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Tin dioxide-based nanomaterials as anodes for lithium-ion batteries

Minkang Wang,[a] Tianrui Chen,[b] Tianhao Liao,[a] Xinglong Zhang,[a] Bin Zhu,[a] Hui Tang (ID) *[a] and Changsong Dai (ID) *[b]

The development of new electrode materials for lithium-ion batteries (LIBs) has attracted significant attention because commercial anode materials in LIBs, like graphite, may not be able to meet the increasing energy demand of new electronic devices. Tin dioxide (SnO_2) is considered as a promising alternative to graphite due to its high specific capacity. However, the large volume changes of SnO_2 during the lithiation/delithiation process lead to capacity fading and poor cycling performance. In this review, we have summarized the synthesis of SnO_2-based nanomaterials with various structures and chemical compositions, and their electrochemical performance as LIB anodes. This review addresses pure SnO_2 nanomaterials, the composites of SnO_2 and carbonaceous materials, the composites of SnO_2 and transition metal oxides, and other hybrid SnO_2-based materials. By providing a discussion on the synthesis methods and electrochemistry of some representative SnO_2-based nanomaterials, we aim to demonstrate that electrochemical properties can be significantly improved by modifying chemical composition and morphology. By analyzing and summarizing the recent progress in SnO_2 anode materials, we hope to show that there is still a long way to go for SnO_2 to become a commercial LIB electrode and more research has to be focused on how to enhance the cycling stability.

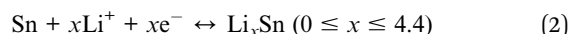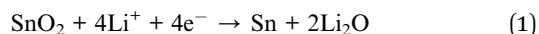## 1. Introduction

Lithium-ion batteries (LIBs) have been widely used in modern electronic equipment, such as laptops, mobile phones, and mechanical devices for their high energy densities, long cycle life, and environmental friendliness.[1–6] As an important component of LIBs, electrode materials are responsible for energy storage and cycling life of LIBs.[7–11] Currently, graphite is the main anode in commercial LIBs owing to its good stability.[12–14] However, it cannot fully meet the increasing energy demand for batteries due to its low theoretical specific capacity (372 mA h g^{-1}).[15–18] In order to solve this problem, much work has been focused on exploring alternative materials with high specific capacity.[19–26]

Potential candidates like metal oxides have been widely researched due to their high theoretical specific capacities, such as MnO,[27–30] MnO_2,[31–36] Mn_3O_4,[37–40] Fe_2O_3,[41–45] Fe_3O_4,[46–50] Co_3O_4,[51–54] and SnO_2.[55–57] Among these materials, SnO_2 has attracted significant attention due to its low cost, natural abundance, and high theoretical specific capacity (782 mA h g^{-1} of bulk SnO_2). SnO_2 is superior to other metal oxides as it has a low charge and discharge potential, *i.e.*, an average charge and

discharge potential of 0.5 V and 0.3 V *vs.* Li/Li$^+$, respectively,[58] resulting in LIBs with higher energy density. However, the commercial use of SnO_2 as an anode material is still hindered by poor cycling stability and inferior rate performance, which is attributed to the electrochemical reaction mechanism of SnO_2 during lithiation/delithiation. For SnO_2-based anode material for LIBs, the electrochemistry includes two steps, shown as follows:[59–61]

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \qquad (1)$$

$$Sn + xLi^+ + xe^- \leftrightarrow Li_xSn \ (0 \leq x \leq 4.4) \qquad (2)$$

In the first reaction, SnO_2 reacts with Li$^+$ and electrons to generate Sn and Li_2O. It is believed as an irreversible process, and this is the main reason why SnO_2 suffers severe capacity deterioration in the initial lithiation process.[62] In the second reaction, Sn obtained from the first step reacts with Li$^+$ and electrons to reversibly generate Li_xSn alloys. The alloying and dealloying processes represent discharging and charging processes of SnO_2-based anode material, respectively.[63] However, Li-alloying anode materials like Li_xSn and Li_xSi, possess the disadvantages of limited cycle life and severe capacity loss because of large volume changes, pulverization, and continuous formation of solid electrolyte interphase (SEI) during the alloying/dealloying process. Therefore, owing to this irreversible phase transformation process during lithiation/delithiation, the commercial use of SnO_2 is largely hampered.
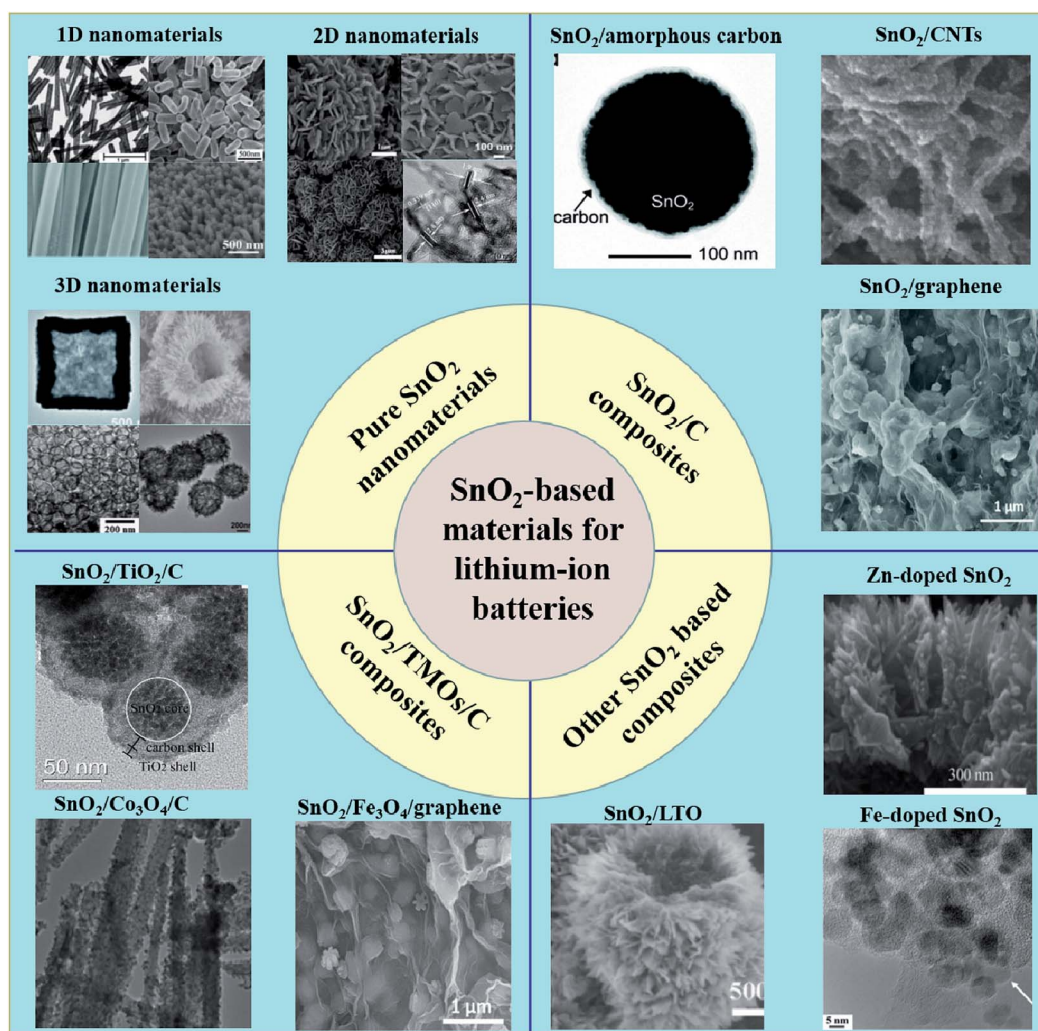
[a]School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, 611731, China. E-mail: tanghui@uestc.edu.cn

[b]School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China. E-mail: changsd@hit.edu.cn

In order to solve these problems and to improve the electrochemical performance of SnO_2, researchers have synthesized many SnO_2-based anode materials with various well-designed architectures. These SnO_2-based anode materials can be classified into four types, according to their chemical composition. The first category includes pure nanostructured SnO_2 materials, such as one-dimensional (1D) nanorods (NDs), nanotubes (NTs)[64–68] and nanowires (NWs),[69–74] two-dimensional nanobelts,[75,76] nanosheets[77–82] and nanoplates,[83–85] three-dimensional (3D) hollow nanostructures,[86–92] and hierarchical nanostructures.[93] Nanosized materials shorten transmission distance for electrons and Li^+ and also help to reduce the extent of volume changes during the electrochemical process. In addition, it has been reported that the reduction reaction of SnO_2 nanomaterials becomes reversible or partly reversible, which improves the lithium storage capacity and reduces the capacity loss during the charge/discharge process.[94] So the theoretic capacity of SnO_2 nanomaterials can be increased up to 1495 mA h g^{-1}. The second category includes the composites of SnO_2 and carbonaceous materials,[95–97] such as SnO_2/carbon

nanotubes (CNTs),[98–101] SnO_2/hollow carbon spheres,[102–104] SnO_2/graphene[105–110] and SnO_2/amorphous carbon. Carbonaceous materials improve the conductivity of the composites and also provide abundant nanosized voids as buffers to decrease the effect of large volume changes during the charge/discharge process.[111–113] The third category includes the composites of SnO_2, transition metal oxides, and carbonaceous materials (SnO_2/TMOs/C). Various composites of SnO_2 and transition metal oxides (SnO_2/TMOs) have been synthesized in the past 20 years, such as SnO_2/Fe_2O_3,[114–117] SnO_2/Co_3O_4,[118,119] SnO_2/TiO_2,[120–122] SnO_2/ZnO[123] and SnO_2/MoO_3 (ref. 124) and they showed enhanced lithium storage capacity compared to pure SnO_2 anode material.[125] It has been reported that the introduction of TMOs, such as Fe_2O_3 (ref. 126) and Co_3O_4,[127] can effectively enhance the capacity because the transition metal nanoparticles in the composite can reversibly convert the extra Li_2O into Li^+; thus, influencing the charge/discharge processes. However, cycling stability and rate performance of the composites still need to be further improved. Therefore, based on SnO_2/TMOs materials, much work has been done to

Scheme 1 Schematic presentation of different SnO_2-based anode materials for LIBs.

synthesize the composites of SnO_2, TMOs, and carbonaceous materials (SnO_2/TMOs/C),[128–131] like Fe_3O_4/SnO_2/rGO,[132] SnO_2@C@Fe_3O_4 (ref. 133) and SnO_2/MoO_3/C.[134,135] SnO_2/TMOs/C materials more effectively alleviate the impact of volume changes and improve conductivity, leading to better electrochemical performance as an anode, compared to the SnO_2/TMOs materials.[136,137] The fourth category includes some other tin dioxide-based compounds, such as heteroatom-doped SnO_2 (ref. 138 and 139) (Fe-doped SnO_2,[140] Zn-doped SnO_2 (ref. 141)), $Li_4Ti_5O_{12}$/SnO_2 (ref. 142) and SnO_2/C_3N_4.[143]
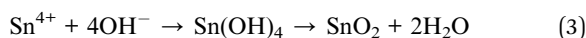
In this article, we provide the recent progress in the research of these four major types of SnO_2-based anode material, as mentioned above (Scheme 1). For the following sections, we will introduce the various SnO_2-based nanomaterials as well as their corresponding synthesis methods and electrochemical performance. We hope this review article will serve as a good reference for further research.

