This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: M. Han, Y. Mu and J. Yu, Mater. Adv., 2020, DOI: 10.1039/D0MA00140F.
Nanoscopically and uniformly distributed SnO$_2$@TiO$_2$/C composite with highly mesoporous structure and bichemical bonds for enhanced lithium ion storage performances†

Meisheng Han$^{a,b}$, Yongbiao Mu$^a$, and Jie Yu$^{a,c}$

$^a$Songshan Lake Materials Laboratory Dongguan, Guangdong 523808, China

$^b$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

$^c$Shenzhen Engineering Lab for Supercapacitor Materials, Shenzhen Key Laboratory for Advanced Materials, School of Material Science and Engineering, Harbin Institute of Technology, Shenzhen, University Town, Shenzhen 518055, China

Abstract

The ultralow volume deformation (<4%) and low cost have aroused great interest in using TiO$_2$ as anode of lithium ion batteries (LIBs), but its low capacity (168 mAh g$^{-1}$) no more than the half of theoretical capacity limits its practical application in high-energy-density LIBs. In order to solve this problem, here we propose a one-step method for fabrication of the SnO$_2$@TiO$_2$/C nanocomposite, which features a superior nanoarchitecture with mesopores, interfacial chemical bonds, vast phase boundaries, carbon coating, and ultrasmall nanocrystals. These nanostructures endow SnO$_2$@TiO$_2$/C with a high capacity of 830.7 mAh g$^{-1}$ at 0.5 C after 100 cycles, an excellent cyclability over 1000 cycles with negligible capacity loss per cycle (0.004%) at 10 C, and high lithium ion transport rate within a few seconds for one cycle. Importantly, the full cell with prelithiated SnO$_2$@TiO$_2$/C as anode and commercial
LiCoO$_2$ as cathode achieves a high energy density of 328.4 Wh kg$^{-1}$ at 0.1 C and 245.9 Wh kg$^{-1}$ at 1 C, which are superior to those of previously reported TiO$_2$-based materials.

**Introduction**

Titanium dioxide (TiO$_2$) has been regarded as a promising anode material in the rechargeable lithium ion batteries (LIBs) due to low cost, non-toxicity, and ultralow volume change (<4%) during lithium ion intercalation/deintercalation.$^{1,2}$ TiO$_2$ possesses a series of allotropes, such as anatase,$^{3,4}$ rutile,$^{5,6}$ and TiO$_2$-B.$^{7,8}$ Among them, anatase TiO$_2$ has been widely investigated due to its inherent crystal structure for lithium ion storage.$^{9,10}$ However, the low theoretical capacity (168 mA h g$^{-1}$), corresponding to the formula of Li$_{0.5}$TiO$_2$, of anatase TiO$_2$, cannot meet the ever-increasing demand of high-energy-density LIBs, thus limiting its practical use.$^3$

In order to enhance the capacity of TiO$_2$, a large number of efforts have been made: (i) preparing nanostructures like nanoparticles,$^3$ nanotubes,$^4$ nanosheets,$^{11}$ and nanomembranes$^{12}$; (ii) fabricating mesoporous composites$^{13,14}$; (iii) forming phase boundaries$^{11}$; and (iv) constructing interfacial chemical bonds$^{1,15}$. Specifically, the design of nanostructures and mesoporous structure is intended to increase the contact area of active material with electrolyte and shorten the transport distance of lithium ions, thus ensuring more sufficient reaction between lithium ion and active material to increase the reversible capacity. Additionally, the capacity can be enhanced by diminishing particle size to nanoscale, which can increase the number of interfaces between materials to accommodate more lithium ions.$^{16,17}$ Similarly, introducing
multi-phase compounds can increase the capacity by generating numerous phase boundaries to provide additional lithium ion storage sites.\textsuperscript{11} Furthermore, the formation of chemical bonds between multi-phases can create a strong interfacial force, which can not only enhance the structural stability of active material and achieve a high capacity retention, but also can enhance the capacity by increasing the diffusion depth of lithium and enabling more active materials to react with lithium ions.\textsuperscript{1,15} Accordingly, the TiO$_2$-based anode with these structures can be assumed to deliver satisfactory capacity. Thus far, several TiO$_2$-based anode materials with similar structures have been reported. For example, an anatase TiO$_2$ nanoparticle with mesoporous structure prepared by atomic layer deposition based sacrificial carbon template was shown to have a capacity of 158.4 mAh g$^{-1}$ with capacity retention of 80\% after 100 cycles at 1 C and a rate capability of 105 mA h g$^{-1}$ at 5 C.\textsuperscript{3} Additionally, a nanocomposite with ultrathin anatase TiO$_2$ nanosheets embedded into TiO$_2$-B nanodomains and vast phase boundaries formed within them was also reported to enhance the lithium ion storage capacity, with a specific capacity of 280 mAh g$^{-1}$ at 0.5 C, 190 mAh g$^{-1}$ after 1000 cycles and capacity retention of 86\% at 10 C.\textsuperscript{11} Moreover, a TiO$_2$/graphene nanocomposite with strong Ti-O-C chemical bonds in the interfaces synthesized by hydrothermal reaction exhibited a capacity of 206.7 mAh g$^{-1}$ at 3 C, 140.3 mAh g$^{-1}$ after 100 cycles and capacity retention of 87.7\% at 30 C.\textsuperscript{18} Furthermore, a high capacity of 227.2-274.0 mAh g$^{-1}$ with good cyclability and rate performance during 200-800 cycles at a current density of 10 C or lower was obtained by a TiO$_2$@C nanocomposite prepared by hydrothermal reaction followed by
carbonization and a TiO$_2$@reduced graphene oxide nanocomposite synthesized by aerosol-assisted spray drying followed by calcination.

