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## 1 Introduction

The development of advanced energy conversion systems such as Lithium-ion batteries (LIBs) is an important way to alleviate the world's energy shortage and global warming problems. LIBs with high power density and high energy density used at electric vehicles, energy storage systems and smart grids are increasingly demanding,<sup>1,2</sup> but conventional LIBs are not sufficient to meet these demands, so new electrode materials with high capacity and low cost have become a hot research topic in recent years.<sup>3</sup> As the most successful anode material in commercial LIBs at present, graphite has several fatal problem. Firstly, the operating voltage of graphite is below 0.2 V *versus* Li/Li<sup>+</sup>, which is close to the lithium deposition voltage. Lithium dendrites may be generated during the repeated charge and discharge process, resulting in internal short circuit and serious safety risks.<sup>4</sup> Compared with graphite, TiO<sub>2</sub> has a relatively high lithium insertion/extraction voltage of about 1.7 V, which can effectively avoid lithium dendrites. Secondly, the volume expansion of TiO<sub>2</sub> during charge and discharge (<4%) is much smaller than that of graphite (10%). However the theoretical capacity of TiO<sub>2</sub> is 335 mA h g<sup>-1</sup>, which is similar to that of graphite (372 mA h g<sup>-1</sup>).<sup>5</sup> Therefore, TiO<sub>2</sub> is one of the candidates materials to replace graphite for its excellent safety.<sup>6,7</sup> However, as a wide bandgap semiconductor material, TiO<sub>2</sub> has poor electronic conductivity ( $10^{-12}$  to  $10^{-7}$  S cm<sup>-1</sup>) and low Li<sup>+</sup>

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## Titanium dioxide-based anode materials for lithium-ion batteries: structure and synthesis

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Lithium-ion batteries (LIBs) have high energy density, long life, good safety, and environmental friendliness, and have been widely used in large-scale energy storage and mobile electronic devices. As a cheap and non-toxic anode material for LIBs, titanium dioxide (TiO<sub>2</sub>) has a good application prospect. However, its poor electrical conductivity leads to unsatisfactory electrochemical performance, which limits its large-scale application. In this review, the structure of three TiO<sub>2</sub> polymorphs which are widely investigated are briefly described, then the preparation and electrochemical performance of TiO<sub>2</sub> with different morphologies, such as nanoparticles, nanowires, nanotubes, and nanospheres, and the related research on the TiO<sub>2</sub> composite materials with carbon, silicon, and metal materials are discussed. Finally, the development trend of TiO<sub>2</sub>-based anode materials for LIBs has been briefly prospected.

diffusion rate ( $10^{-15}$  to  $10^{-9}$  cm<sup>2</sup> s<sup>-1</sup>). To address these problems, current solutions are included: (1) Nanostructures designing to reduce ionic and electronic transport distances,<sup>8</sup> which facilitates the electron/ion transport by increasing the contact area of electrolyte/electrode material. (2) Composites designing to take advantages of the high conductivity of carbon and metal materials and the high capacity of silicon materials, which improves the overall conductivity of electron and lithium by the synergistic effect, thereby improving the electrochemical performance. In this paper, the structure and performance of TiO<sub>2</sub> are firstly briefly described, and then the research progress of TiO<sub>2</sub> nanostructures designing and composites designing which are two aspects to enhance the electrochemical performance are reviewed, and finally, the development trend of TiO<sub>2</sub> has further prospected.

## 2 Crystal structure and lithium storage mechanism of TiO<sub>2</sub>

There are mainly three crystal types of TiO<sub>2</sub>: anatase, rutile and brookite.<sup>9</sup> In addition, there are some rare crystal types, such as

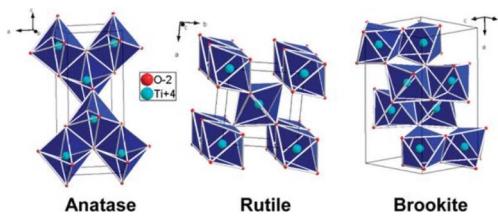


Fig. 1 Anatase, rutile, and brookite crystal structure of TiO<sub>2</sub>.<sup>10</sup>



bronze. The crystal structures of anatase, rutile, and brookite are shown in Fig. 1.<sup>10</sup>

The basic composition of each crystal form is composed of an  $[\text{TiO}_6]^{8-}$  octahedron included of one  $\text{Ti}^{4+}$  and six  $\text{O}^{2-}$ , and different connection modes and arrangement orders constitute different crystal structures of  $\text{TiO}_2$ . The anatase phase is composed of  $[\text{TiO}_6]^{8-}$  octahedron with common edges, and its octahedra distortion is so significantly large that the symmetry is lower than that of the orthorhombic crystal system. The rutile phase is composed of  $[\text{TiO}_6]^{8-}$  octahedrons with common tops and common edges, and its octahedral distortion is smaller than that of anatase, and its symmetry is better than that of anatase. The brookite phase belongs to the orthorhombic system, which consists of six  $\text{TiO}_2$  to form a crystal cells. This crystal structure makes the brookite phase very unstable and therefore rare in nature. Table 1 lists the structure and lithium-storage properties of  $\text{TiO}_2$  polymorphs. Generally speaking, the lithium insertion process of titanium dioxide can be expressed by eqn (1):



The lithium insertion process of anatase  $\text{TiO}_2$  can be divided into three regions (A, B, C) as shown in Fig. 2.<sup>11</sup>

Region A: The open-circuit voltage plunges to 1.8 V, and this region is considered as a small amount of  $\text{Li}^+$  embedded in anatase lattice ( $\text{Li}_x\text{TiO}_2$ ). In the bulk material, only 0.028 Li can be embedded, and reducing the particle size can increase the  $\text{Li}^+$  accommodation capacity. The lithium embedding coefficients of large and small nanoparticles are up to 0.05 and 0.12.

Region B: A plateau appears around 1.75 V, a typical two-phase mechanism.  $\text{Li}^+$  continues to be embedded in  $\text{TiO}_2$  lattice, and the Li-poor phase of tetragonal crystal system changes to the Li-rich phase of orthogonal crystal system, and the two phases coexist. For bulk materials, the lithium content combined with the platform is 0.39 Li/ $\text{TiO}_2$  formulation units.