2. Pure nanostructured SnO_2 materials

2.1 1D nanomaterials

Many 1D nanostructured SnO_2 materials, such as nanorods,[144–146] nanotubes[147–150] and nanowires[151–153] have been synthesized in recent years. 1D SnO_2 nanomaterials usually exhibit superior specific discharge capacity since they can offer extra channels and pathways for electron transmission compared to bulk SnO_2 and SnO_2 powders.[154–156]

2.1.1 SnO_2 nanorods. Pure SnO_2 nanorods can be synthesized via many methods such as chemical vapor deposition (CVD), vapor liquid solid,[157] hydrothermal treatment[158] and spray pyrolysis approach.[159] Among these reported methods, the hydrothermal synthesis of SnO_2 nanorods is the most used routine as it can be conveniently controlled due to its facile operation. The formation mechanism in a hydrothermal system can be summarized as follows:

$$Sn^{4+} + 4OH^- \rightarrow Sn(OH)_4 \rightarrow SnO_2 + 2H_2O \qquad (3)$$

First, $Sn(OH)_4$ forms by the hydrolysis of Sn-based salts in aqueous medium. During the hydrothermal treatment, $Sn(OH)_4$ tends to convert into SnO_2 and subsequently grows along the [001] direction.[160,161] Early in 2003, Zhang et al. fabricated uniform SnO_2 nanorods with diameters of about 8–15 nm and lengths of about 150–200 nm by a one-step procedure under mild conditions.[148] They dissolved sodium dodecyl sulfate and $Sn(OH)_6^{2-}$ salt in a solution consisting of heptane and hexanol by stirring. Then, the homogeneously dispersed solution was transferred into a Teflon-lined autoclave and heated to 200 °C for 18 h. The as-prepared SnO_2 nanorods displayed a crystalline rutile structure. Zhang et al. also discovered that the concentration of $Sn(OH)_6^{2-}$ ions and the ratio of NaOH and $SnCl_4$ determined the shape of the SnO_2 nanorods. It was found that on increasing the concentration of $Sn(OH)_6^{2-}$ from 0.2 M to 0.3 M, the number of nanorods significantly decreased; additionally, on increasing the molar ratio of NaOH to $SnCl_4$ from 10 : 1 to 30 : 1, the aspect ratio of SnO_2 nanorods increased.[162]

In 2004, Cheng et al. investigated a large-scale hydrothermal method to synthesize single-crystalline SnO_2 nanorods with lengths of 15–20 nm and diameters of 2.5–5 nm (Fig. 1A). Sn^{4+} precursor was dissolved in a mixture of water and alcohol, and pH was adjusted 12 and the solution was then heated at 150 °C for 24 h.[163] Based on Zhang and Cheng's work, many groups have synthesized SnO_2 nanorods via hydrothermal methods in other different systems. Guo et al. synthesized SnO_2 nanorods with diameter in the range of 120–260 nm and length up to 2–3 μm by using hexadecyltrimethylammonium bromide as a template (Fig. 1B).[58] Chen et al. synthesized single crystalline SnO_2 nanorods with diameters of 4–15 nm and lengths of 100–200 nm.[145] Xi et al. investigated a new synthesis method of ultrathin SnO_2 nanorods with an average diameter of 2 ± 0.5 nm.[164] Therefore, various SnO_2 nanorods with distinct morphology can be synthesized by controlling hydrothermal conditions.

SnO_2 nanorods can be applied as anode materials in LIBs.[165] Liu et al. synthesized SnO_2 nanorods arrays on a flexible alloy substrate via hydrothermal method. The nanorods arrays have average diameter and length of 60 and 670 nm, respectively (Fig. 1C). Observed by HRTEM images (Fig. 1D) and FFT pattern of HRTEM images (Fig. 1E), SnO_2 nanorod array was growing on substrate along [001] direction, since (001) plane is more loosely packed and has a relatively high surface energy compared to {110} planes.[166] As-collected hierarchical array structure can directly be used as a binder-free electrode for LIBs, which shows good energy performance, including high discharge capacity
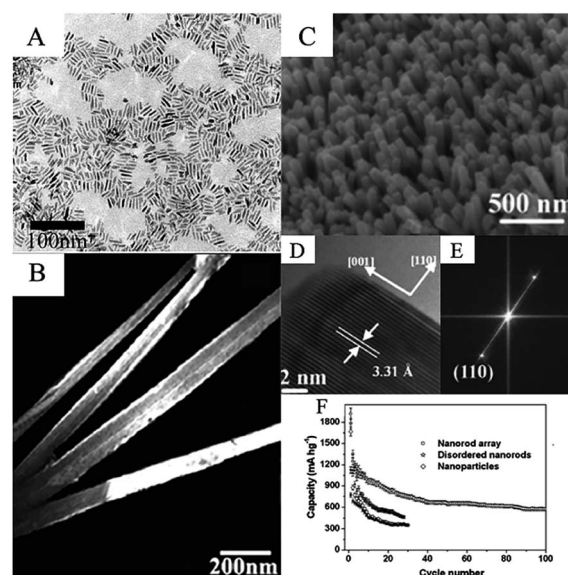

Fig. 1 (A) Transmission electron microscopy (TEM) images of the as-prepared SnO_2 nanorods (adapted with permission from ref. 163 copyright 2004 American Chemical Society). (B) Scanning electron microscopy (SEM) images of long SnO_2 nanorods (adapted with permission from ref. 58 copyright 2004 Elsevier). (C) SEM images, (D) high-resolution TEM (HRTEM) images, (E) FFT patterns of the HRTEM images, and (F) cycling performance of SnO_2 nanorods (adapted with permission from ref. 154 copyright 2009 Royal Society of Chemistry).

(the first discharge is 1918 mA h g^{-1}) and good cycling stability (580 mA h g^{-1} after 100 cycles at 0.1C, with coulombic efficiency of nearly 100%) (Fig. 1F).[154]

2.1.2 SnO$_2$ nanotubes. SnO$_2$ nanotubes have been widely used as anode materials in lithium-ion batteries. Compared to SnO$_2$ nanorods, SnO$_2$ nanotubes usually possess superior lithium storage capacity and cycling stability due to their hollow characteristics.[167] Sacrificial template-based approaches are commonly used in synthesizing this tubular structure. Anodic aluminum anode (AAO), polycarbonate (PC) membrane, SiO$_2$ and ZnO can be served as sacrificial templates in synthesizing metal oxides nanostructures. The synthesis process of SnO$_2$ nanotubes usually includes three steps: (1) infiltration of reactants into the templates; (2) growth of SnO$_2$ with designed shapes and morphology; (3) removal of the template.

Early in 2006, Lai *et al.* reported the preparation of SnO$_2$ nanotubes with a thickness of 10 nm and a length of about 0.4–1.4 μm *via* the electrodeposition method (Fig. 2A). They first electroplated the SnO$_2$ nanoparticles on a gold electrode which was modified with a porous PC membrane. Then, the SnO$_2$ particles were annealed at 650 °C in ambient conditions. The shape and size of the as-prepared nanotubes could be easily controlled by monitoring the charge passed.[66] Meanwhile, Lai *et al.* also reported that the SnO$_2$ nanotubes possessed better crystallinity and uniformity in terms of length and width.

The AAO and PC membrane-template methods have been widely used in the synthesis of metal oxide nanotubes. Wang *et al.* fabricated uniform polycrystalline SnO$_2$ nanotubes *via* this template.[68] They found that the diameter, thickness, length,

and texture of nanotubes can be controlled with template structure, pristine particle size, and heating-rate temperature. As shown in Fig. 2B–D, nanotube walls, with a thickness of about 10–25 nm, were composed of abundant nanocrystallites of 6–15 nm. Furthermore, the SnO$_2$ nanotube electrode showed superior charge/discharge performance compared to SnO$_2$ nanoparticles. The specific capacity of the SnO$_2$ nanotube electrode can be 525 mA h g^{-1} after 80 cycles.[68] They summarized that the improved cycling performance resulted from the following factors, (1) cavities in the nanotubes which provide space and reduce the effect of volume change during lithiation/delithiation process; (2) SnO$_2$ nanotubes provide more active sites for Li$^+$ intercalation and deintercalation; and (3) compared to SnO$_2$ nanoparticles, the SnO$_2$ nanotubes are less movable and result in less agglomeration.[68] Si and SiO$_2$ have been commonly used in the synthesis of hollow nanostructures, including nanotubes. Morphology and shapes of SnO$_2$ nanotubes can be well designed by controlling the shape of the Si templates and the hydrothermal conditions.[168] Ye *et al.* also discovered that the shorter SnO$_2$ nanotubes showed superior electrochemical performance, since the hollow structure in the short nanotubes can alleviate the volume changes.[147] ZnO is another promising sacrificial template used for synthesizing SnO$_2$ nanotube arrays as ZnO can be conveniently synthesized and removed. The as-prepared nanotubes exhibited a diameter and thickness of about 100–300 nm and about 10–20 nm, respectively, composed of nanoparticles with diameters of about 2–5 nm (Fig. 2E and F). The material also showed high capacity and improved cycling performance, *i.e.*, 750–800 mA h g^{-1} after 20 cycles at 0.1C, as shown in Fig. 2G.[64]

2.1.3 SnO$_2$ nanowires. Template-based methods have also been widely used to synthesize SnO$_2$ nanowires. These sacrificial templates contribute to the development of mesoporous and hollow SnO$_2$ nanowires.[63,169] Kim *et al.* fabricated a SnO$_2$ nanowire-based anode material for LIBs by using KIT-6 and SBA-15 SiO$_2$ as hard templates. They first dissolved SnCl$_4$·5H$_2$O and the hard templates in DI water and stirred the mixture at room temperature until Sn^{4+} was adsorbed by templates. Then, the resulting composites were annealed, and the templates were removed from the composites using a NaOH solution. The as-obtained SnO$_2$ nanowires had a diameter of 6 nm and a length greater than 3 μm, and the size of mesoporous SnO$_2$ on the surface of the nanowire was 3.8 nm with a BET surface area of 160 m^2 g^{-1}. Such a porous and interconnected SnO$_2$ nanowire structure showed better lithium storage capacity. The initial discharge and charge capacities of the nanowire anode were 1595 and 800 mA h g^{-1} at 0.2C, respectively, and the discharge capacity remained at 773 mA h g^{-1} after 50 cycles. These observations can be attributed to the mesopores which act as a buffer zone against SnO$_2$ volume expansion.[71]

Researchers have synthesized SnO$_2$ nanowires *via* many methods. For example, Ko *et al.* synthesized SnO$_2$ nanowires on the current collector *via* thermal evaporation at (600 °C). The as-prepared SnO$_2$ nanowires exhibited a highly-ordered single-crystalline phase with a thin diameter of 40–50 nm and length of more than 1 μm (Fig. 3A and B). The SnO$_2$ nanowire-based anode exhibited high specific discharge capacity and good
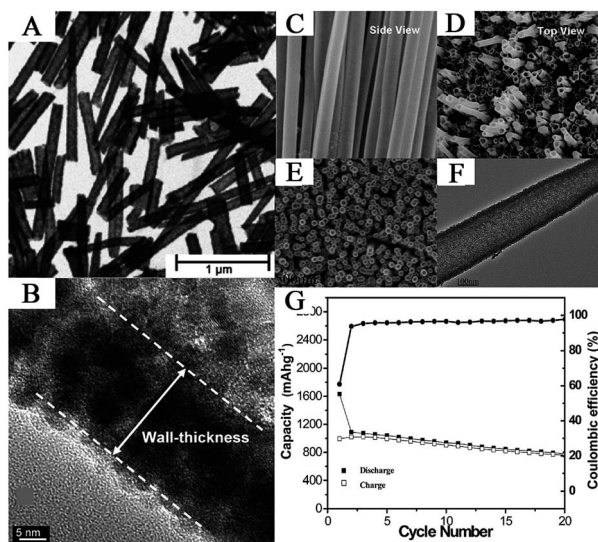