Despite improved lithium ion storage capacity, the above-mentioned TiO$_2$-based nanocomposites are still low in the capacity at various current densities. Besides, the synthesis steps of the these nanocomposites were complex, involving sonicating, stirring, centrifuging, washing, drying, calcinating, and etching, coupled with some repeated operations, suggesting the necessity of a simple fabrication route for preparing the high-capacity TiO$_2$-based nanocomposites with the above-mentioned structures (i-iv) to promote their practical application.

Herein, we propose a one-step method for fabricating a highly mesoporous SnO$_2$@TiO$_2$/C nanocomposite with SnO$_2$ nanocrystals homogeneously dispersed in the TiO$_2$/C matrix and an average size of about 10 nm. The coexistence of multi-phases in the nanocomposites induces numerous phase boundaries and thus the formation of Sn-O-C and Ti-O-C chemical bonds. The addition of high-capacity SnO$_2$ (13.0 wt%), coupled with these structural advantages, endows the SnO$_2$@TiO$_2$/C nanocomposite with a reversible capacity of 830.7 mAh g$^{-1}$ after 100 cycles at 0.5 C, higher than any of the reported TiO$_2$-based anodes at a similar cycle number and current density. Furthermore, the SnO$_2$@TiO$_2$/C is also shown to deliver excellent cyclability and rate performance in half and full cells.

**Experimental**

**Materials**

Tetrabutyl orthotitanate tetramer (C$_{40}$H$_{90}$O$_{13}$Ti$_4$, 99.9%, TOT) and monobutyltin
oxide (C\textsubscript{4}H\textsubscript{10}O\textsubscript{2}Sn, 99.9%, MO) were purchased from Tokyo Chemical Industry (Tokyo, Japan); electrolyte (1 M LiPF\textsubscript{6} in a mixture of ethylene carbonate/diethylene carbonate/dimethyl carbonate at a volume ratio of 1:1:1) from DoDoChem; acetylene black, Li foil, Cu foil, Al foil, polyvinylidene fluoride (PVDF), Celgard 2400 membrane, n-methyl-2-pyrrolidone (NMP), and lithium cobaltate (LiCoO\textsubscript{2}) from MTI Corporation; the stabilized lithium metal power (SLMP) from FMC Lithium Co.

Preparation of TiO\textsubscript{2}/C and SnO\textsubscript{2}@TiO\textsubscript{2}/C

The precursor solution was obtained by dissolving 0.2 g MO in 1 g TOT, then transferring the solution into a reaction vessel and sealing it in a glove box under an argon environment. SnO\textsubscript{2}@TiO\textsubscript{2}/C was prepared by heating the vessel to 600 °C at 10 °C min\textsuperscript{-1}, maintaining it for 0.5 h in a tube furnace with flowing Ar, and then cooling to room temperature naturally. Meanwhile, the TiO\textsubscript{2}/C was synthesized by heating pure 1 g TOT under the same condition.

Characterization

The morphology, structure, and composition of the obtained samples were characterized by scanning electron microscopy (SEM, Hitachi S-4700), transmission electron microscopy (TEM, FEI Talos F200x) with the X-ray energy dispersive spectrometer (EDS), accelerated surface area and porosimetry system (Micromeritics ASAP 2010), X-ray diffractometer (XRD, D/max-2500/PC, Rigaku), Raman spectrometer (Renishaw RM-1000), X-ray photoelectron spectrometer (XPS, Thermo Scientific Escalab 250Xi), thermogravimetric analyzer (TGA, STA449 F3 Jupiter), and inductively coupled plasma atomic emission spectrometer (ICP-AES). The
electrical conductivity of the samples was tested with a powder electrical resistivity tester (ST-2722, Suzhou Jingge Electronic Co., Ltd., China).

**Electrochemical measurement**

The electrodes were prepared by coating the mixture of active materials, acetylene black, and PVDF at a weight ratio of 8:1:1 on Cu foil, followed by drying at 80 °C for 12 h in a vacuum oven. The mass of active material loaded on each electrode was about 1.2 mg cm\(^{-2}\). The electrochemical performances were measured via assembling a 2032 coin-type cell in a glove box filled with pure argon, which consisted of prepared electrode, Li foil, Celgard 2400 membrane, and electrolyte. The electrochemical performances of cells were measured on a Land CT2001A battery-test system (Wuhan Land Electronic co., China) in the voltage range of 0.01-3.00 V (vs. Li/Li\(^+\)) and the current densities of 1-50 C (1 C=168 mA g\(^{-1}\)). The electrochemical impedance spectra (EIS) were measured in the frequency range of 10\(^5\) to 10\(^2\) Hz with an amplitude of 5 mV, and the cyclic voltammogram (CV) in the voltage range of 0.01 to 3.00 V (vs. Li/Li\(^+\)) at scanning rates of 0.1-10 mV s\(^{-1}\) on a CHI 760D electrochemical workstation (Shanghai CH Instruments Co., China). In the full cell, the cathode electrode consisted of LiCoO\(_2\) (90 wt%), PVDF (5 wt%), and acetylene black (5 wt%) on Al foil, and the N/P ratio was 1.1 at the mass loading of 2.0 and 10.5 mg cm\(^{-2}\) for SnO\(_2@\)TiO\(_2@\)C and LiCoO\(_2\), respectively. Before assembling the coin-type full cell, the SnO\(_2@\)TiO\(_2@\)C electrode was pre-lithiated by using the commercial SLMP to improve its first Columbic efficiency (CE). The specific process has been reported in our previous report.\(^{15}\) For full-cell testing, the cycling curves
were measured at 0.1 C (1 C=0.14 A g⁻¹) and rate curves were tested at 0.2-1 C in the voltage window of 1.0-3.6 V. All cells were tested at room temperature.

