.27 nm (Fig. S6), which can be indexed to $\{101\}$ facets of SnO_2 , indicating the exposure of $\{101\}$ surface of the SnO_2 nanosheets. The results show that the highly alkaline environment is the key parameter for the formation of 2D nanosheets and their exposure of $\{101\}$ facets. However, the dimensions of nanosheets produced in the absence of PVP are much smaller than that of PVP-stabilized $\text{SnO}_{2-\delta}$ nanosheets. The effect of PVP amount was also investigated by increasing from 0.5 g to 7.0 g (Fig. S7), confirming that PVP can regulate the uniformity of the as-produced $\text{SnO}_{2-\delta}$ hierarchical aggregates and greatly improve the yield to >80 wt.%. Moreover, the specific surface area of $\text{SnO}_{2-\delta}$ can be greatly increased to $82 \text{ m}^2/\text{g}$ when PVP was introduced during the synthesis, much larger than that of without PVP (only $31 \text{ m}^2/\text{g}$) (Fig.

S8).

Fig. 6. (a) TEM image of the black $\text{SnO}_{2-\delta}$ product obtained after annealing the as-prepared nonstoichiometric $\text{SnO}_{2-\delta}$ hierarchical architectures (namely the *yellow* $\text{SnO}_{2-\delta}$) at 450°C for 2h in N_2 . (b) High-magnification TEM image of the nanosheets and (c) HRTEM image taken from the cross-section of single $\text{SnO}_{2-\delta}$ nanosheets with inset showing the black powder.

To further verify and utilize the capped PVP or its carbonized derivate (Fig. 6), we annealed the as-prepared $\text{SnO}_{2-\delta}$ hierarchical architectures under inert atmosphere in order to avoid the oxidation of Sn^{2+} species, and found that the yellow powder became black after annealing at 450°C for 2h in N_2 (denote as *black* $\text{SnO}_{2-\delta}$; Fig. 2a vs. 6c). Fig. 6a shows that the black $\text{SnO}_{2-\delta}$ product maintains the hierarchical architectures composed of nanosheets, which display no apparent change of the sheet-like morphology (Fig. 6b). Furthermore, the HRTEM image taken from the cross-section of single nanosheets reveals the lattice spacing of 0.27 nm (Fig. 6c), indicating the exposed surface can be indexed to (101) facet. However, no apparent carbon coating on the nanosheet surface is observed, possibly due to the ultrathin carbon coating in the atomic scale (or carbon-doping).

The electrochemical properties of the as-prepared nonstoichiometric $\text{SnO}_{2-\delta}$ with carbonized-PVP capping (denote as *yellow* $\text{SnO}_{2-\delta}$) and its black $\text{SnO}_{2-\delta}$ counterpart obtained by annealing yellow $\text{SnO}_{2-\delta}$ in N_2 (denote as *black* $\text{SnO}_{2-\delta}$) were investigated in view of their potential application as anode materials for lithium ion batteries. Fig. 7a compares the initial two cycles of CV curves of the yellow and black $\text{SnO}_{2-\delta}$ electrodes, which show similar profiles. In the first cycle, both electrodes display two broad reduction peaks: one in the range of 0-0.25 V can be ascribed to the Li-Sn alloying process ($\text{Sn} + x\text{Li}^+ + xe^- \rightarrow 4\text{Li}_x\text{Sn}$, $0 \leq x \leq 4.4$),[36] while the

another reduction peaks at around 1.0 V are different from the previous reports,[25, 36] which may correspond to the formation of electrolyte interphase (SEI) and the reduction of $\text{SnO}_{2-\delta}$ into metallic Sn and Li_2O . [37] This peak disappears in the subsequent cycles, indicating the reaction is irreversible. In the anodic process, the oxidation peak at around 0.57 V in both electrodes can be ascribed to the dealloying of Li_xSn . Besides, the broad peaks at about 1.2 and 1.8 V are due to the re-oxidation of freshly produced metallic Sn grains in the Li_2O matrix.[38, 39]

Fig. 7. Electrochemical properties of the as-prepared yellow $\text{SnO}_{2-\delta}$ and its black $\text{SnO}_{2-\delta}$ counterpart. (a) Cyclic voltammogram (CV) curves at a scan rate of 0.2 mV/s in the range of 0.01-2.0 V. (b, c) Initial galvanostatic discharge-charge profiles of at a current density of 400 mA/g in the range of 0.01-2.0 V. (d) The comparative cycle performance of the yellow and black $\text{SnO}_{2-\delta}$ electrodes at a current density of 400 mA/g, and that of $\text{SnO}_{2-\delta}$ with no PVP (no PVP was introduced during synthesis) and the white SnO_2 (obtained after annealing yellow $\text{SnO}_{2-\delta}$ in air) at a lower current density of 100 mA/g, in the range of 0.01-2.0 V.