Fig. 2 (A) TEM image of SnO$_2$ nanotubes (adapted with permission from ref. 66 copyright 2006 Royal Society of Chemistry). (B) HRTEM image of SnO$_2$ nanotubes for measuring thickness, (C) FESEM image of the side view, and (D) FESEM images of the top view of SnO$_2$ nanotubes (adapted with permission from ref. 68 copyright 2005 American Chemical Society). (E) TEM image, (F) HRTEM image, and (G) discharge capacity *vs.* cycle number of SnO$_2$ nanotube arrays on Ti substrates (adapted with permission from ref. 64 copyright 2011 American Chemical Society).
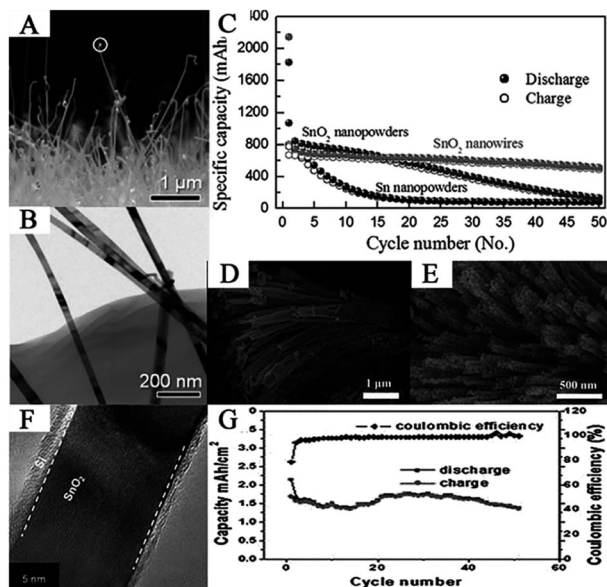
Fig. 3 (A) Cross-sectional FESEM image, (B) TEM image, and (C) comparative cycling performance of the SnO$_2$ nanowires (adapted with permission from ref. 72 copyright 2009 IOP Publishing). (D and E) SEM images of SnO$_2$ porous nanowire bundles (adapted with permission from ref. 170 copyright 2011 Royal Society of Chemistry). (F) HRTEM image, and (G) cycling performance of the SnO$_2$@Si nanowires (adapted with permission from ref. 73 copyright 2013 Royal Society of Chemistry).

cycling performance, *i.e.*, 2140 mA h g^{-1} at the first cycle and 510 mA h g^{-1} at the 50th cycle at 1C (Fig. 3C).[72] Ding *et al.* reported a facile strategy for the synthesis of SnO$_2$ nanowire arrays using SBA-15 nanorods as a template by infiltrating molten SnCl$_2$ into the channels of the SBA-15 nanorods followed by calcination and removal of the template.[69] Han *et al.* investigated the synthesis of porous SnO$_2$ nanowire bundles with a high yield *via* solution-based approaches. This hierarchical nanostructure is made up of SnO$_2$ nanowires with an overall diameter of 80–120 nm and an average length of 6 μm (Fig. 3D). Moreover, the as-prepared nanowires have a highly porous structure composed of numerous nanocrystals.[170] Ren *et al.* synthesized 3D hierarchical SnO$_2$ nanowire arrays on carbon cloth by first, a CVD method for SnO$_2$ nanowires, followed by a Plasma Enhanced-CVD (PECVD) method for Si thin film coating. The SnO$_2$@Si nanowire arrays can directly serve as a flexible and binder-free anode for LIBs. In this unique structure, SnO$_2$ nanowires act as a lithium storage material and a conductive matrix to support Si; in addition, the thin Si layer acts as a buffer for SnO$_2$ to reduce the effect of volume changes (Fig. 3F). Anodes based on such novel hierarchical structures showed excellent electrochemical performance with discharge capacity of 2.13 mA h cm^{-2} in the first cycle and 1.386 mA h cm^{-2} after 50 cycles, *i.e.*, 65% of the first cycle (Fig. 3G).[73] Thus, in this section, different synthesis methods for SnO$_2$ nanowires, corresponding morphologies, and electrochemical properties have been presented, demonstrating that SnO$_2$ nanowires are promising anode materials for LIBs.

2.2 2D nanomaterials

Due to the difficulty of synthesizing well-defined 2D SnO$_2$ nanomaterials, obtaining a large variety of 2D SnO$_2$ nanostructures is significantly harder than 1D and 3D nanomaterials. The anisotropic crystal growth of SnO$_2$, in the formation process, limits the synthesis of 2D nanomaterials.[82] In order to overcome this problem, *in situ* growth of SnO$_2$ nanosheets on physical or chemical substrates has been widely investigated.[171,172] Among these fabrication processes, SnO$_2$ nanosheets grown on physical substrates, such as metal foam,[49,173–175] foil,[77,154,176–178] carbon cloth[78,179] and graphite paper[180–183] can be directly used as binder-free and current-collector free electrode in LIBs due to excellent conductive and supportive properties of such substrates. Meanwhile, some organic macromolecules can be used as chemical templates to fabricate SnO$_2$ nanosheets. These substrates could provide a growth plane for SnO$_2$ nanosheets and inhibit self-aggregation during the lithiation/delithiation processes.[184] Moreover, SnO$_2$ nanosheets have a tendency to assemble into complex structures, such as nanosheet arrays, clusters, and spheres, which usually exhibit superior lithium storage capacities due to their highly interconnected and hierarchical nanostructures.[184–187]

Zhao *et al.* fabricated SnO$_2$ nanosheet arrays on Ni foam with a thickness of 20 nm and a length of 500 nm (Fig. 4A) *via* a hydrothermal method. Nickel foam, *i.e.*, a 3D macroporous conductive network, was used as a supportive substrate to fabricate SnO$_2$ nanosheet arrays, which can be directly used as a binder-free anode in LIBs. Due to the high electroactive surface area, ultrathin sheets, and shorter electron transport pathways, the nanosheets exhibited excellent electrochemical properties. The novel anode showed an initial discharge capacity of approximately 1800 mA h g^{-1} and remained at 674.9 mA h g^{-1} after 50 cycles at 0.5C (Fig. 4B).[79] Moreover,
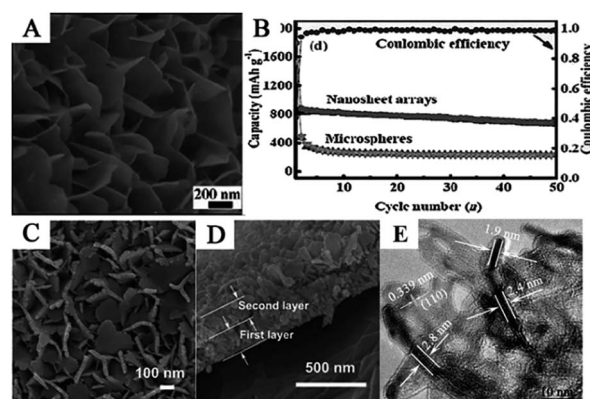

Fig. 4 (A) SEM image, and (B) cycling performance of hierarchical SnO$_2$ nanosheet arrays on nickel foam (adapted with permission from ref. 79 copyright 2014 Wiley). (C) Top view, and (D) cross-sectional FESEM images of SnO$_2$ nanosheets double layer on Ti foil (adapted with permission from ref. 77 copyright 2014 Royal Society of Chemistry). (E) HRTEM image of ultrathin SnO$_2$ nanosheets of less than 5 nm (adapted the permission from ref. 80 copyright 2015 American Chemical Society).

interconnected single and double layer SnO_2 nanosheets were also fabricated on three different conductive substrates, *i.e.*, Ti, Cu foil, and flexible graphite paper, as integrated binder-free electrodes for LIBs. The nanosheets were interconnected with each other to form a hierarchical network, and the thickness of a single SnO_2 nanosheet layer was about 250 nm (Fig. 4C and D). The electrodes delivered high specific capacity, excellent cycling stability, and good rate capability.[77,79] Zhu *et al.* reported an ultra-rapid, low-cost, and simple microwave-assisted synthesis of ultrathin SnO_2 nanosheets with a thickness of less than 5 nm (Fig. 4E). The ultrathin SnO_2 nanosheets exhibited significantly enhanced electrochemical lithium storage properties with a high reversible capacity of 757.6 mA h g^{-1} at a current density of 200 mA g^{-1} up to 40 cycles. The ultrathin 2D nanosheets can significantly reduce the ion diffusion paths and allow faster phase transitions; furthermore, the sufficient external surface interspace and porous configuration successfully accommodate the large volume changes.[77,78,80]

Many complex hierarchical SnO_2 nanostructures were also assembled by 2D SnO_2 nanosheets. Flower-like SnO_2 assembled by many SnO_2 nanosheets, with an average thickness of 100 nm, have been synthesized on a flexible carbon cloth using CVD at 750 °C.[78] SEM images (Fig. 5A) show that as-prepared flower-like SnO_2 nanostructures were formed by an assembly of numerous nanosheets with a thickness of 100 nm. Ding *et al.* synthesized hollow spheres assembled from SnO_2 nanosheets (Fig. 5B), using sulfonated polystyrene hollow spheres (sPSHSs) as a template; the surface of the sPSHS is covered with $-SO_3-$ functional groups. Therefore, the Sn^{2+} ions can easily interact with these templates *via* electrostatic forces and subsequently grow into SnO_2 nanosheets, assisted by mercaptoacetic acid. Moreover, sPSHSs templates are beneficial for minimizing the gas outflux during the template removal process, which helps the retention of the final structure.[188–191] The as-prepared

samples showed a superior cycling capacity retention compared to other SnO_2 nanoflowers assembled by SnO_2 nanosheets as well as SnO_2 nanoparticles, indicating the positive effect of the unique nanostructure (Fig. 5C).[87] Wei *et al.* fabricated nanoporous SnO_2 nanosheets *via* a simple one-step ultrasonic-assisted chemical precipitation strategy with poly-vinylpyrrolidone (PVP) as a soft template. Due to the porous nanosheet structure, it exhibited high capacity, *i.e.*, an initial discharge capacity of 2231 mA h g^{-1} at 0.2 A g^{-1}, and excellent cycling performance, *i.e.*, an initial discharge capacity of 710 mA h g^{-1} and 606 mA g^{-1} at 1.6 A g^{-1} and 4 A g^{-1}, respectively, which remained at 497 mA h g^{-1} and 280 mA h g^{-1} after 60 cycles, respectively (Fig. 5D).[81]

2.3 3D nanomaterials

In recent years, 3D SnO_2 structures have attracted significant attention.[86] Various 3D nanostructures have been synthesized, such as hollow spheres[91,192–194] and microboxes.[195–197] Furthermore, many new synthetic methods to prepare SnO_2 hollow structures, including Ostwald ripening,[198–200] Kirkendall effect,[201–204] removable templates[195] and chemically induced self-assembly[192,205] have been reported.