Results and discussion

Fig. 1 shows the SEM images of TiO₂/C. In Fig. 1a, TiO₂/C exhibits a spherical shape with an average size of 2.5 μm due to high vapor pressure, with its formation mechanism being discussed in detail in our previous reports.²⁰,²¹ Interestingly, adding MO into TOT led to the formation of nanoparticles with an average size of 15 nm (Fig. 1b), indicating MO addition facilitates nanocomposite formation in the vapor pressure-induced reaction process.¹⁵

![SEM images of TiO₂/C (a) and SnO₂@TiO₂/C (b).](image)

Fig. 1 SEM images of TiO₂/C (a) and SnO₂@TiO₂/C (b).

In the XRD patterns (Fig. 2a), the two samples show the diffraction peaks at 25.3, 37.8, 48.1, 53.9, 54.9, 62.6, 68.7, 75.1, and 82.7 °, corresponding, respectively, to the (101), (004), (200), (105), (211), (204), (116), (215), and (224) crystal planes of anatase TiO₂ (JCPDS:21-1272), suggesting the successful synthesis of anatase TiO₂. Besides, SnO₂@TiO₂/C exhibits four peaks at 26.6, 33.8, 51.8, and 66.1 °, corresponding, respectively, to the (110), (101), (211), and (301) crystal planes of crystalline SnO₂ (JCPDS No. 41-1445), indicating the formation of SnO₂. In the Raman spectra with the insert for the enlarged image of SnO₂@TiO₂/C in the range of
100-835 cm$^{-1}$ (Fig. 2b), the two samples show the obvious Raman peaks of anatase TiO$_2$ at around 148.7, 392.4, 506.6, and 630.9 cm$^{-1}$ (Fig. 2b), corresponding to the E$_g$, B$_{1g}$, A$_{1g}$, and E$_g$ modes, as well as two peaks around 1323.8 and 1590.5 cm$^{-1}$, corresponding to the D and G peaks of carbon materials, respectively, indicating the existence of anatase TiO$_2$ and free carbon. Obviously, the SnO$_2$@TiO$_2$/C exhibits the Raman peak of SnO$_2$ at about 770 cm$^{-1}$, suggesting the presence of SnO$_2$ in the sample. Meanwhile, the D peak arises from a double resonance process involving a phonon and a defect, while the G peak is attributed to in-plane vibrations and E$_{2g}$ symmetry. Due to the overlap of the D and G peaks, peak fitting was performed, and additional peaks appeared at about 1240 and 1500 cm$^{-1}$, labeled as I and D", respectively. The I peak is related with disorder in the graphitic lattice or sp$^2$-sp$^3$ bonds, while the D" peak is known to occur in the presence of amorphous carbon. Besides, the intensity ratio of D and G (I$_D$/I$_G$) peaks indicates the disorder degree of the graphitic structure, which is close to each other for the two samples (0.68 for SnO$_2$@TiO$_2$/C and 0.67 for TiO$_2$/C), suggesting a similar disorder degree for the carbon in both of them. Furthermore, the high ratio of I$_D$/I$_G$ indicates the existence of vast defects in the carbon, which favors lithium ion storage.

The content of the elements in the precursor and the two samples are shown in Table S1, ESI†. The obtained samples are seen to retain the elements of the precursor apart from H. Furthermore, compared with the precursor, the obtained samples show an increase in the mass percentages of Ti and Sn elements while a decrease in the mass percentages of C and H. These results suggest that a large number of
C,H-containing substances were produced by the decomposition of precursors at a high temperature, which could not be converted into solid under high pressure, leading to a decrease in the mass of C and H. According to the XPS results (Fig. S1, ESI†), the atomic ratio of O and Ti is around 2.11, approaching the theoretical value of TiO$_2$, and the atomic ratio of O and Sn is about 2.02, close to the theoretical value of SnO$_2$, indicating the formation of TiO$_2$ and SnO$_2$. Additionally, the two samples show two XPS peaks around 465.2 and 459.4 eV due to binding energies of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ of anatase TiO$_2$, respectively, (Fig. 2c) further suggesting the formation of anatase TiO$_2$. The SnO$_2$@TiO$_2$/C samples exhibit two Sn 3d peaks of Sn$^{4+}$ 3d$_{3/2}$/3d$_{5/2}$ at around 495.9/487.5 eV (Fig. 2d), again indicating the formation of SnO$_2$.24,25 The two samples also show a wide peak of O 1s from 528.8 to 534.4 eV, which can be fitted into five peaks (Figs. 2e and f): Ti-O bonds at 530.7 eV,26,27 Ti-O-C bonds at 531.2 eV,26,27 Sn-O/C=O at 531.5 eV,28 Sn-O-C at 532.3 eV,28 and C-O-C at 533.1 eV,26,28 confirming the formation of Ti-O-C and Sn-O-C bonds. The C 1s peaks of the two samples are fitted into three peaks (Figs. 2g and h): C=C/C-C at 284.8 eV,22 Ti-O-C at 285.4 eV,26,29 and C-O/C-O-Sn at 286.2 eV,30 further confirming the formation of the Ti-O-C and Sn-O-C bonds. The percentage of Ti-O-C bonds increases from 20.7 for TiO$_2$/C to 25.5% for SnO$_2$@TiO$_2$/C (Table S2, ESI†), due to the production of more interfaces between TiO$_2$ and C by the smaller-sized TiO$_2$ nanoparticles in the SnO$_2$@TiO$_2$/C. Additionally, Sn-O-C bonds increase from 0 to 4.1% with the addition of MO into TOT (Table S2, ESI†). The high content of Ti-O-C and Sn-O-C bonds favors lithium ion storage. Since the XPS technique can
only detect the surface (several nanometers) composition of the material, the XPS spectra of SnO$_2$@TiO$_2$/C in the deeper area were also tested to further confirm the presence of chemical bonds of Ti-O-C and Sn-O-C bonds inside the sample. Briefly, the sample powders were compressed into a thin plate, followed by bombarding it with argon ions for 30 min, and testing the bombarded area by XPS. The XPS results (Fig. S2, ESI†) are consistent with the data in Figs. 2c-h, indicating that the chemical bonds of Ti-O-C and Sn-O-C are distributed in the whole SnO$_2$@TiO$_2$/C sample. ICP-AES results reveal the mass percentages of Sn/Ti as 0/50.3 and 10.2/36.8 wt%, indicating that the mass contents of SnO$_2$/TiO$_2$/C are 0/83.9/16.1 wt% and 13.0/61.3/25.7 wt%, corresponding to TiO$_2$/C and SnO$_2$@TiO$_2$/C, respectively (Table S3, ESI†). The TG curves (Fig. 2i) show that the mass percentages of residuals post high temperature oxidation are 84.1 and 74.7%, corresponding to TiO$_2$/C and SnO$_2$@TiO$_2$/C, respectively, suggesting that the respective carbon content is 15.9 and 25.3 wt%, which are consistent with the ICP-AES results.
Fig. 2 (a) XRD, (b) Raman spectra, (c-h) XPS spectra of Ti 2p (c), Sn 3d (d), O 1s (e,f), C 1s (g, h), and (i) TG curves of TiO$_2$/C (I) and SnO$_2$@TiO$_2$/C (II).