Region C: The voltage decreases continuously and linearly below 1.7 V. The smaller the size of anatase crystal in this region, the larger the insertion amounts of  $\text{Li}^+$ .

The lithium-storage mechanism of other crystal types is rarely reported. The insertion of  $\text{Li}^+$  in  $\text{TiO}_2$  rutile is highly anisotropic, preferentially occurring in the *c*-axis,<sup>12</sup> tending to be one-dimensional, due to the large difference between the (*ab*-plane) *a*-axis and *c*-axis  $\text{Li}^+$  diffusion coefficients. *c*-Axis pore channels are narrow, with a radius of 4 nm for octahedral

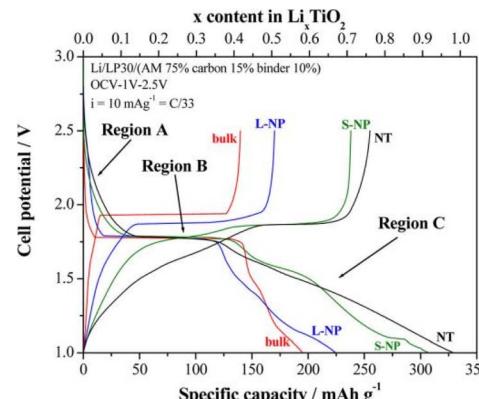


Fig. 2 The voltage–capacity curves of anatase  $\text{TiO}_2$ .<sup>11</sup>

vacancies and 6 nm for  $\text{Li}^+$ , so that only a small amount of  $\text{Li}^+$  can be embedded at room temperature. With the insertion of  $\text{Li}^+$ , the diffusivity of  $\text{Li}^+$  in rutile decreases, further limiting the embedding of  $\text{Li}^+$ . The process of  $\text{Li}^+$  embedding brookite  $\text{TiO}_2$  is also limited by structure, and the diffusion process is mainly along the direction of *c*-axis where the resistance is low. But the lithium storage mechanism is still unclear.

### 3 Pure nanostructured $\text{TiO}_2$ materials

$\text{TiO}_2$  materials have disadvantages such as low electrical conductivity, poor cycle performance and rate performance, however nanostructured  $\text{TiO}_2$  electrode materials have the advantages of large surface area and short ion diffusion distance,<sup>16</sup> so the researchers are devoted to preparing various  $\text{TiO}_2$  nanomaterials. In terms of dimensions,  $\text{TiO}_2$  nanomaterials can be divided into zero-dimensional ( $\text{TiO}_2$  nanoparticles<sup>17,18</sup>), one-dimensional ( $\text{TiO}_2$  nanowires,  $\text{TiO}_2$  nanorods,  $\text{TiO}_2$  nanotubes, *etc.*<sup>19–23</sup>), two-dimensional ( $\text{TiO}_2$  nanosheets<sup>24–26</sup>), three-dimensional ( $\text{TiO}_2$  nanoflowers,  $\text{TiO}_2$  nanospheres,  $\text{TiO}_2$  nanotrees, *etc.*<sup>27–29</sup>). The studies find that the particle size, morphology, and surface area of nano- $\text{TiO}_2$  have obvious effects on its electrochemical performance. When the particle size decreases,  $\text{TiO}_2$  nanomaterials have a larger active material/electrolyte contact area and shorter ion diffusion distance,<sup>30</sup> which can effectively improve the rate performance and high-current charge-discharge performance. The unique morphology can alleviate the volume expansion during lithiation/delithiation processes, and improve the cycle

Table 1 Structure and lithium-storage properties of  $\text{TiO}_2$  polymorphs<sup>13–15</sup>

Polymorph	Crystal structure	Density (g cm <sup>-3</sup> )	Band gap energy (eV)	Unit cell (Å)	Li <sup>+</sup> insertion (mol)/specific capacity (mA h g <sup>-1</sup> )	
					Bulk	Nano
Anatase	Tetragonal ( <i>I4<sub>1</sub>/amd</i> )	3.79	3.20–3.23	<i>a</i> = 3.79, <i>c</i> = 9.51	0.5/168	1.0/335
Rutile	Tetragonal ( <i>P4<sub>2</sub>/mnm</i> )	4.13	3.02–3.04	<i>a</i> = 4.59, <i>c</i> = 2.96	0.1/34	0.85/285
Brookite	Orthorhombic ( <i>Pbca</i> )	3.99	3.14–3.31	<i>a</i> = 9.17, <i>b</i> = 5.46, <i>C</i> = 5.14	0.1/34	1.0/335



stability. The larger surface area can increase active material/electrolyte contact area, and thinner wall thickness can reduce the diffusion distance of  $\text{Li}^+$ , which is beneficial to improve the electrochemical performance.

### 3.1 Zero-dimensional $\text{TiO}_2$

**$\text{TiO}_2$  nanoparticles.**  $\text{TiO}_2$  nanoparticle synthesis methods mainly include the sol-gel method,<sup>31,32</sup> hydrothermal method, template method, and microemulsion method. The size of  $\text{TiO}_2$  nanoparticles is about 10–20 nm,<sup>33,34</sup> and their electrochemical performance is better than that of micron  $\text{TiO}_2$  particles.<sup>35</sup> However, it is easy to agglomerate in the process of charging and discharging, which speeds up the capacity decay, and its cycle stability is poor.<sup>36</sup> The morphology of the material is a key factor affecting the electrochemical performance,<sup>37</sup> so the synthesis of  $\text{TiO}_2$  nanoparticles is a feasible method to improve the performance of LIBs.