In 2006, Lou *et al.* investigated a one-pot template-free synthesis of hollow SnO_2 nanostructures, based on an unusual inside-out Ostwald ripening mechanism. The synthesis process was performed in an ethanol–water ($EtOH–H_2O$) mixed solvent with K_2SnO_3 as the precursor, followed by a hydrothermal treatment. Lou *et al.* discovered that the concentration of the precursor and the ratio of EtOH in the mixed solvent determined both the particle size and morphology of the product. Moreover, the addition of urea or thiourea in the synthetic mixtures was also found to increase the product yield, morphological yield to nearly 100%, and a well-dispersed monodispersity (Fig. 6A–C). Such hollow SnO_2 nanosphere-based anode material exhibited high discharge capacity and good cycling performance, *i.e.*, an initial discharge capacity of 1140 mA h g^{-1}, which is comparable to the theoretical capacity of graphite after more than 40 cycles.[86]

Porous hollow SnO_2 micro-boxes have been synthesized *via* a selective leaching strategy using $ZnSn(OH)_6$ as the precursor. $ZnSn(OH)_6$ micro-boxes were first formed through a modified one-pot co-precipitation method and subsequently, the Zn species were removed *via* a selective leaching strategy. The TEM image (Fig. 6D) shows that the thickness of the shell was about 100 nm.[195] Hu *et al.* used a template-and additive-free hydro-thermal route to prepare a uniquely shaped SnO_2 material that comprised of a hollow spherical morphology with uniform diameter and very thin petal-like nanosheets grown perpendicularly on the surface of the spheres, resembling a "chestnut cupule" (Fig. 6E). In contrast to conventional SnO_2 materials, this unique morphology significantly improved the storage capacity and cycling performance of SnO_2 as an anode material for lithium and sodium ion batteries.[206]

In addition, 3D hierarchical SnO_2 nanomaterials can be assembled by 0D, 1D, and 2D SnO_2 nanomaterials. For example, 0D crystalline SnO_2 nanoparticles were successfully assembled
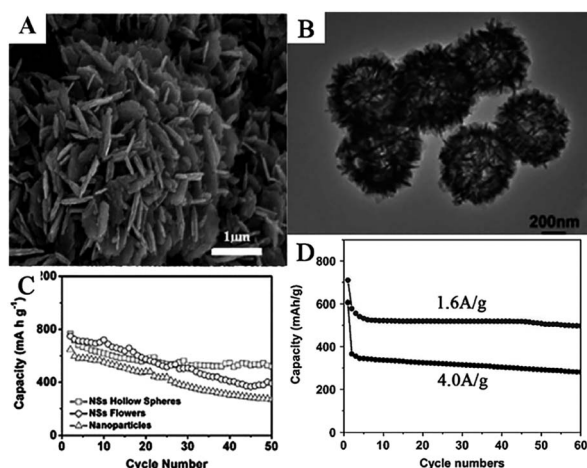

Fig. 5 (A) SEM images of flower-like SnO_2 nanosheets (adapted with permission from ref. 78 copyright 2014 Elsevier). (B) TEM image, and (C) cycling performance of SnO_2 nanosheets hollow spheres (adapted the permission from ref. 87 copyright 2011 Royal Society of Chemistry). (D) Cycling performance of SnO_2 nanosheets at 1.6 A g^{-1} and 4.0 A g^{-1} (adapted the permission from ref. 81 copyright 2017 Elsevier).
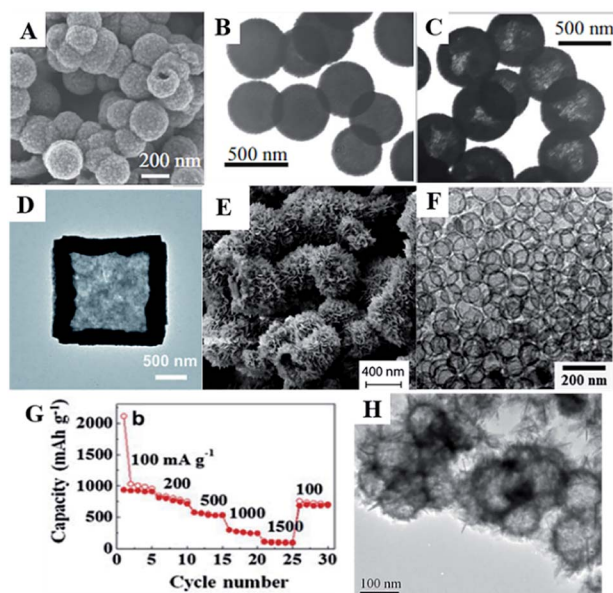
Fig. 6 (A) FESEM images of SnO_2 hollow nanosphere prepared in the solvent of $EtOH : H_2O$ ratio of 1 : 1. (B) TEM images of SnO_2 hollow nanosphere prepared with the value of EtOH in the solvent of $EtOH–H_2O = 37.5\%$. (C) TEM images of SnO_2 hollow nanosphere prepared with the value of EtOH in the solvent $EtOH–H_2O = 37.5\%$ and 0.1 M urea (adapted the permission from ref. 86 copyright 2006 WILEY). (D) TEM images of SnO_2 microboxes (adapted the permission from ref. 195 copyright 2016 Royal Society of Chemistry). (E) SEM images of SnO_2 hierarchical hollow microspheres (adapted the permission from ref. 205 copyright 2017 Royal Society of Chemistry). (F) TEM images, and (G) rate performance of SnO_2 hollow spheres (adapted with permission from ref. 91 copyright 2012 Elsevier). (H) TEM image of the hierarchical SnO_2 (adapted with permission from ref. 210 copyright 2010 American Chemical Society).

into a high-order nanostructure of hollow core–shell. First, $SnCl_4$ was dissolved in a mixture of DI water and ethanol to form a homogeneous solution which was heated to 180 °C for 24 h. Then, the collected sediments were calcined in air to remove carbon by oxidation. FESEM showed that the mesospheres had an overall dimension of 1–3 μm, and the surface of the spheres was formed by small aggregated SnO_2 nanoparticles (11 nm). The shell was estimated to be approximately 200 nm in thickness. This unique SnO_2 nanostructure could store an exceedingly large amount of Li^+ and cycled well for a pure phase SnO_2 anode.[207–209] Hollow urchin-like SnO_2 nanospheres have been fabricated using ultrathin nanorods *via* a solvothermal route. The diameters of urchin-like nanospheres and nanorods are about 300 and 100 nm, respectively. The as-obtained hollow urchin-like SnO_2 nanospheres with ultrathin 1D nanorods exhibited high capacity and excellent rate discharging performance. The 1st, 2nd, 20th, and 50th discharge capacities were 1881 mA h g^{-1}, 1090 mA h g^{-1}, 781 mA h g^{-1}, and 719 mA h g^{-1}, respectively, at a current density of 100 mA g^{-1}. Upon changing the discharge–charge rates to 0.2, 0.4, 0.8, 1, 2, and 0.4C, the capacities of urchin-like SnO_2 were maintained at 815, 687, 601, 446, 282, and 520 mA h g^{-1}, respectively, while for commercial SnO_2, the capacities were

only 828, 677, 512, 386, 246, 133, and 375 mA h g^{-1}, respectively. The retention of the reversible capacity of the hollow nanosphere electrodes was better than that of commercial SnO_2 samples.[210] Furthermore, SnO_2 hollow nanospheres can also be synthesized by sol–gel methods.[91] The size of the hollow spheres is controlled by using different-sized templates. As-prepared SnO_2 shells are almost amorphous and exhibit a rutile phase after annealing at 600 °C. The size of the SnO_2 hollow spheres ranges from 25 to 100 nm (Fig. 6F), and the thickness of the shell is constantly 5 nm despite the size of the hollow spheres. Due to the nanosized hollow sphere and thin shell thickness, SnO_2 hollow spheres show excellent electrochemical performance. The smallest hollow sphere of SnO_2 (25 nm) exhibited a high reversible capacity of 750 mA h g^{-1} as well as good rate performance, *i.e.*, 700 mA h g^{-1} at 0.2 A g^{-1} and 530 mA h g^{-1} at 0.5 A g^{-1} (Fig. 6G).[91] Hierarchical SnO_2 hollow nanostructures can also be assembled by 2D nanosheets. As shown in Fig. 6H, the hierarchical SnO_2 shows high capacities and excellent cycle performance as an anode material for LIBs. The improved electrochemical properties could be ascribed to the large surface area, enhanced structure stability, and short diffusion length for both lithium ions and electrons.[211]

3. Composites of SnO_2 and carbonaceous materials

3.1 SnO_2 with carbon nanotubes (CNTs)

Nanocomposites of SnO_2 and CNTs reportedly exhibit improved lithium storage capacities compared to pure SnO_2 materials.[212] This can be attributed to the flexible nature and superior conductivity of the CNTs, which alleviates the internal stress caused during the charge/discharge process[213–215] and enhances the electron transportation. With increased conductivity and surface area, such nanocomposites show enhanced lithium storage capability.[216,217]

Wen *et al.* reported an *in situ* synthesis of mesoporous SnO_2 on the surface of multi-walled CNTs (MWCNTs) through a hydrothermal method utilizing CTAB as the structure-directing agent. The MWCNTs/SnO_2 hybrid electrodes showed great electrochemical performance and cycling stability. This can be attributed to the synergistic effects of the unique combination of properties including their one-dimensional hollow structure, high-strength with flexibility, excellent electric conductivity, and large surface area, which helped alleviate the effect of volume expansion, shorten the distance of Li^+ diffusion, and contribute to the transmission of electrons.[100,218–221]

In another hydrothermal system, Du *et al.* synthesized SnO_2/MWCNT composites by a simple solvothermal method and subsequent heat treatment at 360 °C with $SnCl_2$ and CNTs as reactants. The distribution of SnO_2 nanocrystals can be controlled by changing the molar ratio of Sn^{2+} and CNTs in the precursor. For SnO_2/MWCNTs composites prepared with a molar ratio of Sn : C = 0.3 : 1, a uniform layer of SnO_2 nanocrystals, with a crystal size of about 5 nm, was deposited on the surface of the MWCNTs (Fig. 7A).[222] These composites showed
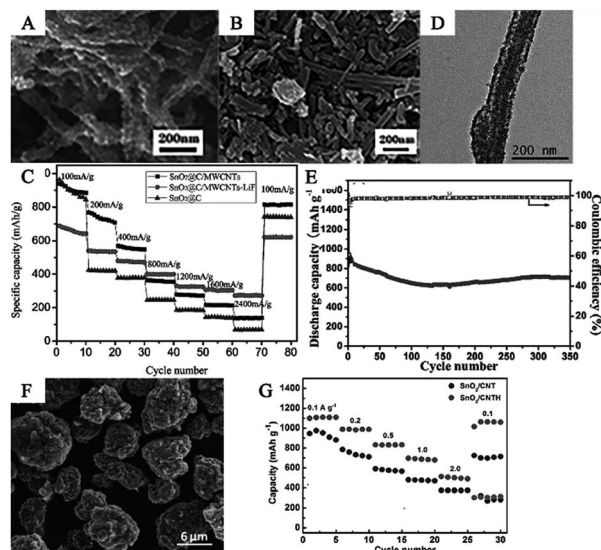
Fig. 7 (A) FESEM image of SnO$_2$/CNT composites prepared with MSn : C = 0.3 : 1 (adapted with permission from ref. 221 copyright 2009 Elsevier). (B) SEM image, and (C) rate performance of SnO$_2$@C/MWCNTs-LiF (adapted with permission from ref. 224 copyright 2019 Elsevier). (D) TEM image and (E) cycling performance of CNT@void@SnO$_2$@C composite (adapted the permission from ref. 225 copyright 2015 Elsevier). (F) SEM image, and (G) rate performance of SnO$_2$/CNTH composites (adapted with permission from ref. 226 copyright 2019 American Chemical Society).

very stable cycling retention, of up to 100 cycles, because of nanosized materials and the introduction of CNTs.[201,223] Jin et al. prepared SnO$_2$/MWCNTs electrodes via a hydrothermal method at 150 °C for 24 h. The SnO$_2$ nanoparticles with diameters of less than 3 nm were uniformly loaded onto the surface of MWCNTs. The MWCNT/SnO$_2$ nanocomposites exhibited a high reversible capacity of 420 mA h g^{-1} even after 100 cycles.[137,224]