Fig. 7b and c display the voltage profiles of the yellow $\text{SnO}_{2-\delta}$ and black $\text{SnO}_{2-\delta}$ electrodes, and both show broad plateau at around 1.0 V, which disappears in the subsequent discharge-charge cycles. This result indicates that the electrodes undergo irreversible reactions, which are consistent with the CV measurements. Initial discharge/charge capacities are 1095/676 and 1370/904 mA h/g

for the yellow $\text{SnO}_{2-\delta}$ and black $\text{SnO}_{2-\delta}$ electrodes, respectively, which give corresponding initial Coulombic efficiencies of ~62% and ~66%. The subsequently Coulombic efficiencies increase from 2nd cycle onward and maintain high values of > 90% (Figure S9), indicating the high reversible of lithium insertion-extraction. Interestingly, the charge capacities in both electrodes increase in the following cycles, indicating the successive activation of the electrode materials, which are also revealed by the CV measurements (Fig. 7a). Fig. 7d compares the cycle performance of the two electrodes cycled at a current density of 400 mA/g in the range of 0.01-2.0 V. Obviously, the black $\text{SnO}_{2-\delta}$ electrode demonstrates the better cycle performance, exhibiting a discharge capacity of 616 mA h/g after 60 cycles, which is much higher than that of yellow $\text{SnO}_{2-\delta}$ electrode (493 mA h/g). As compared with the 3D Sn^{2+} self-doped (8 at.%) and 1D $\text{Sn}^{2+}/\text{Ti}^{4+}$ co-doped (12 at.%) $\text{SnO}_{2-\delta}$ hierarchical nanostructures in our previous report,[36] both yellow and black $\text{SnO}_{2-\delta}$ electrodes demonstrate much better cycle performance, which can be mainly attributed to the increased specific surface area from 21 and 26 to 82 m²/g. Moreover, the electrochemical performance is relatively better than that of ever-reported SnO_2 hierarchical nanostructures.[21, 24, 25] For example, Wang *et al.*[21] reported that SnO_2 nanosheets exhibited a discharge capacity of 559 mA h/g after 20 cycles at 78.2 mA/g in 0.05-3.0 V. Chen *et al.*[25] demonstrated that SnO_2 nanosheets showed a discharge capacity of ~400 mA h/g at 400 mA/g after 50 cycles in 0.01-1.2 V. In order to further explore this improvement in electrochemical behaviors, the cycle performances of $\text{SnO}_{2-\delta}$ without PVP capping and the white SnO_2 (without both PVP capping and Sn^{2+} doping) are shown in Fig. 7d, which exhibit much lower discharge capacities of ~316 and 210 mA h/g after 60 cycles even at a lower current density of 100 mA/g, respectively. The results suggest that the carbonized-PVP capping can greatly enhance the capacity retention and cycle stability.

Conclusions

In summary, we have demonstrated a facile large-scale fabrication of nonstoichiometric $\text{SnO}_{2-\delta}$ nanosheets with exposed {101} facets via microwave hydrothermal method, in which $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was used as tin source and Sn^{2+} dopant, and PVP was used as capping agent to stabilize the as-produced $\text{SnO}_{2-\delta}$ nanosheets in the highly alkaline aqueous solution. More importantly, NaOH functioned as a directing agent, which together with PVP contributed to the preferential crystal growth at the (121) planes and thus the exposure of {101} dominated surfaces in the single-crystalline $\text{SnO}_{2-\delta}$ nanosheets. Mössbauer spectrum revealed the presence of a large amount of Sn^{2+} (17 at.%), and FTIR and XPS analysis showed the presence of PVP or its derivate, which underwent carbonization during the hydrothermal reaction under microwave irradiation. When used as anode materials for lithium ion batteries, the nonstoichiometric $\text{SnO}_{2-\delta}$ capped with

carbonized PVP (yellow color) or carbon-coating (black color) showed enhanced lithium storage properties, which were attributed to the synergistic contributions of the Sn^{2+} self-doping, carbonized-PVP (or carbon) capping, and the unique hierarchical structures composed of ultrathin, flexible nanosheets. More importantly, the 3D hierarchical nanostructures with open porous structure, large specific surface area and oriented alignment not only facilitated the diffusion of electrolyte and lithium ions but also to maintain the structural integrity of the electrodes. Following our best knowledge, the developed synthetic strategy is the first one allowing for the tailored exposure of reactive {101} facet of SnO_2 with simultaneous self-doping of Sn^{2+} , which is promising for study of the facet- and defect-dependent physicochemical properties in the field of gas sensing, catalysis, and photovoltaics.

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