Fig. 3 shows the high angle annular dark field (HAADF) image and its corresponding EDS mapping images. Ti, O, and C elements are seen to be uniformly distributed on the surface of TiO$_2$/C spheres (Fig. 3a-d). The average size of TiO$_2$ particles in the TiO$_2$/C spheres is shown to be about 45 nm by measuring the crushed powder, with a decrease of 10 nm in the size of nanoparticles after adding MO into TOT (Fig. 3f), which agrees with the SEM observation (Fig. 1b). In Fig. 3g, carbon layers can be seen at the edge of the sample, confirming the presence of carbon coating. Fig. 3h shows the lattice fringes of the (101) crystal plane of anatase TiO$_2$ and (110) crystal plane of SnO$_2$, corresponding, respectively, to the highest diffraction peaks of TiO$_2$ at 25.3° and SnO$_2$ at 26.6° (Fig. 2a). Besides, it can be clearly
observed that the nanocrystals are well interconnected by C, combined with the existence of vast chemical bonds of Ti-O-C and Sn-O-C, suggesting that the nanocomposite possesses the superior nanoarchitecture of C/C-O-Ti/TiO$_2$/Ti-O-C/C/C-O-Sn/SnO$_2$/Sn-O-C/C. In Fig. 3i, the selected area electron diffraction (SAED) pattern shows the Debye-Scherrer ring patterns of the (101), (004) and (211) crystal planes of anatase TiO$_2$ as well as the (110) and (221) crystal planes of SnO$_2$, further confirming the existence of TiO$_2$ and SnO$_2$ nanocrystals. In Fig. 3j-n, HAADF and its corresponding EDS elemental mapping images show the even distribution of Ti, Sn, O, and C elements, verifying the homogeneous dispersion of TiO$_2$, SnO$_2$, and free carbon in the nanocomposite. The homogeneous dispersion structure at the nanoscale could induce numerous phase boundaries or interfaces, contributing to lithium ion storage.

**Fig. 3** (a) High angle annular dark field image and the corresponding EDS elemental mapping images of Ti (b), O (c), and C (d) of TiO$_2$/C sphere; (e) TEM image of crushed TiO$_2$/C sphere; (f) TEM image, (g,h) HRTEM image, and (i) the
corresponding SAED pattern of SnO$_2$@TiO$_2$/C; (j) HAADF image and the corresponding EDS elemental mapping images of Ti (k), Sn (l), O (m), and C (n) of SnO$_2$@TiO$_2$/C.

Fig. 4 shows the Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore-size distribution of the samples determined by Nitrogen adsorption-desorption isotherms. The two samples exhibit a typical type-IV isotherm, indicating that they possess a mesoporous structure. Due to the formation of nanostructure, the SnO$_2$@TiO$_2$/C has a significantly higher value than TiO$_2$/C in BET surface area (143.3 m$^2$ g$^{-1}$ versus 11.8 m$^2$ g$^{-1}$) and pore volume (0.86 cm$^3$ g$^{-1}$ versus 0.06 cm$^3$ g$^{-1}$), with mesopores centered at 5.3 nm for the former and 11.1 nm for the latter. Comparatively, the disadvantage for the highly mesoporous structure of the SnO$_2$@TiO$_2$/C nanocomposite is involved in the increase of the active material specific surface area, contributing to the formation of more solid electrolyte interface (SEI) film during the first cycle and decreasing the first Coulombic efficiency (CE). However, this disadvantage can be improved by the commercial prelithiation technique.$^{15}$ Accordingly, the low CE of our SnO$_2$@TiO$_2$/C anode is not an obstacle to its practical application. More importantly, the porous structure possesses several advantages: (i) favoring the contact of active material with electrolyte; (ii) shortening diffusion distance of Li$^+$; (iii) facilitating the storage of additional Li$^+$; (iv) accommodating the volume change of active material upon cycling, thus leading to enhanced capacity, cycling life, and rate performance.$^{13,14}$ Collectively, the preparation of porous structure is favorable for lithium ion storage.
Fig. 4 Nitrogen adsorption-desorption isotherms and pore-size distribution of TiO$_2$/C (a,b) and SnO$_2$@TiO$_2$/C (c,d).