In order to further improve electrochemical properties of the SnO$_2$/CNTs hybrid nanomaterials, many groups have synthesized various SnO$_2$/CNTs-based anode materials. For example, Liang et al. synthesized SnO$_2$@C/MWCNTs-lithium fluoride (LiF) composite nanomaterials (Fig. 7B). Carbon-coated SnO$_2$ (SnO$_2$@C) was prepared by a spray drying method, with water-soluble asphalt as the carbon source and MWCNTs as the conductive agent. The conductivity was significantly enhanced, and the extent of volume expansion of the SnO$_2$ was reduced. Compared to SnO$_2$/CNTs, the presence of LiF enhanced the stability of the SEI film and improved the coulombic efficiency and capacity retention rate of the electrode. After 200 cycles, the SnO$_2$@C/MWCNTs-LiF anode still maintained 70.1% of the capacity retention rate and the specific capacity was held at 274 mA h g^{-1} at 2400 mA g^{-1}, compared with 136 mA h g^{-1} for the SnO$_2$@C/MWCNTs anode (Fig. 7C).[225] Tian et al. fabricated a tube-in-tube nanostructure, denoted as CNT@void@SnO$_2$@C, by a facile hydrothermal method and subsequent carbonation with polysaccharide as the carbon source, SiO$_2$ as the sacrificial template, and NH$_4$F as the etchant. The CNT@void@SnO$_2$@C exhibited one-dimensional nanostructures with average

diameters of about 100–150 nm and hollow structures filled with abundant voids (Fig. 7D). Tian et al. interpreted the formation mechanism as follows: (1) the crystallization and deposition of SnO$_2$ could occur prior to the polycondensation of glucose; (2) the formation rate of SnO$_2$@polysaccharide was faster than the etching rate of SiO$_2$ by NH$_4$F due to the slow etching process of SiO$_2$ by NH$_4$F solution under hydrothermal condition; and (3) the large void-space between the SnO$_2$@polysaccharide and CNT, formed after the SiO$_2$ coating layer, was etched away completely. The CNT@void@SnO$_2$@C exhibited good electrochemical properties, delivering a reversible capacity of 702.5 mA h g^{-1} at 200 mA g^{-1} even after 350 cycles (Fig. 7E). This indicated that the unique tube-in-tube nanostructure, as well as the one-dimensional void space, which formed between the inner CNT and outer SnO$_2$@C nanotubes, contributed significantly to the electrochemical performance.[226] Liu et al. synthesized ultrafine SnO$_2$ (6–7 nm)/carbon nanotube hairball (SnO$_2$/CNTH) composites with a 3D hierarchical structure (Fig. 7F), which was prepared by spray drying and a solvothermal method. Fig. 7G shows that SnO$_2$/CNTH exhibited superior electrochemical performance and improved the lithium storage capacity compared to conventional SnO$_2$/CNT. The improved electrochemical performance can be attributed to the increased conductivity and enhanced electrode reactivity due to the 3D hierarchical cross-linked structure. This structure can also address the large volume changes upon cycling.[227]

3.2 SnO$_2$ with amorphous carbon

Hydrothermal treatment followed by carbonization is the most common method for synthesizing SnO$_2$/amorphous carbon nanomaterials.[228–230] There are mainly two synthesis routes of SnO$_2$/amorphous carbon; one is to treat Sn^{2+} or Sn^{4+} salt with the precursor of carbon,[231–236] and the other is to deposit a carbon layer on the as-prepared SnO$_2$ nanostructures.[237,238] Conventional amorphous carbon can be derived from glucose,[239,240] sucrose[241,242] and many organic compounds.[243] The morphology and shapes of the nanostructures can be adjusted by the hydrothermal and annealing conditions.

Various SnO$_2$/C nanomaterials have been synthesized in recent years, such as carbon-coated SnO$_2$ NPs,[244–247] carbon-coated SnO$_2$ nanorods,[248,249] carbon-coated SnO$_2$ nanowires[151,217] and carbon-coated SnO$_2$ nanotubes.[57] Different structures and morphologies of SnO$_2$ are known to lead to different electrochemical performance. In 2008, Lou et al. prepared SnO$_2$/C composite hollow spheres. The mesoporous SnO$_2$ hollow spheres were embedded in 3D carbon networks (Fig. 8A). The carbon networks act as a physical buffering cushion for the intrinsic large volume change and electronically conducting pathways. Compared to SnO$_2$ hollow spheres and graphite, these SnO$_2$/carbon hollow spheres were able to deliver a reversible lithium storage capacity of 473 mA h g^{-1} after 50 cycles (Fig. 8B).[99] In 2009, Lou et al. also synthesized a thin layer of carbon-coated SnO$_2$ nano-colloids (Fig. 8C) and coaxial SnO$_2$@carbon hollow nanospheres (Fig. 8D) by a simple hydrothermal method followed by carbonization; both
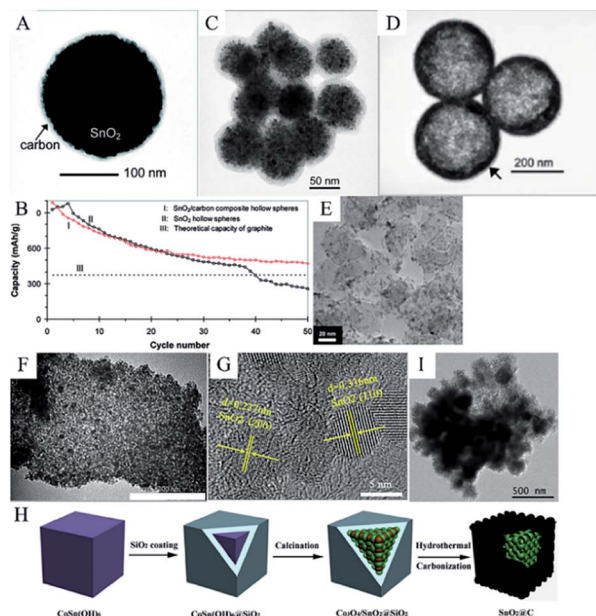
Fig. 8 (A) TEM image, and (B) cycling performance of SnO_2/carbon composites hollow spheres (adapted with permission from ref. 99 copyright 2008 American Chemistry Society). (C) TEM image of carbon-coated SnO_2 nanocolloids obtained after carbonization at 550 °C (adapted with permission from ref. 239 copyright 2009 American Chemical Society). (D) TEM image of SnO_2@carbon hollow nanospheres (adapted with permission from ref. 240 copyright 2009 Wiley). (E) TEM image of nanosized SnO_2/carbon composites (adapted with permission from ref. 248 copyright 2009 Elsevier). (F) TEM image, and (G) HRETM image of SnO_2/RHPC composite materials (adapted with permission from ref. 231 copyright 2019 Elsevier). (H) The fabrication schematic of SnO_2@non-smooth carbon. (I) TEM image of SnO_2 quasi-nanocubes@non-smooth carbon (adapted with permission from ref. 255 copyright 2019 Elsevier).

exhibited improved electrochemical performance.[57,250] Courtel *et al.* reported an *in situ* synthesis of SnO_2 nanoparticles (5–10 nm)/carbon composite materials using the polyol method by oxidizing $SnCl_2 \cdot 2H_2O$ in the presence of a carbon matrix. The TEM image (Fig. 8E) show that the SnO_2 nanoparticles were uniformly embedded in the carbon matrix. Based on the nanostructure, the as-obtained composites showed an improved lithium storage capacity of 370 mA h g^{-1} at 200 mA g^{-1} and a lower capacity fading compared to commercial SnO_2 (50 nm).[251]

While the morphology and structure of SnO_2 influence the electrochemical properties of the SnO_2/C composites, different carbonaceous materials also influence the performance of the composite. Xu *et al.* prepared composites of SnO_2/ordered mesoporous carbon (SnO_2/OMC) through a hydrolysis process. OMC, a novel kind of carbon material, has been widely used in LIBs due to its large surface area, high conductivity, and highly porous structure; it promotes the diffusion of lithium ions and electrolyte. The SnO_2/OMC composites delivered a good cycling performance with a reversible capacity of 395.6 mA h g^{-1} for up to 50 cycles.[252] Shi *et al.* synthesized SnO_2/rice-husk-based porous carbon composites (RHPC) *via* a simple melt-

impregnation method with a heat treatment route. RHPC can be easily and cheaply obtained by convenient carbonization and activation of rice husk. The TEM images (Fig. 8F and G) show that the SnO_2 nanoparticles with the average size of 4 nm can be loaded on the RHPC matrix. The cycling measurements showed that the discharge capacity of the RHPC/SnO_2 anode at the current density of 100 mA g^{-1}, at the 50th cycle, was 550 mA h g^{-1}, which demonstrated that in contrast to pure SnO_2 anodes, the cycling performance of the RHPC/SnO_2 anode was remarkably enhanced by the introduction of the RHPC matrix. It also demonstrates that biomass-sourced carbonaceous materials like RHPC[253–255] have promising applications in LIBs due to their low cost and porous structure.[233] Tian *et al.* fabricated non-smooth carbon-coated SnO_2 quasi-nanocubes. Generally, in SnO_2/C nanocomposites, nanostructured SnO_2 is usually coated with smooth carbon, which is easily fabricated from organically sourced carbon *via* hydrothermal or CVD methods.[90,256] However, it is believed that SnO_2-coated 3D non-smooth carbon usually shows better lithium storage properties owing to the substantial free space and larger surface area of the 3D structure.[257] In this work, Tian *et al.* synthesized the hybrid nanostructures *via* multiple hydrothermal and calcination methods (Fig. 8H). As shown by the TEM images (Fig. 8I), the porous SnO_2 quasi-nanocubes were coated by a carbon layer with a rough surface. The introduction of 3D non-smooth carbon can reduce the transmission length of electrons and Li$^+$ and increase the electrochemical reaction sites. Based on such 3D porous structures, the SnO_2@C anode displayed extraordinary cycling performance and outstanding rate capability, maintaining a capacity of 1089.5 mA h g^{-1} at 200 mA g^{-1}, even after 400 cycles, as well as 479.2 mA h g^{-1} at 3000 mA g^{-1}.[257]

It is worth mentioning that even though the amorphous carbon layer can enhance the cycling stability and conductivity of the composites, it has a relatively low lithium storage capacity compared to SnO_2. Therefore, the ratio of the carbon layer and the SnO_2 nanomaterial determines the capacity and cycle life of the composites.

3.3 SnO_2/graphene

As an important 2D carbon material, graphene has quickly gained importance in material science in recent years. Due to its excellent mechanical properties and superior conductivity, graphene has been widely studied in LIBs.[258–260] Compared to CNTs and amorphous carbon, graphene exhibits higher specific discharge capacity, high surface area, good mechanical properties, and high chemical stability;[261–263] thus, SnO_2/graphene, as an anode material in LIBs, shows better electrochemical performance.[264–268]

Graphene can be used as a supporting substrate for the synthesis of hierarchical SnO_2 nanostructures. For example, Ding *et al.* fabricated 2D SnO_2 nanosheets grown on a graphene oxide (GO) support *via* a facile hydrothermal method. The SnO_2 nanosheets were uniformly embedded in the GO support, approximately 100 nm in length and 5–10 nm in thickness (Fig. 9A). This unique SnO_2/GO hybrid structure exhibited
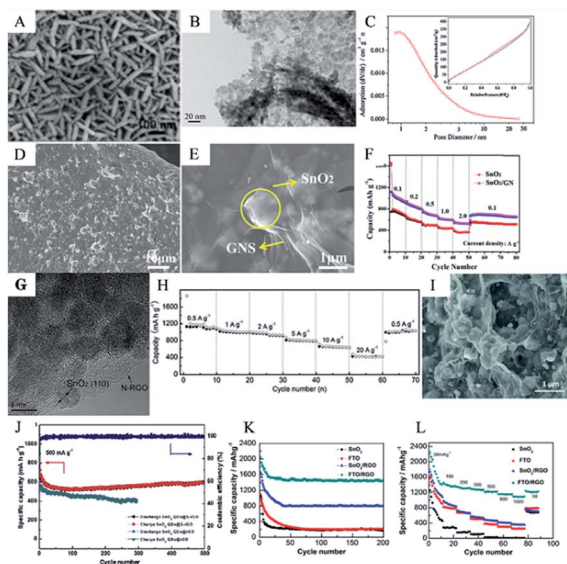
Fig. 9 (A) SEM image of SnO$_2$ nanosheets/graphene (adapted with permission from ref. 170 copyright 2011 Royal Society of Chemistry). (B) TEM image and (C) nitrogen adsorption–desorption isotherms of SnO$_2$ nanoparticles/graphene (adapted with permission from ref. 169 copyright 2017 Elsevier). (D and E) SEM images and (F) rate performance of SnO$_2$/GN on Ni foam (adapted with permission from ref. 267 copyright 2018 Elsevier). (G) HRTEM image and (H) rate performance of SnO$_2$NC@N-RGO (adapted with permission from ref. 173 copyright 2013 Wiley). (I) SEM images of SnO$_{2-x}$/N-rGO (adapted with permission from ref. 280 copyright 2018 Royal Society of Chemistry). (J) Cycling stability of SnO$_2$QDs@S-rGO (adapted with permission from ref. 277 copyright 2018 Elsevier). (K) Cycling performance and (L) rate performance of FTO/rGO (adapted with permission from ref. 109 copyright 2015 American Chemical Society).