Partheeban *et al.*<sup>38</sup> used melamine as a soft template to prepare anatase phase  $\text{TiO}_2$  nanoparticles with an average size of 10–20 nm. It showed excellent electrochemical performance with an initial discharge capacity of 272  $\text{mA h g}^{-1}$  at 1C, a slight decrease of about 240  $\text{mA h g}^{-1}$  after 50 cycles, and still had a capacity of 208  $\text{mA h g}^{-1}$  after 1000 cycles. Zhang *et al.*<sup>39</sup> designed a two-step hydrothermal method for the preparation of brookite phase mesocrystalline  $\text{TiO}_2$  using amorphous titanate as a precursor and oxalic acid as a structural guide (see Fig. 3), which maintained a capacity of 105.7  $\text{mA h g}^{-1}$  after 500 cycles at 5C. Ouardi *et al.*<sup>40</sup> used titanium tetrakisopropanol and sodium alginate as titanium precursor and template, respectively, and then calcined to prepare nano-sized  $\text{TiO}_2$ . At 0.1C,  $\text{TiO}_2$  anode calcined at 300 °C and 450 °C had reversible capacities of 266  $\text{mA h g}^{-1}$  and 275  $\text{mA h g}^{-1}$  in the first cycle, respectively. Coulomb efficiencies are 70% and 75%, respectively. The cycling performances and capacities of  $\text{TiO}_2$  nanoparticles is depicted in Table 2.

### 3.2 One-dimensional $\text{TiO}_2$

**$\text{TiO}_2$  nanowires.** Compared with  $\text{TiO}_2$  nanoparticles,  $\text{TiO}_2$  nanowires exhibit some advantages such as stable and reversible capacity<sup>41</sup> and excellent rate performance. Common methods for the preparation of  $\text{TiO}_2$  nanowires include the hydrothermal method, which can control the morphology and particle size by adjusting the solution concentration, titanium source, reaction temperature and reaction time, *etc.* The obtained products have better purity, controllable crystalline shape, uniform particles, and a simple operation process with

low pollution.<sup>42</sup> In addition to the hydrothermal method, sol-gel method<sup>43</sup> and template method<sup>44</sup> are also commonly used.

Wang *et al.*<sup>45</sup> prepared  $\text{TiO}_2$  nanowires containing anatase phase and a small amount of bronze phase by hydrothermal method with diameters of 40–80 nm and lengths of 400–1500 nm, and had a capacity of 280  $\text{mA h g}^{-1}$  after 40 cycles at 140  $\text{mA g}^{-1}$  with a coulombic efficiency close to 98%. Wu *et al.*<sup>46</sup> used the hydrothermal method to prepare anatase  $\text{TiO}_2$  nanowires with initial discharge/charge capacities of 260  $\text{mA h g}^{-1}$  and 224  $\text{mA h g}^{-1}$  at 20  $\text{mA g}^{-1}$ , respectively, and the reversible capacity remained around 216  $\text{mA h g}^{-1}$  in the 20th cycle. At a current density of 200  $\text{mA g}^{-1}$ , the discharge capacity was about 159  $\text{mA h g}^{-1}$  at the 20th cycle, which showed good cycling stability. Wang *et al.*<sup>47</sup> synthesized porous linear  $\text{TiO}_2$ . And the synthesis process consisted of two steps, firstly, the synthesis of titanium ethanoate precursor nanowires by microwave-assisted solvothermal method, followed by the conversion of titanium ethanoate nanowires into porous  $\text{TiO}_2$  nanowires with diameters of about 0.4–2  $\mu\text{m}$  and lengths of 2–20  $\mu\text{m}$ , having a high surface area of 252  $\text{m}^2 \text{g}^{-1}$ . Its unique nanoporous structure results in better electrolyte permeability and faster diffusion rates of electrons and  $\text{Li}^+$ , as well as better buffering volume changes during charge/discharge cycles. The cycling performances and capacities of  $\text{TiO}_2$  nanowires is depicted in Table 3.

**$\text{TiO}_2$  nanorods.**  $\text{TiO}_2$  with cone, strip, shuttle, dumbbell, and rod shapes are generally referred to as  $\text{TiO}_2$  nanorods in a broad sense.  $\text{TiO}_2$  nanorods are mainly prepared by solvothermal and hydrothermal methods,<sup>48–51</sup> and their microscopic morphology is affected by the reaction temperature and reaction time, and an appropriate increase in reaction temperature is beneficial to the orientation and alignment of nanorods. In LIBs, shorter and finer nanorods are beneficial for the diffusion and transport of  $\text{Li}^+$ .

Seisenbaeva *et al.*<sup>52</sup> prepared anatase phase nanorods, using a one-step hydrothermal method. It had homogeneous mesopores, high porosity, a surface area of about 300  $\text{m}^2 \text{g}^{-1}$ , and initial charge/discharge capacities of 299  $\text{mA h g}^{-1}$  and 225  $\text{mA h g}^{-1}$  at C/15, respectively. Ji<sup>53</sup> sintered titanium foil coated with sodium hydroxide solution at 800 °C to prepare  $\text{TiO}_2$  nanorods, which mainly consisted of rutile phase, with a width of about 500 nm and a thickness of about 5  $\mu\text{m}$ . At the same time, they also studied the effect of different temperatures on  $\text{TiO}_2$  nanorods. Santhi *et al.*<sup>54</sup> used a hydrothermal method to synthesize  $\text{TiO}_2$  nanorods at different pH value and it was showed that when pH = 7, the length of nanorods was about 300–350 nm and the diameter was about 70–100 nm. When the pH was

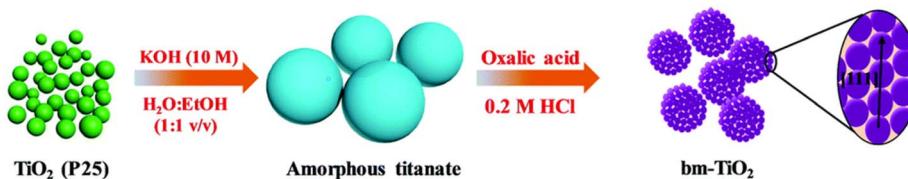


Fig. 3 Preparation process of mesomorphic  $\text{TiO}_2$  with brookite phase.<sup>39</sup>



Table 2 Cycling performances and capacities of  $\text{TiO}_2$  nanoparticles<sup>a</sup>

$P_m$	$C_d$	Initial coulombic efficiency	$I_{dc}/\text{mA h g}^{-1}$	$C_n$	$R_c/\text{mA h g}^{-1}$	Areal capacities ( $\text{mA h cm}^{-2}$ )	Ref.
$T_m$	1C	50%	272	50	240	0.41	38
$H_m$	5C	58%	—	500	105.7	0.13	39
$T_m$	0.1C	75%	364	100	180	—	40

<sup>a</sup>  $P_m$ —preparation method,  $T_m$ —template method,  $H_m$ —hydrothermal method,  $C_d$ —current density,  $I_{ce}$ —initial coulombic efficiency,  $I_{dc}$ —initial discharge capacity,  $C_n$ —cycle numbers,  $R_c$ —remaining capacity,  $A_c$ —areal capacities.