Fig. 5 shows the charge/discharge and cycling curves of the two samples. Different from the first charge/discharge curve of TiO$_2$/C, SnO$_2$@TiO$_2$/C exhibits two potential plateaus below 0.6 V in the charge/discharge curves, attributed to the delithiation/lithiation of SnO$_2$.$^{21,31}$ Additionally, SnO$_2$@TiO$_2$/C does not show obvious delithiation plateaus of anatase TiO$_2$ at 2.15 V, probably due to the contribution of SnO$_2$ and higher carbon content.$^{15}$ The reversible capacity of active material has been reported to be associated with the relative content of each component, particle size, and the number of phase boundaries and chemical bonds at the interface.$^{15,21}$ Due to low theoretical capacity of anatase TiO$_2$, adding high-capacity active material can greatly enhance the capacity of TiO$_2$-based anodes, such as SnO$_2$ and amorphous carbon. Owing to low electrical conductivity (EC) of anatase TiO$_2$, adding materials with higher EC can considerably improve the electrical connectivity of the whole electrode, enabling more active materials to react with lithium ions and thus increasing the specific capacity.$^{21}$ The EC is shown to increase with a rise in the carbon content (Table S4, ESI†). As previously reported, active materials with a nanoscale size possess higher specific capacity than their corresponding bulk materials, because nano-sized materials can remarkably shorten
lithium ion diffusion distance and achieve a deeper lithiation to enhance the capacity.\textsuperscript{3,4} Introducing more components into the active materials can generate more phase boundaries to store extra lithium ions and enhance the reversible capacity.\textsuperscript{11} The formation of chemical bonds in the interface of each phase can increase interfacial defects, EC, and structure stability, thus achieving higher capacity and cyclability.\textsuperscript{1,15} In Fig. 5b and Table S5, ESI†, the SnO$_2$@TiO$_2$/C is seen to have higher specific capacity (830.7 mAh g$^{-1}$) than TiO$_2$/C (169.6 mAh g$^{-1}$) after 100 cycles due to its larger amount of SnO$_2$, C, Sn-O-C, and Ti-O-C bonds as well as higher EC (Table S2-4, ESI†).

The electrochemical performance of SnO$_2$@TiO$_2$/C was further investigated. Fig. 5c shows its voltage profiles at a different cycle number. The first discharge and charge capacities are 1141.2 and 823.4 mAh g$^{-1}$, respectively, with the first CE of 72.2%. The low CE has been reported to arise from the formation of SEI layer and Li$_2$O.\textsuperscript{15,21} The subsequent charge/discharge curves retain a similar shape, indicating the high stability of the electrode structure during cycling. After 100 cycles, a high reversible capacity of 830.7 mAh g$^{-1}$ is observed, corresponding to capacity retention of 100.9%. The increased post-cycling capacity may result from interfacial Li$^+$ storage and electrochemical activation.\textsuperscript{15} In the present study, the obtained reversible capacity (830.7 mAh g$^{-1}$) is higher than that of any previously reported TiO$_2$-based anode (Table S6, ESI†), due to the formation of a large number of phase boundaries, chemical bonds, and mesoporous sites in the nanocomposite, facilitating the storage of more lithium ions and thus increasing the capacity.\textsuperscript{1,11,13} Additionally, adding a
high amount of SnO$_2$ and C also contributes to the enhancement of capacity, leading to a high reversible capacity of 1419.5 mAh g$^{-1}$ for the SnO$_2$/C nanocomposite (Fig. S3, ESI†). Fig. 5d shows the CV curves of SnO$_2$@TiO$_2$/C, with the presence of the characteristic anodic peaks at about 2.12 V and cathodic peaks at about 1.73 V of anatase TiO$_2$.\textsuperscript{9,10} Besides, the three anodic peaks and two cathodic peaks below 0.7 V belong to the delithiation and lithiation behaviors of SnO$_2$, respectively.\textsuperscript{21,31} Interestingly, the presence of a pair of oxidation and reduction peaks in 1.27 and 0.91 V is not the typical delithiation/lithiation behavior of TiO$_2$, SnO$_2$, or C, which may attribute to the formation of a new reversible lithium ion storage site by phase boundaries, defects, interfacial chemical bonds, and mesoporous structure. Fig. 5e shows the Nyquist plots at a different cycling number. The EIS were fitted to an equivalent circuit (Fig. S4, ESI†), where $R_s$ is the electrolyte resistance, corresponding to the intersection of the high-frequency oblique line and the horizontal axis;\textsuperscript{32} $R_{ct}$, the charge transfer resistance, corresponding to the diameter of the depressed semicircle;\textsuperscript{32} $W$, the Warburg impedance of Li$^+$ ion diffusion, corresponding to the low-frequency slope line.\textsuperscript{32} The values of $R_s$ and $R_{ct}$ at a different cycle number are shown in Table S7, ESI†. With a rise in the cycle number, the Rs value is shown to gradually increase, suggesting the increase of electrolyte resistance with increasing cycling number. Meanwhile, the $R_{ct}$ value is seen to increase after the 1st cycle due to the formation of SEI layer, followed by a gradual decrease, probably due to electrochemical activation on cycling.\textsuperscript{15} The decrease of $R_{ct}$ favors the enhancement of capacity and cyclability. In Fig. 5f, the long cycling life is shown to
be at 10 C, with a high specific capacity of 438.5 mAh g⁻¹ at 0.004% capacity loss per cycle after 1000 cycles as well as an average CE of 99.72% during 2-1000 cycles, indicating the high reversibility of electrode during cycling. The lithium ion transport of SnO₂@TiO₂/C was investigated by measuring the rate capability at the current densities of 0.5 to 50 C (Fig. 5g and h), and the shape of charge/discharge curves remains unchanged at different current densities, indicating that the electrode structure is stable during rate testing. The rate capacities are measured as 827.4, 742.2, 647.8, 516.8, 400.6, 333.5, and 217.7 mAh g⁻¹ at 0.5, 1, 2, 5, 10, 20, and 50 C, respectively, with a high capacity of 217.7 mAh g⁻¹ at 50 C, sufficiently proving the excellent rate performance of SnO₂@TiO₂/C. Importantly, the specific capacity returns to almost 100% of the initial capacity with the current density back to 0.5 C, confirming that the electrode structure is still highly stable even after high current charging and discharging. Our SnO₂@TiO₂/C nanocomposite is superior to other TiO₂-based anodes in cycling and rate performances (Table S6, ESI†). Especially, the rate capability is comparable and even superior to that of other anodes, such as Sn-based anode, SiOₓSiOᵧ membrane, Si nanotube, Nb₁₈W₁₆O₉₃, Li₄Ti₅O₁₂ nanowire, and graphite/Si/carbon composite (Table S8, ESI†).
Fig. 5 (a) First charge/discharge curves; (b) Cycling curves at 0.5 C of TiO$_2$/C (I) and SnO$_2$@TiO$_2$/C (II); (c) Charge/discharge curves at different cycles; (d) CV curves; (e) Nyquist plots; (f) Cycling performance at 10 C; (g) Charge/discharge curves at different current densities; (h) rate performance of SnO$_2$@TiO$_2$/C.