enhanced lithium storage properties with high reversible capacities, i.e., an initial discharge capacity of 1666 mA h g^{-1}, and good cycling performance, i.e., 518 mA h g^{-1} after 50 cycles at 400 mA h g^{-1}.[171] Additionally, due to its mechanical properties and electronic conductivity, graphene can serve as the carbon matrix to accommodate the SnO$_2$ nanoparticles. In 2017, Shi et al. investigated a facile microwave-assisted hydrothermal method to synthesize a composite of SnO$_2$ and graphene, which took only 30 min and did not require any chelating agents. As shown by TEM images (Fig. 9B) and the nitrogen adsorption–desorption isotherms (Fig. 9C), Shi et al. found that ultra-small SnO$_2$ nanoparticles were well dispersed on the surface of the graphene, with an average particle size of about 3–8 nm. It also showed superior lithium storage capability. The charge/discharge capacity of this material was 969.4/978.6 mA h g^{-1} after 100 cycles at 200 mA h g^{-1}.[269] Binder-free multilayered SnO$_2$/graphene on Ni foam was fabricated via a dip-coating method. SnO$_2$ nanoparticles and grapheme were alternatively coated on to the Ni foam to obtain a sandwich-like structure. As shown in SEM images in Fig. 9D and E, SnO$_2$ nanoparticles were uniformly distributed on the surface of the Ni foam and wrapped tightly in GN. Such a multilayered nanostructure showed superior electrochemical performance due to the following factors: (1) 3D porous Ni foam serves as a conductive network

and binder-free current which is beneficial for electron and ion diffusion; (2) the graphene layer improves the conductivity of anode material and buffers the SnO$_2$ volume changes; and (3) the extent of volume change of the SnO$_2$ nanoparticles is lower than that of bulk SnO$_2$. Owing to such porous Ni foam frameworks and sandwich-like structures, the SnO$_2$/graphene composites exhibited good rate performance and excellent cycling stability. High capacities, i.e., 708 and 609 mA h g^{-1} were achieved at current densities 1 and 2 A g^{-1}, respectively (Fig. 9F). Furthermore, the SnO$_2$/GN electrode delivered a high capacity of 757 mA h g^{-1} after 500 cycles at 1 A g^{-1}.[174]

Moreover, it is worth mentioning that atom-doped graphene can also be used as a carbon matrix for SnO$_2$, which effectively enhances the electrochemical performance of the composites. Heteroatoms in graphene can act as anchor sites that prevent aggregation and exfoliation of the SnO$_2$ anchored on graphene; this helps improve the cycling stability of such anode materials.[270–274] Liu et al. synthesized SnO$_2$ nanoparticles anchored on chlorinated graphene (SnO$_2$@rGO-Cl) as binder-free electrodes that exhibit a long cycling life, of up to 400 cycles, with a discharge capacity of 1008 mA h g^{-1} via a facile strategy using a one-step heat treatment at low temperature.[275] Liu et al. found that Cl-doping can enhance the electrical conductivity of graphene and the Cl–Sn bonds can prevent the exfoliation of SnO$_2$ nanoparticles during the charge/discharge process; thus, improving the electrochemical properties of SnO$_2$-based hybrid nanomaterials. SnO$_2$/nitrogen-doped graphene (N-rGO) was also applied as an anode in LIBs. It is believed that N-doped carbonaceous materials enhance the electronic conductivity and SEI film stability.[276–278] Zhou et al. fabricated SnO$_2$@N-rGO via a hydrazine monohydrate vapor reduction approach for anchoring SnO$_2$ nanocrystals uniformly into N-rGO (Fig. 9G). Due to the bond formed between SnO$_2$ and graphene, and the void pores dispersed in N-rGO, the as-prepared hybrid materials displayed superior mechanical properties and lithium storage capacity. SnO$_2$@N-rGO anode showed a reversible charge capacity of 1346 mA h g^{-1} after 500 cycles; furthermore, as the current density increased from 0.5 to 1, 2, 5, 10, and 20 A g^{-1}, their discharge capacity varied from 1074 to 994, 915, 782, 631, and 417 mA h g^{-1}, respectively (Fig. 9H).[279] Wu et al. synthesized the SnO$_{2-x}$/N-rGO hybrid material through electrostatic adsorption-induced self-assembly together with a thermal reduction process. This treatment induced the generation of the oxygen vacancies on the surface of SnO$_2$ hollow nanospheres; thus, building up a long-range and bi-continuous transfer channel for rapid electron and ion transport. Meanwhile, SnO$_{2-x}$ hollow spheres are well-wrapped by graphene sheets; thus, enhancing the conductivity of the anode material (Fig. 9I). Due to these structural advantages, the as-obtained SnO$_{2-x}$/N-rGO electrode exhibited excellent robust cycling stability, i.e., about 912 mA h g^{-1} after 500 cycles at 0.5 A g^{-1} and 652 mA h g^{-1} after 200 cycles at 1 A g^{-1}, and superior rate capability, i.e., 309 mA h g^{-1} at 10 A g^{-1}.[280] Sulfur-doped graphene (S-rGO) also proved to be a feasible anode material for LIBs.[281] Compared to the C atom, the S atom has a larger volume and lower electronegativity, which is beneficial for the diffusion of Li$^+$ and electrons. For instance, Wu et al. successfully loaded

SnO_2 quantum dots (QDs) on sulfur-doped reduced graphene oxide (S-rGO), and it exhibited excellent lithium storage with a high specific capacity of 897 mA h g^{-1} and a long cycling stability with 88% capacity retention after 500 cycles (Fig. 9J).[282] The abovementioned results demonstrate that heteroatoms can tailor the electronic structure of carbon and create topological defects in the carbon lattice.[281,283]

Apart from doped-graphene, atom-doped SnO_2, such as fluorine-doped tin oxide[138] and antimony-doped tin oxide[122] can also be used with pristine graphene as an anode material.[284–287] For example, Xu et al. has successfully fabricated composites of fluorine-doped tin oxide (FTO) and rGO from a colloidal solution containing FTO nanocrystals and rGO by a hydrothermal treatment; the FTO nanocrystals were tightly embedded in the RGO nanosheets. As an anode material, the FTO/RGO composite showed high structural stability during the lithiation and delithiation processes. The conductive FTO nanocrystals help form stable and thin SEI films. Moreover, the FTO/RGO composite retains a discharge capacity as high as 1439 mA h g^{-1} after 200 cycles at 100 mA g^{-1} (Fig. 9J), and 1148 mA h g^{-1} at 1000 mA g^{-1} (Fig. 9K).[109]

3.4 Complex SnO_2/C nanostructure

Compared to 1D or 2D carbonaceous materials, complex 3D carbonaceous matrices usually show better electrochemical properties due to their high specific surface area and porous structure, which is beneficial in suppressing volume changes.[288] In recent years, various SnO_2/C complex hybrid nanomaterials have been reported, such as the combination of CNTs and amorphous carbon,[288] and CNTs and graphene.[283,289,290] These complex hierarchical SnO_2/C nanostructures often show superior electrochemical properties, making them an important research subject.

A sandwich structure with carbon nanofiber, SnO_2, and nanofiber bundle for carbon-coating (C@SnO_2@C) has been fabricated by using collagen fiber (CF), which is a typical fibrous protein extracted from cattle skin and is used as a bio-template as well as the carbon source. FESEM image (Fig. 10A) and TEM image (Fig. 10B) show that the average diameter of the SnO_2 nanofiber bundle was about 5–10 μm and a layer of SnO_2 was sandwiched between the carbon nanofiber and the carbon coating layer. Such hierarchical architectures of the C@SnO_2@C nanofiber bundle guaranteed a good balance between electron transport and Li+ diffusion kinetics. Thus, efficient ambipolar diffusion and reduced volume changes of SnO_2 were obtained to ensure structural integrity with high cycling stability.[162]

A porous 3D core–shell structured CNT@SnO_2 composite, with a graphene coating (CNT@SnO_2@G), has been synthesized via a two-step hydrothermal method. The first step consists of the synthesis of CNT@SnO_2, and then, CNT@SnO_2@G is formed in the subsequent step. FESEM image (Fig. 10C) and TEM image (Fig. 10D) show that CNT@SnO_2 (about 20–40 nm in width) particles was distributed across the graphene sheets and was encased in the graphene coating, which suppressed the formation of SEI layers on the surface of the CNT@SnO_2@G.
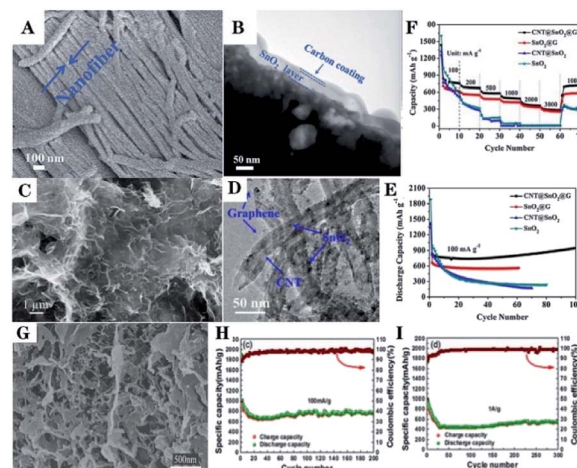

Fig. 10 (A) FESEM image, and (B) TEM image of C@SnO_2@C nanofiber bundle (adapted with permission from ref. 162 copyright 2016 Royal Society of Chemistry). (C) FESEM image, (D) TEM image, (E) cycling performance, and (F) rate performance of CNT@SnO_2@G (adapted with permission from ref. 263 copyright 2017 Elsevier). (G) SEM image, (H) cycling performance, and (I) rate performance of SnO_2@G-SWCNT materials (adapted with permission from ref. 289 copyright 2017 American Chemical Society).

The as-prepared CNT@SnO_2@G electrode exhibited outstanding lithium storage capability, including a large specific capacity, remarkable cycling stability, and excellent rate capability (Fig. 10E and F).[265]

SnO_2 nanoparticles anchored on an aerogel based on 3D graphene-single walled carbon nanotube (SnO_2@G-SWCNT), as shown in Fig. 10G, has been fabricated by a hydrothermal self-assembly process.[291] The 3D G-SWCNT matrix provides a flexible conductive matrix and a more porous network to support SnO_2. This is beneficial for facilitating electronic and ionic transportation and mitigating the volume changes of the SnO_2 during lithiation/delithiation; thus, leading to enhanced electrochemical performance of the SnO_2 anodes for LIBs. The discharge capacity remained 758 mA h g^{-1} at 100 mA g^{-1} after 200 cycles (Fig. 10H) and 537 mA h g^{-1} at 1 A g^{-1} after 300 cycles (Fig. 10I).[291]

4. SnO_2/TMOs/C

The composites of SnO_2 and transition metal oxides (TMOs) have been considered as promising anode materials for LIBs.[292–294] By the introduction of metal oxides, the reversible decomposition of Li_2O can be increased because TMOs can convert extra Li_2O into Li+;[295–297] thus, enhancing their cycling stability, rate performance, and rate capability. However, the electrochemical performance of SnO_2/TMOs is unsatisfactory because of low conductivity and large volume expansion, leading to poor cycling stability.[136] In order to overcome these problems, much work has been focused on the fabrication of SnO_2/TMOs/C materials in recent years. Supported and coated by carbonaceous material and TMOs, the structural stability and conductivity of SnO_2 can be significantly improved. This

section will cover synthesis methods, morphology, and electrochemical performance of SnO_2/TMOs/C.[298–302]