Table 3 Cycling performances and capacities of  $\text{TiO}_2$  nanowires<sup>a</sup>

$P_m$	$L/\text{nm}$	$D/\text{nm}$	$C_d$	$C_n$	$R_c/\text{mA h g}^{-1}$	Ref.
$H_m$	400–1500	40–80	140 $\text{mA g}^{-1}$	40	280	45
$H_m$	250	20	200 $\text{mA g}^{-1}$	20	159	46
$S_m$	2000–20 000	400–2000	0.2C	51	114.4	47

<sup>a</sup>  $P_m$ —preparation method,  $H_m$ —hydrothermal method,  $S_m$ —solvochemical method,  $L$ —length,  $D$ —diameter,  $C_d$ —current density,  $C_n$ —cycle numbers,  $R_c$ —remaining capacity.

increased to 9, the morphology was changed from rod-like structure to a platelet-like nanostructure.

**TiO<sub>2</sub> nanotubes.** TiO<sub>2</sub> nanotubes have a hollow structure that better satisfies the requirements for high surface area and relatively short conductive paths.<sup>55,56</sup> The main preparation methods are microwave, hydrothermal synthesis,<sup>57</sup> template, and anodic oxidation,<sup>58</sup> among which the anodic oxidation method is simple and easy to operate.<sup>59</sup>

Gong *et al.*<sup>60</sup> used the anodic oxidation method to prepare TiO<sub>2</sub> nanotubes with different diameters and lengths, and TiO<sub>2</sub> nanotubes arrays with diameters ranging from 30 nm to 90 nm could be obtained by controlling the anodic oxidation voltage. Xu *et al.*<sup>61</sup> used the hydrothermal method to prepare anatase TiO<sub>2</sub> nanotubes with a diameter of about 10 nm and a length about 200–400 nm. At 36  $\text{mA g}^{-1}$ , the first charge–discharge capacities were 290  $\text{mA h g}^{-1}$  and 238  $\text{mA h g}^{-1}$ , respectively. At the 20th cycle, the reversible capacity was still about 200  $\text{mA h g}^{-1}$ , and the coulomb efficiency is about 98%. Fasakin *et al.*<sup>62</sup> obtained TiO<sub>2</sub> nanotubes with average length, thickness, and diameter of 4  $\mu\text{m}$ , 17 nm, and 20 nm, respectively. After stirring and hydrothermal treatment, the surface area of TiO<sub>2</sub> nanoparticles increased from the original 8  $\text{m}^2 \text{g}^{-1}$  to 62  $\text{m}^2 \text{g}^{-1}$ . The initial capacity of the original TiO<sub>2</sub> nanoparticles at a current density of 36  $\text{mA g}^{-1}$  was 98  $\text{mA h g}^{-1}$ , which decreased to 38  $\text{mA h g}^{-1}$  at the 100th cycle. While the TiO<sub>2</sub> nanotubes showed an initial capacity of about 123  $\text{mA h g}^{-1}$  at a current density of 36  $\text{mA g}^{-1}$  and showed a capacity of 142  $\text{mA h g}^{-1}$  at the 100th cycle, which increased by about 17% relative to the initial value. The cycling performances and capacities of TiO<sub>2</sub> nanotubes is depicted in Table 4.

**TiO<sub>2</sub> nanofibers.** Nanofibers are representative one-dimensional wire-like nanomaterials due to their high aspect ratio that have nanoscale diameter and large length, fast charge transfer and large specific surface area. Nanofibers can provide a continuous transport path to promote charge transfer and ion

diffusion, reduce charge transfer resistance, and greatly improve electrode kinetics. At the same time, the high specific surface area of nanofibers can provide a large reaction contact area and a large number of active sites.<sup>66</sup> One-dimensional nanofibers are prepared by hydrothermal or solvent thermal synthesis,<sup>67</sup> chemical vapor deposition,<sup>68</sup> and electrostatic spinning.<sup>69–71</sup> Among them, electrostatic spinning method is most commonly used, simple and easy to achieve mass production.<sup>72–74</sup> Porous and continuous titanium dioxide nanofibers with large specific surface area can be prepared by the method. And the diameter, length and surface morphology of nanofibers can be controlled by adjusting the parameters of electrospinning process.

Zhuang *et al.*<sup>75</sup> synthesized TiO<sub>2</sub>–B nanofibers with a specific surface area of 112  $\text{m}^2 \text{g}^{-1}$ , high thermal stability and high crystallinity by steam thermal method. The initial capacity was 193.8  $\text{mA g}^{-1}$ , which dropped to 189.5  $\text{mA g}^{-1}$  after 100 cycles at 1C, with a good capacity retention rate of 97.8%. Luo *et al.*<sup>76</sup> synthesized unique MoO<sub>2</sub>-modified TiO<sub>2</sub> nanofibers by electrospinning and layer-by-layer (LBL) self-assembly processes. It consisted of a TiO<sub>2</sub> nanofiber core and a thin metal-like MoO<sub>2</sub> nanolayer. MoO<sub>2</sub>-modified TiO<sub>2</sub> nanofibers showed 514.5  $\text{mA h g}^{-1}$  after 50 cycles at 0.2C. Zhu *et al.*<sup>77</sup> used electrospinning and sintering processes to prepare nanofibers, which showed stable performance at the end of 800 cycles at 150  $\text{mA g}^{-1}$ , with a capacity retention of about 136  $\text{mA h g}^{-1}$ .