The reasons for the high capacity of SnO$_2$@TiO$_2$/C are further explored by estimating the pseudocapacity contribution in the total capacity using CV curves at different scanning rates (Fig. 6a). The relationship between scanning rate ($v$) and peak current ($i_p$) satisfies the following equation (1):

$$\log(i) = a \log(v) + \log(b)$$  \hspace{1cm} (1)

Where $a$ and $b$ are empirical parameters. The 0.5 $a$-value indicates a diffusion-controlled behavior and the 1 $a$-value represents an ideal pseudocapacitive behavior. The $a$-value can be calculated as the slope from the plots of Log($i$) versus Log($v$) at peaks 1-3 (Fig. 6b). The $a$-value for peak 1, peak 2, and peak 3 is calculated as 0.51, 0.53, and 0.70, respectively (Fig. 6b), indicating that the diffusion- and pseudocapacitive-controlled behaviors are responsible for the high capacity of SnO$_2$@TiO$_2$/C. The relationship of total capacity at a given $v$ and voltage (V) is shown in the following equation (2):

$$i(V) = k_1 v^{1/2} + k_2 v$$  \hspace{1cm} (2)

Where the values of $k_1 v^{1/2}$ and $k_2 v$ represent the diffusion- and pseudocapacitive-controlled process, respectively. An increase of $v$ from 0.2 to 10 mV s$^{-1}$ witnesses an increase from 35.1 to 82.3% in the percentage of pseudocapacitive contribution (Fig. 6c), suggesting the significant role of pseudocapacitive-controlled
behavior in the total capacity, especially at a high \( v \). The specific pseudocapacitive contribution at a scanning rate of 1 mV s\(^{-1}\) is presented in the red area (Fig. 6d). The high pseudocapacitive contribution in SnO\(_2@\)TiO\(_2\)/C nanocomposite can be attributed to the following three reasons: (i) vast phase boundaries between TiO\(_2\), SnO\(_2\), and C can offer extra Li\(^+\) storage sites; (ii) the formation of a large number of interfacial chemical bonds can induce numerous defects as additional Li\(^+\) storage sites; (iii) the mesoporous structure can accommodate excess Li\(^+\).

**Fig. 6** (a) CV curves at different scanning rates; (b) The line relationship of Log(\( i \)) vs Log(\( v \)) at peaks 1-3 marked in (a); (c) The percentages of pseudocapacitive contribution at different scanning rates; (d) The detailed pseudocapacitive contribution at a scanning rate of 1 mV s\(^{-1}\) of SnO\(_2@\)TiO\(_2\)/C.

The practicality of the SnO\(_2@\)TiO\(_2\)/C anode was confirmed by testing the delivery capacity of a full cell assembled with prelithiated SnO\(_2@\)TiO\(_2\)/C anode and LiCoO\(_2\) cathode. The full cell exhibits a high capacity of 142.2 mAh g\(^{-1}\), a capacity retention of 93.3\% after 100 cycles at 0.1 C (Fig. 7a and b) and a superior rate performance with a capacity of 110.7 mAh g\(^{-1}\) at 1 C (Fig. 7c and d), which are higher than the values of the reported full cells of graphite/LiCoO\(_2\) and graphite/LiFePO\(_4\).\(^{33-35}\) The gravimetric energy density of the full cell can be calculated by the following equation (3):\(^{36}\)
Energy density (Wh kg\(^{-1}\)) = \left( \frac{C_{\text{cathode}} \times m_{\text{cathode}}}{m_{\text{cathode}} + m_{\text{anode}}} \right) \times V

(3)

Where \(C_{\text{cathode}}\) is the specific capacity calculated based on the mass of cathode; \(V\), the nominal voltage of 2.75V; \(m_{\text{cathode}}/m_{\text{anode}}\), the active mass of cathode and anode, respectively. Accordingly, the gravimetric energy density is calculated as about 328.4 Wh kg\(^{-1}\) at 0.1 C and 245.9 Wh kg\(^{-1}\) at 1 C, which is comparable to that of graphite/LiCoO\(_2\) full cell (335 Wh Kg\(^{-1}\) at 0.1 C),\(^{37-39}\) and superior to that of the reported full cell of TiO\(_2\)-based anode.\(^{40-41}\) In previous reports,\(^{41}\) the nominal voltage is shown as about 2 V in the TiO\(_2\)/LiCoO\(_2\) full cell. In our case, the enhanced nominal voltage may be ascribed to (i) the addition of low-working potential crystalline SnO\(_2\) (0.2-0.8 V)\(^{21}\) and amorphous carbon (below 0.5 V) and (ii) the formation of a new lithium ion storage site, with a pair of oxidation and reduction peaks present, respectively, in 1.27 and 0.91 V, as confirmed by CV curves. It should be mentioned that the energy density should be calculated based on the mass of the whole cell, including both the active materials (cathode material, Li anode and electrolyte) and the inactive materials (conductive carbon, binder, current collectors, tabs, separator and packaging material). However, our research focuses on improving the capacity of anode materials. For the whole battery, when the areal capacity of the active material is constant, the mass of the anode material tends to decrease with an increase of its capacity, which can improve the energy density of the battery. The mass values of inactive materials and electrolyte should be a fixed value in batteries, but they are absent in equation 3, because they are unclear for us. In academic studies, researchers
are more inclined to use the simplified equation 3 to calculate energy density, because it still makes sense in that the higher the energy density calculated by this simplified equation, the higher the energy density when calculated with all materials included, suggesting the reference value of this calculated density.