4.1 SnO_2/Fe_2O_3/C

Fe_2O_3 has been considered as another promising anode material for LIBs due to its large theoretical capacity (1007 mA h g^{-1}) and low cost.[303,304] However, the short carrier diffusion length inhibits lithiation/delithiation processes. It has been reported that SnO_2/Fe_2O_3 showed an improvement in photocatalysis, energy storage, and gas sensing.[303,305–307] Furthermore, the SnO_2/Fe_2O_3/C electrode showed better lithium storage capability.[308] In this composite, SnO_2 possesses a high intrinsic conductivity and a shortened charge diffusion distance, while Fe_2O_3 facilitates the reversible decomposition of Li_2O and prevents Sn aggregation during charging and discharging.[309]

In 2014, Wu *et al.* proposed a facile hydrothermal method to synthesize a ternary phased SnO_2/Fe_2O_3/SWCNTs composite. As shown in Fig. 11A, the composites of SnO_2 and Fe_2O_3 nanoparticles were well distributed and firmly anchored on to SWCNTs, which serve as a buffer and conductive matrix. Nanosized Fe_2O_3/SnO_2 composites can suppress the effect of volume changes and particle agglomeration. The SnO_2/Fe_2O_3/SWCNTs electrode showed a high reversible capacity, superior cycle performance, and high rate capability. It delivered a capacity of 692 mA h g^{-1} at 200 mA g^{-1} after 50 cycles. Even at a rate as high as 2000 mA g^{-1}, this composite could still maintain its capacity at 656 mA h g^{-1} (Fig. 11B).[310]

The growth of SnO_2 on Fe_2O_3 and subsequent carbon coating on SnO_2/Fe_2O_3 is another common synthesis route for SnO_2/Fe_2O_3/C. Du *et al.* synthesized γ-Fe_2O_3@SnO_2@C porous core–shell nanorods. They first formed FeOOH nanorods *via* a hydrothermal process, which served as a template for the subsequent SnO_2 deposition process in another hydrothermal system. After the deposition of SnO_2 on the FeOOH nanorods, the as-synthesized FeOOH@SnO_2 nanorods were coated with

a carbon layer *via* another hydrothermal process and carbonized under N_2 at 500 °C for 2 h (Fig. 11C). The TEM image (Fig. 11D) shows that SnO_2 can successfully grow on the Fe_2O_3 nanostructure with well-defined interfaces. The thickness of the SnO_2 layer is 5–10 nm, which is composed of SnO_2 nanoparticles with a diameter of about 3–5 nm, and the core nanorod is highly porous. Such a porous core–shell hybrid nanorod-based electrode showed good cycling and rate performance due to the improvement of conductivity and structural stability by the introduction of carbon and Fe_2O_3.[115]

4.2 SnO_2/Co_3O_4/C

Many studies have concentrated on improving electrochemical properties of SnO_2 and Co_3O_4 by designing and synthesizing unique nanostructures. Like most transition metals, the presence of Co can improve the reversibility of the reduction reaction of Li_2O and further enhance the reversible capacity.[311–315] As shown in Fig. 12A, Co_3O_4@SnO_2@C core–shell nanorods have been synthesized *via* a hydrothermal method followed by carbonization. Fig. 12B and C show that SnO_2 nanoparticles uniformly coated the surface of Co_3O_4 nanorods and that the coating was smooth and uniform, with a thickness of 5–10 nm. Such materials exhibited improved cycling performance and higher specific capability as an anode material for LIBs (860 mA h g^{-1} after 50 cycles at 0.2 A g^{-1}). This result demonstrated that the combination of SnO_2 and Co_3O_4, into an integrated core–shell nanorod structure, exhibited a better and more elegant synergistic effect during the charge/discharge processes.

SnO_2/Co_3O_4@N-doped carbon (NC) usually shows better lithium storage properties compared to most SnO_2/Co_3O_4/C materials.[316] Wang *et al.* successfully designed and fabricated SnO_2/Co_3O_4/NC nanoflakes *via* a combined strategy of CVD and template synthesis.[119,317] HRTEM images (Fig. 12D) show that SnO_2/Co_3O_4 nanoparticles were uniformly distributed on the NC nanoflakes. By adjusting the ratio of the precursor and reaction conditions, they found that the SnO_2/Co_3O_4@NC ($R_{Sn/}$
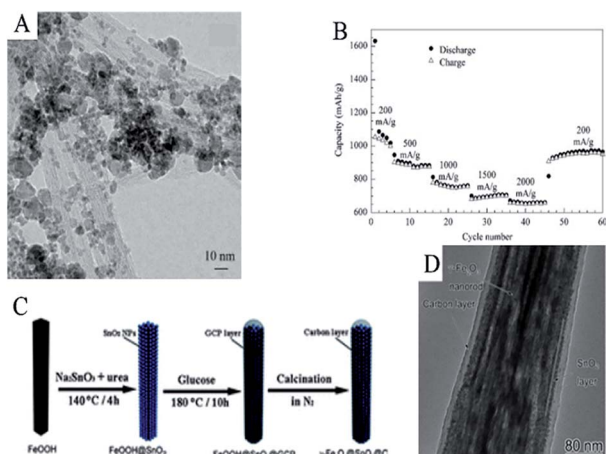

Fig. 11 (A) TEM image, and (B) rate performance of SnO_2/Fe_2O_3/SWCNTs (adapted with permission from ref. 308 copyright 2014 Elsevier). (C) TEM images, and (D) schematic illustration of the synthesis of γ-Fe_2O_3@SnO_2@C core–shell nanorods (adapted with permission from ref. 115 copyright 2013 Royal Society of Chemistry).

Fig. 12 (A) Schematic illustration of the fabrication of Co_3O_4@SnO_2@C core–shell nanorods. (B) TEM image, and (C) HRTEM images of Co_3O_4@SnO_2@C core–shell nanorods (adapted with permission from ref. 313 copyright 2012 Royal Society of Chemistry). (D) HRTEM image and, (E) cycling performance of SnO_2/Co_3O_4@NC-1 nanoflakes (adapted with permission from ref. 119 copyright 2019 Elsevier).

$_{Co} = 1:1)$ nanoflakes-based electrode demonstrated excellent lithium storage capability, *i.e.*, a discharge capacity of 1450.3 mA h g^{-1} after 300 cycles at 200 mA h g^{-1} (Fig. 12E). The superior lithium storage of such materials may result from the synergistic effect between the combination of SnO$_2$ and Co$_3$O$_4$ and better conductivity caused by the N-doped carbon matrix.[119]

Therefore, in SnO$_2$/Co$_3$O$_4$/C composites, SnO$_2$ and Co$_3$O$_4$ display a synergistic enhancement effect. It can provide additional active sites for lithium storage and shorten the lithium diffusion distance. Additionally, the carbon layer can greatly improve the electrode conductivity and restrain volume changes during the lithiation/delithiation processes.

4.3 SnO$_2$/TiO$_2$/C

SnO$_2$, as one of the most extensively investigated anode material, which offers a high specific capacity. However, poor cycling stability, due to large volume expansion and subsequent pulverization during Li$^+$ insertion/extraction processes, greatly restricts its application as an anode material.[130,318–320] In contrast, TiO$_2$ exhibits negligible volume change (less than 4%) and stable electrochemical properties, but its application is limited due to its low specific capacity.[321–325] Furthermore, SnO$_2$ and TiO$_2$ have complementary characteristics in LIBs, *i.e.*, Sn^{4+} and Ti^{4+} possess similar radii and the lattice matching of SnO$_2$ and TiO$_2$ is good.[326–328] Considering the facts mentioned above, in order to promote cycling stability of SnO$_2$, various SnO$_2$/TiO$_2$ based hybrid materials have been synthesized.[329–334]

Mesoporous SnO$_2$@C@TiO$_2$ nanochains have been synthesized by first fabricating SnO$_2$@C core–shell nanochains *via* a hydrothermal method and subsequent continuous mechanical stirring of the solution of SnO$_2$@C and tetrabutyl titanate (C$_{16}$H$_{36}$O$_4$Ti). It is noticeable that the SnO$_2$ core is composed of SnO$_2$ nanoparticles with a diameter of 2–6 nm and is coated by a thin carbon layer (2–6 nm) as well as a TiO$_2$ layer (about 8 nm) (Fig. 13A). In this 3D hierarchical structure, the carbon layer and the TiO$_2$ layer can effectively improve cycling stability and discharge capacity, *i.e.*, the initial discharge capacity of

807 mA h g^{-1} and 369 mA h g^{-1} after 100 cycles at 100 mA h g^{-1}.[298]

Xie *et al.* reported the synthesis of hierarchical TiO$_2$/SnO$_2$ hollow spheres coated with graphitized carbon (HTSO/GC-HSs) by a multi-step approach. As shown in Fig. 13B, titanate-silicone gel particles were first reacted with SnCl$_2$ *via* a sol–gel process to obtain core–shell hybrid structures, which were further coated with a polysaccharide *via* a hydrothermal process and subsequent carbonization in Ar atmosphere. As shown in Fig. 13C, the as-prepared mesoporous HTSO/GC-HSs had a yolk–shell structure and elements Sn, Ti, O and C were found to be uniformly distributed in this hierarchical hollow nanostructure. Additionally, they also found that due to the uniform distribution of SnO$_2$, TiO$_2$, and the carbon layer, a solid solution was formed which could effectively suppress the effect of volume changes during the charge/discharge process. The specific discharge capacity remained at about 680 mA h g^{-1} at 1 A g^{-1} after 500 cycles, which demonstrates the excellent cycling performance of HTSO/GC-HSs at high current densities (Fig. 13D).[301]

SnO$_2$/TiO$_2$/C combines the high capacity of SnO$_2$ with the long cycle life and high rate capability of TiO$_2$.[335,336] Furthermore, carbonaceous materials can inhibit agglomeration and pulverization of SnO$_2$ and enhance the conductivity of TiO$_2$.[337,338] Therefore, SnO$_2$/TiO$_2$/C present an important area of research for the future.

4.4 SnO$_2$/TMOs/graphene

In the previous sections, we have discussed the synthesis methods, morphologies, and electrochemical performance of some representative SnO$_2$/TMOs/C anode materials. We classified them into different categories according to metal oxides because different TMOs greatly influence the physical and chemical properties of such complex materials due to different reaction mechanisms. In addition, different carbonaceous materials used in SnO$_2$/TMOs/C also influence the electrode performance in LIBs. Among these complex materials, much work has been focused on the fabrication of SnO$_2$/TMOs/graphene materials in recent years. Compared to amorphous carbon and CNTs, graphene shows higher lithium storage capacity.[339–342] Additionally, graphene, as a supportive matrix and conductive network, displays excellent mechanical properties and electronic conductivity, which is conducive to improvement in cycling stability and rate performance of SnO$_2$. Therefore, effectively combining SnO$_2$, TMOs, and graphene, to synthesize high-performance and practical anode material, has been a popular research subject in recent years.[46,275,343–345]

Wang *et al.* synthesized a Fe$_3$O$_4$/SnO$_2$/rGO (FSG) composite *via* a facile hydrothermal method. SEM images (Fig. 14A) and elemental mapping show that FSG consists of SnO$_2$ and Fe$_3$O$_4$ nanoparticles with diameters of about 10–100 nm, uniformly distributed on the surface of the rGO. In this composite, rGO served as a conductive and robust matrix to prevent aggregation of Fe$_3$O$_4$ and SnO$_2$ nanoparticles on rGO. As shown in Fig. 14B, the nanocrystallites of Fe$_3$O$_4$ and SnO$_2$ tend to link with each other, which is beneficial for suppressing both, *i.e.*, the
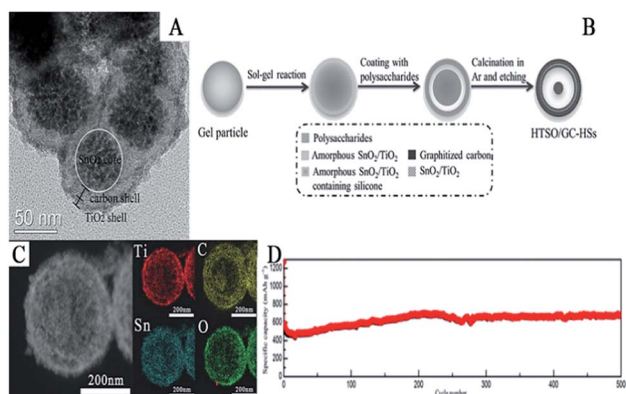