### 3.3 Two-dimensional TiO<sub>2</sub>

**TiO<sub>2</sub> nanosheets.** TiO<sub>2</sub> nanosheets<sup>78</sup> have a larger surface area, larger electrode/electrolyte contact area, and shorter Li<sup>+</sup> and electron transport paths. Compared with nanoparticles, it shows higher reversible charge/discharge capacity, better rate performance, and excellent cycling stability. And compared to mesoporous sphere, it shows shorter Li<sup>+</sup> diffusion paths. It has been synthesized by magnetron sputtering, multiple spin coating, sol–gel, and hydrothermal methods.<sup>79,80</sup>

Liu *et al.*<sup>81</sup> synthesized nanosheet-structured porous TiO<sub>2</sub> with a thickness of 5–10 nm by the solvothermal method, with an initial discharge capacity of 216  $\text{mA h g}^{-1}$  at a high current density of 10C and maintained at 200  $\text{mA h g}^{-1}$  after 200 cycles with a capacity retention rate of 92.6%. Wang *et al.*<sup>82</sup> used the multiple spin-coating methods on a fluorine-doped tin oxide substrate to prepare TiO<sub>2</sub> nanosheets arrays. More importantly, the size and shape can be controlled and the nanosheets arrays can be arranged on the substrate in an orderly and horizontally



Table 4 Cycling performances and capacities of  $\text{TiO}_2$  nanotubes<sup>a</sup>

$P_m$	$T/\text{nm}$	$C_d$	Initial coulombic efficiency	$C_n$	$R_c/\text{mA h g}^{-1}$	Areal capacities ( $\text{mA h cm}^{-2}$ )	Ref.
$H_m$	—	$36 \text{ mA g}^{-1}$	82%	20	200	0.44	61
$H_m$	17	$36 \text{ mA g}^{-1}$	94%	100	142	0.497	62
$T_m$	40	1C	72.2%	500	150	3.58	63
$A_{\text{om}}$	17	$320 \text{ mA g}^{-1}$	—	50	179	—	64
$H_m$	3–4.5	0.1C	65%	50	265	1.33	65

<sup>a</sup>  $P_m$ —preparation method,  $H_m$ —hydrothermal method,  $T_m$ —template method,  $A_{\text{om}}$ —anodic oxidation method,  $T$ —thickness,  $C_d$ —current density,  $I_{ce}$ —initial coulombic efficiency,  $C_n$ —cycle numbers,  $R_c$ —remaining capacity,  $A_c$ —areal capacities.

homogeneous manner. Dai *et al.*<sup>83</sup> successfully prepared ultra-thin  $\text{TiO}_2$  nanosheets with a large surface area and fast electron transfer using a hydrothermal method with P123 as a soft template.

### 3.4 Three-dimensional $\text{TiO}_2$

**TiO<sub>2</sub> nanoflowers.**  $\text{TiO}_2$  nanoflowers are nanomaterials with unique morphology and flower-like structure, which are of interest because of simple preparation, high surface area, and large porosity, and the three-dimensional structure has faster charge transfer capability and faster reaction rate on the surface.  $\text{TiO}_2$  nanoflowers are synthesized by hydrothermal and precipitation methods, which are simple, non-toxic, and cost-effective, but the morphology of nanoflowers is difficult to control.<sup>84</sup>

Zhang *et al.*<sup>85</sup> synthesized homogeneous and hierarchical flower-like morphologies of  $\text{TiO}_2$  with a diameter of  $124 \pm 5 \text{ nm}$  by solvothermal method followed by hydrogenation. And the petals of  $\text{TiO}_2$  nanoflowers consisted of nanosheets with a thickness of  $10 \pm 1.2 \text{ nm}$ . After hydrogen reduction,  $\text{Ti}^{3+}$  or oxygen vacancies were introduced into the  $\text{TiO}_2$  nanoflowers structure. The hydrogenated  $\text{TiO}_2$  nanoflowers exhibited high capacity, excellent rate performance, and better cycling stability, with an initial discharge capacity of  $179.6 \text{ mA h g}^{-1}$  and the 200th discharge capacity of  $177.1 \text{ mA h g}^{-1}$  at 10C, with a capacity retention rate of 98.4% after 200 cycles. While the unhydrogenated  $\text{TiO}_2$  nanoflowers presented an initial capacity of  $130.1 \text{ mA h g}^{-1}$  at a high current density, which decreased to  $121.4 \text{ mA h g}^{-1}$  after 200 cycles with a capacity retention rate of 93.4%. Pavasupree *et al.*<sup>86</sup> hydrothermally synthesized flower-like  $\text{TiO}_2$  with a mesoporous structure. And it was composed of slightly curved nanosheets with a width of about 50–100 nm and a thickness of a few nanometers (see Fig. 4). The average pore size of  $\text{TiO}_2$  nanosheets was about 3–4 nm, and the BET surface area and pore volume were about  $642 \text{ m}^2 \text{ g}^{-1}$  and  $0.774 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Gao *et al.*<sup>87</sup> synthesized  $\text{TiO}_2$  nanoflowers by a hydrothermal synthesis route in saturated sodium chloride solution.

**TiO<sub>2</sub> hollow spheres.**  $\text{TiO}_2$  hollow spheres have good surface permeability, easily adjustable diameter and shell thickness.<sup>88</sup> Hollow structure alleviates the volume change during the insertion/extraction of  $\text{Li}^+$ , and increases the contact area of active material/electrolyte, effectively improving the transport rate of  $\text{Li}^+$  and electrons in the electrode.<sup>89–91</sup> The template

method is considered as a representative method of preparing hollow structures. It is grown on the template to form a core-shell structure, and then the template is removed. However, the template method faces some challenges, such as difficult to obtain uniform coatings due to compatibility issues between template and shell materials.<sup>92,93</sup> And template-free, solvothermal<sup>94</sup> (see Fig. 5), and sol-gel methods<sup>95</sup> are commonly used for the synthesis of  $\text{TiO}_2$  hollow spheres.