**Fig. 7** (a) The charge/discharge curves at 0.1 C; (b) The cycling performance at 0.1 C; (c) The charge/discharge curves at different current densities; (d) Rate performance of full cells. The capacity is calculated based on the mass of LiCoO$_2$.

The high stability of electrode structure was verified by SEM and TEM analysis of the electrode after 2000 cycles at 10 C. In the SEM images, the electrode surface is observed to be intact (Fig. S5a and b, ESI†), without any cracks in the nanoparticles (Fig. S5c and d, ESI†). These results confirm the high structural stability of SnO$_2$/TiO$_2$/C nanocomposites during cycling, which is ascribed to the unique
nanoarchitecture of SnO$_2$@TiO$_2$/C (Fig. 8). Specifically, carbon coating on the surface of TiO$_2$ and SnO$_2$ nanocrystals can greatly suppress the structural volume change, enhance electrical conductivity, and inhibit the aggregation of nanocrystals, thus improving the cyclability and rate performance.$^{42,43}$ Additionally, the formation of Ti-O-C and Sn-O-C bonds in the interfaces can promote interfacial charge transfer and enhance the structural stability of SnO$_2$@TiO$_2$/C, thus contributing to a fast lithium ion transport and long cycling life.$^{15}$ Furthermore, the phase boundaries and mesoporous structure can afford the storage of additional Li$^+$ and thus achieve a high capacity.$^{42,43}$ Finally, the ultrasmall nanocrystals can supply enormous active storage sites and shorten Li$^+$ diffusion distance, thus facilitating high capacity and enhancing rate capability.$^{42,43}$

![Fig. 8 A schematic illustration of lithium ion storage mechanism in the SnO$_2$@TiO$_2$/C nanoarchitecture.](image)

**Conclusion**

In this research, we propose a one-step pressure-induced vapor phase method for fabricating a chemically bonded SnO$_2$@TiO$_2$/C nanocomposite with a highly
mesoporous structure as well as SnO₂ and TiO₂ nanocrystals of a size about 10 nm. The fine multi-component nanocrystals are shown to induce a large amount of phase boundaries, defects, interfacial chemical bonds, and mesoporous structures, endowing the SnO₂@TiO₂/C nanocomposite with a high reversible capacity of 830.7 mAh g⁻¹ after 100 cycles at 0.5 C, 438.5 mAh g⁻¹ after 1000 cycles at 10 C, and 217.7 mAh g⁻¹ at 50 C in the half cell. In the full cell, a high energy density of 328.4 and 245.9 Wh Kg⁻¹ is achieved at 0.1 and 1 C, respectively. These lithium ion storage performances are superior to those of previously reported TiO₂-based anodes. 

Acknowledgements

The work was provided technical support by “Ceshigo Research Service agency for TEM, “www.ceshigo.com”.

Conflict of Interest

There are no conflicts of interest to declare.

References

1 S. Cao, Z. Xue, C. Yang, J. Qin, L. Zhang, P. Yu, S. Wang, Y. Zhao, X. Zhang and R. Liu, Nano Energy, 2018, 50, 25-34.

2 S. Wang, Y. Yang, W. Quan, Y. Hong, Z. Zhang, Z. Tang and J. Li, Nano Energy, 2017, 32, 294-301.

3 K. J. Hong and S. O. Kim, Energy Storage Mater., 2016, 2, 27-34.

4 M. Zhang, K. Yin, Z. D. Hood, Z. Bi, C. A. Bridges, S. Dai, Y. S. Meng, M. P. Paranthaman and M. Chi, J. Mater. Chem. A, 2017, 5, 20651-20657.

5 F. Shahvaranfard, M. Altomare, Y. Hou, S. Hejazi, W. Meng, B. Osuagwu, N. Li, C.
J. Brabec and P. Schmuki, *Adv. Funct. Mater.*, 2020, 1909738.

6 C. Gao, T. Wei, Y. Zhang, X. Song, Y. Huan, H. Liu, M. Zhao, J. Yu and X. Chen, *Adv. Mater.*, 2019, 31, 1806596.

7 S. Liu, Z. Wang, C. Yu, H. B. Wu, G. Wang, Q. Dong, J. Qiu, A. Eychmüller and X. W. (David) Lou, *Adv. Mater.*, 2013, 25, 3462-3467.

8 Y. Ren, Z. Liu, F. Pourpoint, A. R. Armstrong, C. P. Grey and P. G. Bruce, *Angew. Chem. Int. Edit.*, 2012, 51, 2164 -2167.

9 S. Tian, A. Xing, H. Tang, Z. H. Bao and G. M. Wu, *J. Mater. Chem. A.*, 2014, 2, 2896-2900.

10 R. Mo, Z. Lei, K. Sun and D. Rooney, *Adv. Mater.*, 2014, 26, 2084-2088.

11 Q. Wu, J. Xu, X. Yang, F. Lu, S. He, J. Yang, H. Fan and M. Wu, *Adv. Energy Mater.*, 2015, 5, 1401756.

12 S. Huang, L. Zhang, X. Lu, L. Liu, L. Liu, X. Sun, Y. Yin, S. Oswald, Z. Zou, F Ding and O. G. Schmidt, *ACS Nano*, 2017, 11, 821-830.

13 Y. Xing, S. Wang, B. Fang, G. Song, D. P. Wilkinson and S. Zhang, *J. Power Sources*, 2018, 385, 10-17.

14 C. Chen, Y. Yang, S. Ding, Z. Wei, X. Tang, P. Li, T. Wang, G. Cao and M. Zhang, *Energy Storage Mater.*, 2018, 13, 215-222.