Fig. 13 (A) TEM images of SnO$_2$@C@TiO$_2$ nanochains (adapted with permission from ref. 296 copyright 2015 Elsevier). (B) Schematic illustration of the synthesis, (C) STEM image, and (D) cycling performance of HTSO/GC-HSs (adapted with permission from ref. 299 copyright 2017 Wiley).
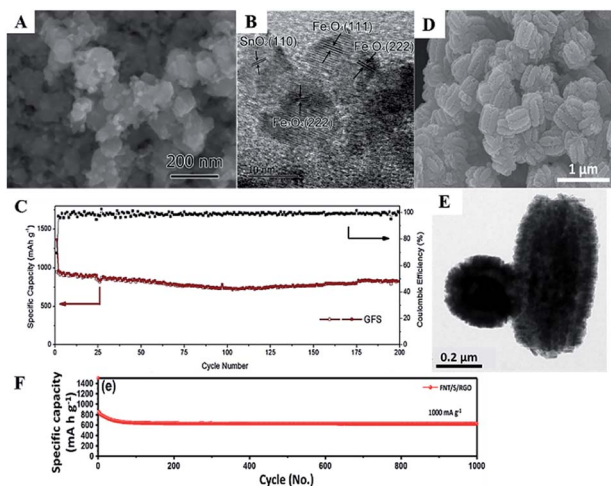
Fig. 14 (A) SEM image, (B) HRTEM image, and (C) cycling performance of FSG (adapted with permission from ref. 132 copyright 2016 Elsevier). (D) SEM image, (E) TEM image from top and side view of CNT/S, and (F) cycling performance of FNT/S/RGO (adapted with permission from ref. 136 copyright 2017 Elsevier).

formation of the SEI film and the volume changes. Such a novel nanostructure can effectively shorten the transport path of Li$^+$ and electrons and helps improve electrolyte penetration. The FSG nanocomposite exhibited a reversible capacity of 947 mA h g^{-1} at a current density of 200 mA g^{-1} in the first cycle and maintained a capacity of 831 mA h g^{-1} after 200 cycles (Fig. 14C).[132]

Lee et al. have synthesized hollow nanostructured α-Fe$_2$O$_3$ nanotubes/SnO$_2$/rGO (FNT/S/G) via a microwave-assisted hydrothermal method. As shown in Fig. 14D, SnO$_2$ nanorods grow on the surface of FNT, and FNT/SnO$_2$ are uniformly anchored on rGO sheets. The diameter and length (Fig. 14E) of FNT/S are about 230 nm and 660 nm, respectively. Lee et al. also compared the electrochemical performance of FNT, FNT/S, and FNT/S/G. As shown in Fig. 14F, FNT/S/G exhibited the highest discharge capacity under all tested current densities. FNT/S was the second best, demonstrating that the introduction of SnO$_2$ and rGO can effectively enhance the lithium storage capability and cycling stability of the anode material. The specific discharge capacity of FNT/S/RGO remained at 629 mA h g^{-1} at 1 A g^{-1} after 1000 cycles.[136,346]

Other SnO$_2$/TMOs/graphene composites like SnO$_2$/TiO$_2$/GN,[338] SnO$_2$/CuO/GN[347] and SnO$_2$/In$_2$O$_3$/GN[348] also exhibit improved electrochemical performance. The introduction of TMOs and graphene effectively improve the lithium storage capacity of SnO$_2$. Graphene serves as a supportive and conductive matrix that inhibits agglomeration and pulverization of SnO$_2$ and TMOs during the charge/discharge process.

5. Other SnO$_2$-based compounds

Li$_4$Ti$_5$O$_{12}$ (LTO) has been considered as a promising anode material for LIBs due to its excellent cycling stability during lithiation/delithiation.[349,350] However, like TiO$_2$, LTO possesses

a lower theoretical capacity than other anode materials (175 mA h g^{-1}) and shows poor rate performance.[351,352] Therefore, in order to improve lithium storage of LTO and cycling performance of SnO$_2$, an effective strategy is to synthesize composites of SnO$_2$ and LTO nanostructures. Ding et al. synthesized hierarchical yolk–shell LTO–SnO$_2$ structures via a two-step hydrothermal method. They first synthesized SnO$_2$ microspheres at 180 °C for 12 h in a hydrothermal system and then, coated LTO on the surface of the SnO$_2$ in another hydrothermal system, followed by calcination at 600 °C for 3 h. SEM images (Fig. 15A) and TEM images (Fig. 15B) clearly show that the yolks are SnO$_2$ microspheres composed of SnO$_2$ nanoparticles, while the shells consist of LTO nanosheets. Hence, this hierarchical coating structure can effectively improve structural stability and suppress the volume changes of SnO$_2$ microspheres; thus, improving the cycling performance and showing high rate capacity.[142]

Heteroatom-doped SnO$_2$ reveals better electrochemical performance compared to pure SnO$_2$. The presence of a dopant may favor the reversible formation of Li$_2$O and improve the conductivity of SnO$_2$; thus, enhancing the specific capacity of the anode material.[353] Various heteroatom-doped SnO$_2$ nanomaterials have been synthesized and tested as anode materials in LIBs.[354–356] For example, Mueller et al. have synthesized carbon-coated Fe-doped SnO$_2$ nanoparticles (Fig. 15C). The discharge capacity of such materials is about 1726 mA h g^{-1} after 10 cycles at 50 mA g^{-1}, which is around twice the theoretical capacity of pure SnO$_2$.[353] Zn-doped SnO$_2$ hierarchical cube-like nanomaterials were fabricated via hydrothermal method. As shown in Fig. 15D and E, the cube is about 2 μm in length and composed of assembled nanorods which are 20–40 nm in diameter. The discharge capacity of Zn-doped SnO$_2$

Fig. 15 5(A) SEM image, and (B) TEM image of LTO−SnO$_2$ composites (adapted with permission from ref. 142 copyright 2018 Elsevier). (C) HRTEM image of carbon-coated Fe-doped SnO$_2$ nanoparticles (adapted with permission from ref. 351 copyright 2015 Elsevier). (D and E) SEM images, and (F) cycling performance of Zn-doped SnO$_2$ nanomaterials (adapted with permission from ref. 355 copyright 2014 Elsevier). (G) SEM image, and (H) cycling performance of Cu/N-doped SnO$_2$ (adapted with permission from ref. 139 copyright 2014 Elsevier).

Table 1 Electrochemical property comparison table of some typical SnO_2-based anode materials for LIBs

Materials	Morphology	Preparation approach	Voltage window (V)	Current density (A g^{-1})	Cycle number	Specific capacity (mA h g^{-1})	Reference
SnO_2 nanorods	Diameter of 60 nm and length of 670 nm	Hydrothermal	0.005–2.5	0.078	100	580	154
SnO_2 nanotube arrays	Diameter of 100–300 nm and thickness of 10–20 nm	Solvothermal and annealing	0.005–2	0.078	20	750–800	64
SnO_2 nanowires	Diameter of 6 nm and length of >3 μm	Solvothermal and annealing	0–1.2	0.156	50	773	71
SnO_2 nanosheet arrays	Thickness of 20 nm and length of 500 nm	Hydrothermal	0.01–1.2	0.391	50	674.9	79
Hollow SnO_2 nanospheres	Size of 100–250 nm	Solvothermal and hydrothermal	0.01–2	0.391	40	1140	86
Urchin-like SnO_2 nanospheres	Diameter of 300 nm	Solvothermal	0.01–3	0.1	50	719	210
SnO_2 nanocrystals/MWCNT composites	Crystal size of 5 nm	Solvothermal and heat treatment	0.01–3	0.1	100	402	223
CNT@void@SnO_2@C	Tube in tube diameter of 100–150 nm	Spray drying	0.01–3	0.2	350	702.5	226
SnO_2/C composite hollow spheres	Size of 150–400 nm	Hydrothermal and carbonation	0–2.5	0.16	50	473	99
SnO_2 nanoparticles/carbon composite	Nanoparticles of 5–10 nm	Polyol method	0.005–1.5	0.2	100	370	251
SnO_2 nanosheets/GO	Length of 100 nm and thickness of 5–10 nm	Hydrothermal	0.01–1.2	0.4	50	518	171
SnO_2 nanoparticles/graphene	Particle size of 3–8 nm	Microwave-assisted hydrothermal	0.01–3	0.2	100	978.6	269
SnO_2@rGO-Cl	Nanoparticle size of 5 nm	Heat treatment	0.01–3	0.2	400	1008	275
CNT@SnO_2@G	Width of 20–40 nm	Hydrothermal	0.01–3	0.1	100	947	265
SnO_2@G-SWCNT	Diameter of 3–5 nm and particle size of 6–8 nm	Hydrothermal	0.01–3	1	300	537	291
SnO_2–Fe_2O_3/SWCNTs nanocomposite	Particle size of 10–50 nm	Hydrothermal	0.01–3	0.2	50	692	310
Co_3O_4@SnO_2@C core–shell nanorods	Thickness of 5–10 nm	Hydrothermal	0.01–2.5	0.2	50	860	313
SnO_2@C@TiO_2 nanochains	SnO_2 for 2–6 nm; thickness of 2–6 nm and 8 nm for carbon and TiO_2	Hydrothermal and subsequent mechanical stirring	0.01–3	0.1	100	369	298
Fe_2O_3 nanotubes/SnO_2/rGO	Diameter of 230 nm and length of 660 nm	Microwave-assisted hydrothermal	0.01–3	1	1000	629	136
Yolk–shell LTO–SnO_2	Diameter of 1.0–1.5 μm	Hydrothermal and calcination	0.01–3	0.175	200	253.2	142
Fe-doped SnO_2 nanoparticles	Diameter of 15 nm	Hydrothermal and calcination	0.01–2	0.05	10	1726	351

composites is 488.3 mA h g^{-1} after 50 cycles at 10 mA g^{-1} (Fig. 15F).[357] Wan *et al.* fabricated Cu/N-doped SnO_2 nanocomposites, as shown in Fig. 15G. They found that with the introduction of Cu/N, the average diameter of SnO_2 became smaller, and the surface became rough, which is beneficial for ion diffusion and suppressing volume expansion. Cu/N-doped SnO_2 electrode materials are known to deliver a discharge capacity of 1939 mA h g^{-1} in the first cycle and remain at 664 mA h g^{-1} after 50 cycles at 0.1C.[139]

6. Conclusions

In this review, we summarized various SnO_2-based nanomaterials as anode materials for lithium-ion batteries (Table 1).

By optimizing the structure and composition of the materials, *i.e.*, by synthesizing nanostructured SnO_2 and making composites with carbonaceous materials or transition metal oxides (TMOs), the surface area and reaction sites of the anode materials can be effectively increased, improving the electrochemical properties of SnO_2-based anode materials. The introduction of carbonaceous materials or TMOs can effectively buffer the internal stresses caused by large volume changes, reduce the irreversible capacity loss, and improve the cycle performance. These aspects lay the foundation for the development and commercialization of high-performance LIBs in the future. Since lithium storage in SnO_2 is accompanied by repeatedly inserting and removing lithium ions, volume changes and irreversible capacity loss of SnO_2 electrode cannot

be completely avoided. Significant research on nanosized SnO₂-based anode materials has been carried out, and while these materials display superior lithium storage capacity and cycling stability, critical issues like volume expansion and pulverization of SnO_2 remain to be solved. Further extensive research is needed before new, non-carbonaceous anode materials, such as SnO_2-based nanomaterials, can be commercialized.

Conflicts of interest

There are no conflicts to declare.

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