Zhen *et al.*<sup>89</sup> synthesized hollow mesoporous  $\text{TiO}_2$  microspheres by a template-free method. It had diameters of about 200–300 nm, mesopore diameters of about 12 nm, microspheres walls of about 200 nm, surface area of  $105 \text{ m}^2 \text{ g}^{-1}$ , the first discharge capacity of about  $215 \text{ mA h g}^{-1}$  at 2C, and a capacity of  $132 \text{ mA h g}^{-1}$  at 2C after 200 cycles. In addition, it also exhibited excellent cycling stability, with the capacity retention of  $100 \text{ mA h g}^{-1}$  at 5C after 800 cycles. Yue *et al.*<sup>96</sup> synthesized mesoporous  $\text{TiO}_2$  microspheres by solvothermal method, and the  $\text{TiO}_2$  microspheres consisted of 6–8 nm nanocrystals with a uniform distribution of 4–8 nm mesopores on the surface. There was a reversible capacity of  $180 \text{ mA h g}^{-1}$  at a current density of 2C after 100 cycles. Zhang *et al.*<sup>97</sup> prepared hollow porous  $\text{TiO}_2$  spheres with a thickness of about

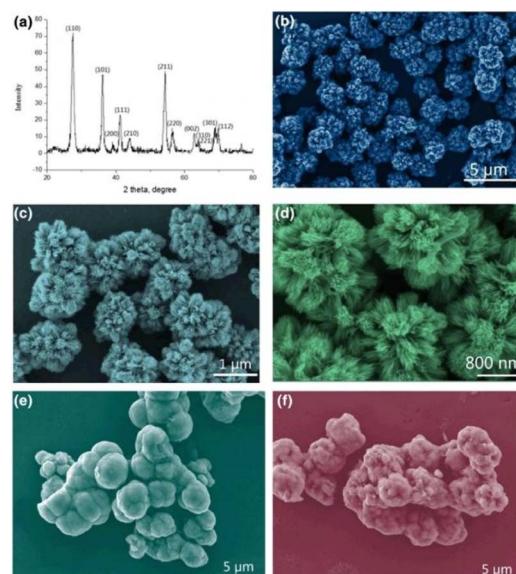


Fig. 4 XRD pattern and FE-SEM images of  $\text{TiO}_2$  nanoflowers.<sup>87</sup>



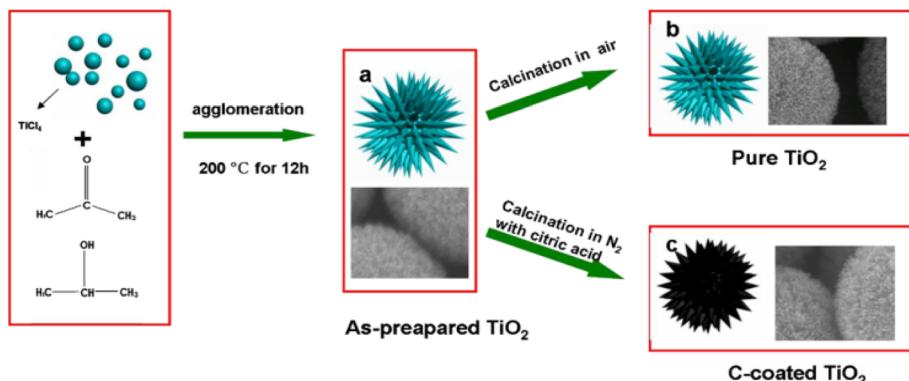


Fig. 5 Schematic diagram of the growth mechanism of TiO<sub>2</sub> microspheres.<sup>94</sup>

450 nm by hydrothermal method (see Fig. 6). This unique hollow porous structure, which facilitated the transport of Li<sup>+</sup>, exhibited excellent electrochemical performance with a reversible capacity of 170 mA h g<sup>-1</sup> at 0.6C after 150 cycles. Sunkara *et al.*<sup>98</sup> prepared mesoporous TiO<sub>2</sub> microspheres at a relatively low temperature using an acoustic-chemical synthesis method, which showed excellent cycling stability with a reversible capacity of 212.3 mA h g<sup>-1</sup> after 100 charge-discharge cycles. The cycling performances and capacities of TiO<sub>2</sub> hollow spheres is depicted in Table 5.

**TiO<sub>2</sub> nanotrees.** TiO<sub>2</sub> nanotrees have the advantages of high surface area, short electron transport path, and unique morphology, which can achieve high capacity.<sup>99–101</sup> The structure of TiO<sub>2</sub> nanotrees has been less studied in recent articles, and how to construct nano-branches with ultra-thin and slender shapes to obtain a large surface area is the exploration direction for TiO<sub>2</sub> nanotrees in LIBs.

Wen *et al.*<sup>99</sup> prepared TiO<sub>2</sub> nanotrees by depositing ultrathin nanoribbons of mixed-phase anatase/bronzite TiO<sub>2</sub> on an array of single-crystal anatase nanowires. The nanotrees branches were a few nanometers thick and 200–260 nm long, and had a discharge capacity of 330 mA h cm<sup>-2</sup> in the second cycle at a current density of 0.1 mA cm<sup>-2</sup> with stable capacity retention over the subsequent 50 charge/discharge cycles. Sun *et al.*<sup>100</sup> prepared TiO<sub>2</sub> nanotrees composed of nanorods, nanoribbons, and nanowires nanounits by a hydrothermal method (see Fig. 7), and the shape of TiO<sub>2</sub> dendrimers was controlled by adjusting the precursor hydrolysis rate and surfactant. Compared with nanoparticles with smooth surfaces, the novel TiO<sub>2</sub> nanostructures have higher surface area and excellent electrochemical performance.

### 3.5 Special shape

In addition, nanostructured TiO<sub>2</sub> with morphologies such as microcone,<sup>102</sup> candied fruit, sea urchin-like, and coral-like morphologies have also been studied, which have larger surface areas due to their unique morphologies and exhibit excellent electrochemical performance. The unique morphology is difficult to control in the synthesis process, and the exploration of synthetic methods with low cost, simple operation, and adjustable morphology will become the focus of future research.

Alireza<sup>103</sup> synthesized coral-like TiO<sub>2</sub> by sol-gel method and investigated the effects of precursor hydrolysis rate, reaction time, type and concentration of acid, reaction temperature, and annealing temperature. The surface of the coral-like structure consists of nanoparticles with a cashew-like shape and a mesoporous structure with a surface area of up to 164 m<sup>2</sup> g<sup>-1</sup>. Caruso *et al.*<sup>104</sup> used a polymer gel template method to obtain wall thicknesses of about 100–150 nm and coral-like TiO<sub>2</sub> with pore sizes ranging from 100 nm to several microns.