15 M Han, Z. Lin and J. Yu, *J. Mater. Chem. A*, 2019, 7, 4804-4812.

16 Q. Wu, J. Xu, X. Yang, F. Lu, S. He, J. Yang, H. Fan and M. Wu, *Adv. Energy Mater.*, 2014, 5, 1401756.

17 A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala and G. Yushin, *Nat.*
18 J. Qiu, C. Lai, Y. Wang, S. Li and S. Zhang, Chem. Eng. J., 2014, **256**, 247-254.

19 A. Mondal, S. Maiti, K. Singha, S. Mahanty and A. B. Panda, J. Mater. Chem. A, 2017, **5**, 23853-23862.

20 M. Han and J. Yu, Diam. Relat. Mater., 2018, **87**, 10-17.

21 M. Han and J. Yu, Energy Technol., 2019, **7**, 1900084.

22 X. Tian, X. Li, T. Yang, K. Wang, H. Wang, Y. Song, Z. Liu, Q. Guo and C. Chen, Electrochim. Acta, 2017, **247**, 1060-1071.

23 Y. Zhou, R. Ma, S. L. Candelaria, J. Wang, Q. Liu, E. Uchaker, P. Li, Y. Chen and G. Cao, J. Power Sources, 2016, **314**, 39-48.

24 Q. Guo, Z. Zheng, H. Gao, J. Ma and X. Qin, J. Power Sources, 2013, **240**, 149-154.

25 S. Kang, X. Chen and J. Niu, Nano Lett., 2018, **18**, 467-474.

26 H.-K. Roh, M.-S. Kim, K. Y. Chung, M. Ulaganathan, V. Aravindan, S. Madhavi, K. C. Roh and K.-B. Kim, J. Mater. Chem. A, 2017, **5**, 17506-17516.

27 S. Sakthivel and H. Kisch, Angew. Chem. Int. Ed., 2003, **42**, 4908-4911.

28 R. Tian, Y. Zhang, Z. Chen, H. Duan, B. Xu, Y. Guo, H. Kang, H. Li and Hezhou Liu, Sci. Rep., 2016, **6**, 19195.

29 D. Li, S. Dai, J. Li, C. Zhang, M. Richard-Plouet, A. Goullet and A. Granier, J. Electron. Mater., 2018, **47**, 7372-7379.

30 L. Sun, H. Si, Y. Zhang, Y. Shi, K. Wang, J. Liu and Y. Zhang, J. Power Sources., 2019, **415**, 126-135.

31 S. Kang, X. Chen and J. Niu, Nano Lett., 2017, **18**, 467-474.
32 X. Zhuang, P. Song, G. Chen, L. Shi, Y. Wu, X. Tao, H. Liu and D. Zhang, *ACS Appl. Mater. Interfaces*, 2017, 9, 28464–28472.

33 Y. S. Jung, P. Lu, A. S. Cavanagh, C. Ban, G.-H. Kim, S. H. Lee, S. M. George, S. J. Harris and A. C. Dillon, *Adv. Energy Mater.*, 2013, 3, 213-219.

34 N.-S. Choi, Y. Lee, S.-S. Kim, S.-C. Shin and Y.-M. Kang, *J. Power Sources*, 2010, 195, 2368-2371.

35 J. Chong, S. Xun, H. Zheng, X. Song, G. Liu, P. Ridgway, J. Wang and V. S. Battaglia, *J. Power Sources*, 2011, 196, 7707-7714.

36 H. J. Kwon, J.-Y. Hwang, H.-J. Shin, M.-G. Jeong, K. Y. Chung, Y.-K. Sun and H.-G. Jung, *Nano Lett.*, 2020, 20, 625-635.

37 H. J. Kim, S. Choi, S. J. Lee, M. W. Seo, J. G. Lee, E. Deniz, J. L. Yong, E. K. Kim and W. Choi, *Nano Lett.*, 2016, 16, 282-288.

38 S. Chen, L. Shen, P. A. van Aken, J. Maier and Y. Yu, *Adv. Mater.*, 2017, 29, 1605650.

39 W. He, Y. Liang, H. Tian, S. Zhang, Z. Meng and W. Q. Han, *Energy Storage Mater.*, 2017, 8, 119-126.

40 H. Xiong, H. Yildirim, E. V. Shevchenko, V. B. Prakapenka, B. Koo, M. D. Slater, M. Balasubramanian, S. K. R. S. Sankaranarayanan, J. P. Greeley, S. Tepavcevic, N. M. Dimitrijevic, P. Podsiadlo and C. S. Johnson, *J. Phys. Chem. C*, 2012, 116, 3181-3187.

41 N. Plylahan, M. Letiche, M. K. S. Barr, B. Ellis, S. Maria, T. N.T. Phan, E. Bloch, P. Knauth and T. Djenizian, *J. Power Sources*, 2015, 273, 1182-1188.
42 M. Han, Y. Mu, F. Yuan, J. Liang, T. Jiang, X. Bai and J. Yu, *J. Mater. Chem. A*, 2020, **8**, 3822-3833.

43 M. Han and J. Yu, *J. Power Sources*, 2019, **414**, 435-443.
A superior nanoarchitecture with vast phase boundaries interconnected via chemical bonds between carbon and ultrasmall nanocrystals shows enhanced Li$^+$ storage performances.
(a) Current vs. Potential
(b) Log v vs. Log i
(c) Contribution ratio
(d) Voltage vs. Li\textsuperscript{+}/Li
enhanced electrical conductivity
improved structural stability and interfacial Li⁺ storage
short Li⁺ diffusion distance

- Li⁺
- C
- O²⁻
- Ti²⁺
- Sn²⁺

571x285mm (96 x 96 DPI)