## 4 Construction of TiO<sub>2</sub> composites

The poor ionic and electronic conductivity of TiO<sub>2</sub> leads to a capacity far below the theoretical value and poor rate performance, which hinders its practical application in LIBs. Although the preparation of TiO<sub>2</sub> nanomaterials with a high surface area exhibits good electrochemical performance, it is still difficult to meet the commercial demand. For this reason, it is usually necessary to compound TiO<sub>2</sub> with other materials, and this review introduces the research progress of different types of TiO<sub>2</sub> composites, mainly from the compounding of TiO<sub>2</sub> with carbon, silicon, metals, and metal oxides.<sup>105</sup>



Fig. 6 Schematic illustration of the probable formation mechanism of hollow porous TiO<sub>2</sub> microspheres.<sup>97</sup>



Table 5 Cycling performances and capacities of  $\text{TiO}_2$  hollow spheres<sup>a</sup>

$P_m$	$D/\text{nm}$	$T/\text{nm}$	$S_a/\text{m}^2 \text{ g}^{-1}$	$C_d$	Initial coulombic efficiency	$C_n$	$R_c/\text{mA h g}^{-1}$	Areal capacities ( $\text{mA h cm}^{-2}$ )	Ref.
$T_{\text{fm}}$	200–300	200	105	5C	—	800	100	0.175	89
$S_m$	500–2000	—	118.1	2C	—	100	180	—	96
$H_m$	—	450	—	0.6C	85.6%	150	170	0.24	97
$S_{\text{om}}$	500	—	59.4	0.25C	89%	100	212.3	0.53	98

<sup>a</sup>  $P_m$ —preparation method,  $T_{\text{fm}}$ —template-free method,  $S_m$ —solvochemical method,  $H_m$ —hydrothermal method,  $S_{\text{om}}$ —sonochemistry method,  $D$ —diameter,  $T$ —thickness,  $S_a$ —surface area,  $C_d$ —current density,  $I_{\text{ce}}$ —initial coulombic efficiency,  $C_n$ —cycle numbers,  $R_c$ —remaining capacity,  $A_c$ —areal capacities.

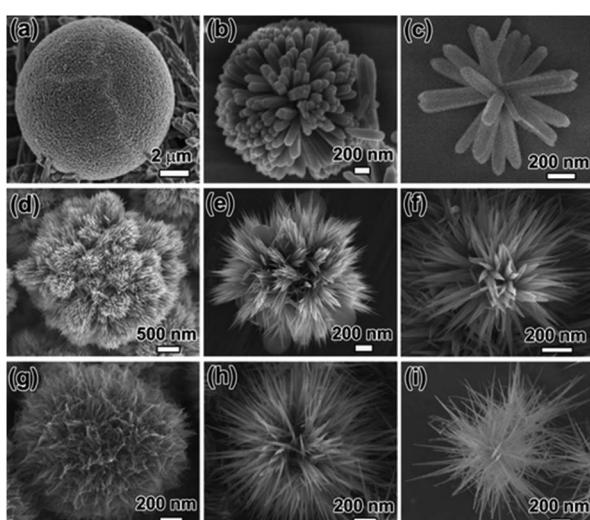


Fig. 7 SEM images of 3D nanotree composed of (a–c) nanorods (d–f) nanoribbons (g–i) nanowires.<sup>100</sup>

#### 4.1 $\text{TiO}_2$ and carbon composite

Using the higher safety performance of  $\text{TiO}_2$  and the excellent electrical conductivity of carbon materials, compounding  $\text{TiO}_2$  with carbon materials is one of the development directions of  $\text{TiO}_2$  anode materials for LIBs.<sup>106–110</sup>  $\text{TiO}_2$  compounded with carbon materials such as graphene, carbon nanotubes, and hard carbon can effectively improve the electrochemical performance.<sup>111,112</sup> On the one hand, the introduction of carbon enhances the overall electrical conductivity of the electrode, and on the other hand, it suppresses the accumulation and agglomeration of  $\text{TiO}_2$  nanostructures, making it easier to diffuse for  $\text{Li}^+$  and electrons.<sup>113</sup>

Zhang *et al.*<sup>114</sup> used hollow porous pollen carbon microspheres as a backbone to load C@ $\text{TiO}_2$  nanoparticles. C@ $\text{TiO}_2$ /3D pollen carbon (CTPC) composites with hollow porous structure were successfully prepared by a simple method (see Fig. 8). The results showed that the CTPC-700 (calcination temperature of 700 °C) composites exhibited excellent electrochemical performance with a high specific capacity of 148  $\text{mA h g}^{-1}$  at 5C after 1000 cycles. Trang *et al.*<sup>115</sup> prepared a composite material consisting of mesoporous  $\text{TiO}_2$  spheres and multi-walled carbon nanotubes by sol-gel and solvochemical methods, which exhibited excellent electrochemical

performance. The first discharge capacity was 269  $\text{mA h g}^{-1}$  at a current density of 1C, and after 100 cycles the capacity decreased by only 3.1%, with a capacity of about 260  $\text{mA h g}^{-1}$ . Lopez *et al.*<sup>116</sup> synthesized a  $\text{TiO}_2$ /carbon fiber composite with first discharge and charge capacities of 683  $\text{mA h g}^{-1}$  and 356  $\text{mA h g}^{-1}$  at 100  $\text{mA g}^{-1}$ , respectively, with a reversible capacity of 290  $\text{mA h g}^{-1}$  after 100 cycles. Liang *et al.*<sup>117</sup> prepared two-dimensional, ultrathin and mesoporous  $\text{TiO}_2$ /reduced graphene using layer-by-layer assembly process. The synergistic effect of ultrathin mesoporous  $\text{TiO}_2$  and reduced graphene nanosheets significantly enhanced the ion diffusion and electronic conductivity. The capacity was maintained at 245  $\text{mA h g}^{-1}$  at 1  $\text{A g}^{-1}$  after 1000 cycles. Mondal *et al.*<sup>118</sup> reported a large-scale preparation of hollow spherical  $\text{TiO}_2$ /reduced graphene composites by aerosol-assisted spray drying method. The  $\text{TiO}_2$ /reduced graphene spheres are porous and consist of 10–20 nm  $\text{TiO}_2$  particles dispersed on the surface of reduced graphene with a surface area of 86  $\text{m}^2 \text{ g}^{-1}$ . It has good electrochemical energy storage performance with a specific capacity up to 174.4  $\text{mA h g}^{-1}$  at a current density of 188  $\text{mA g}^{-1}$  after 200 cycles. The cycling performances and capacities of  $\text{TiO}_2$ /C nanocomposite is depicted in Table 6.

#### 4.2 $\text{TiO}_2$ and silicon composite

Silicon materials have a high theoretical capacity of 4200  $\text{mA h g}^{-1}$  and are abundant in the earth's crust,<sup>119</sup> but the large bulk effect and low electrical conductivity lead to considerable challenges in related research. Silicon materials undergo structural damage during charge/discharge, resulting in lower reversible capacity, poor cycling stability, and rate performance. Although  $\text{TiO}_2$  has minimal volume change during charge/discharge, the theoretical capacity is low at 335  $\text{mA h g}^{-1}$ , which can be increased by compounding with silicon materials.<sup>120</sup>

Fang *et al.*<sup>121</sup> prepared a silicon–titanium core–shell structure consisting of silicon nanoparticles encapsulated in  $\text{TiO}_2$  hollow spheres using hydrolysis and magnesium thermal reduction (see Fig. 9), which maintained a capacity of 804  $\text{mA h g}^{-1}$  after 100 cycles at 0.1C. This excellent cycling stability and high capacity can be attributed to the unique core–shell nanostructure and the synergistic effect between silicon and  $\text{TiO}_2$ . Li *et al.*<sup>122</sup> coated  $\text{TiO}_2$  on the surface of silicon nanoparticles by sol-gel method and maintained a reversible capacity of 1010.7  $\text{mA h g}^{-1}$  after 100 cycles at a current rate of 0.1C.



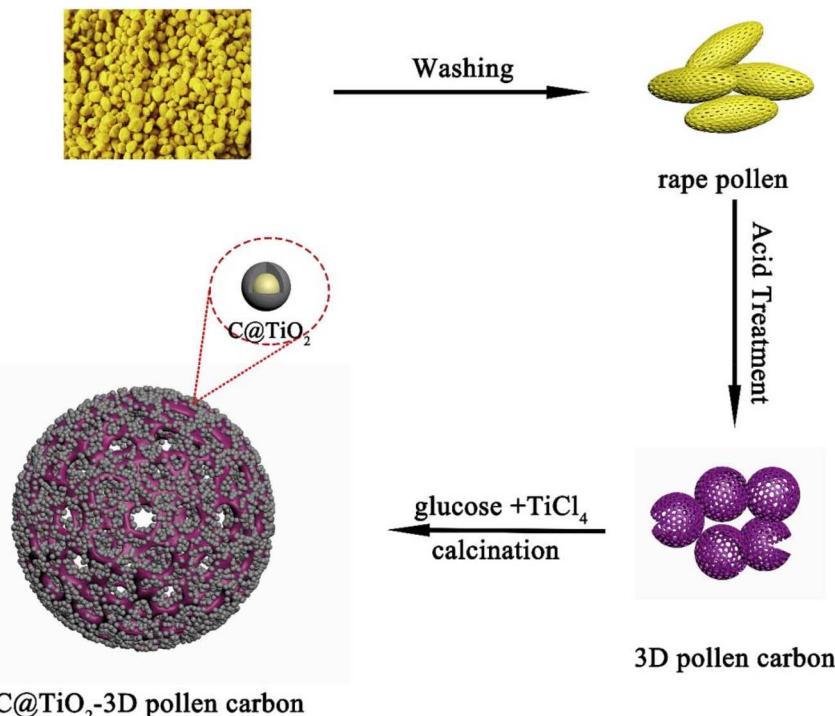


Fig. 8 Schematic illustration of the synthetic process of  $\text{C@TiO}_2$ /3D pollen carbon.<sup>114</sup>

Table 6 Cycling performances and capacities of  $\text{TiO}_2/\text{C}$  nanocomposite<sup>a</sup>

$C_d$	$C_n$	$R_c/\text{mA h g}^{-1}$	$T_c/\text{V}$	Ref.
1C	500	200	0.01–3	111
5C	1000	148	1–3	114
1C	100	269	0–3	115
100 $\text{mA g}^{-1}$	100	290	0.01–3	116
1 A $\text{g}^{-1}$	1000	245	0.01–3	117
188 $\text{mA g}^{-1}$	200	174.4	1–3	118

<sup>a</sup>  $C_d$ —current density,  $C_n$ —cycle numbers,  $R_c$ —remaining capacity,  $T_c$ —tested condition.

Excellent stability can be obtained at high current densities. Jia *et al.*<sup>123</sup> prepared layered nanofiber  $\text{TiO}_2$ /silica composites using natural cellulose material as a template, and their

electrochemical performance improved with increasing titanium content in the composites. For composites with 54.3 wt%  $\text{TiO}_2$  and  $\text{TiO}_2$  nanoparticles of size 12 nm, at 200  $\text{mA g}^{-1}$  current density, it has a capacity of 498.9  $\text{mA h g}^{-1}$  after 200 charge/discharge cycles. Zhou *et al.*<sup>124</sup> prepared spherical  $\text{TiO}_2$ /silica nanoparticles using the sol–gel method. It was shown that the optimal mass ratio of  $\text{TiO}_2$ /silica was 1 : 0.15, the reversible capacity was 720.9  $\text{mA h g}^{-1}$  at a current density of 100  $\text{mA g}^{-1}$ , and the capacity retention was 86.5% after 400 cycles, with a capacity of about 615.9  $\text{mA h g}^{-1}$ . Yan *et al.*<sup>125</sup> successfully coated nano-Si with different contents of nano- $\text{TiO}_2$  to form a new structure of pineapple. When the molar ratio of Si/ $\text{TiO}_2$  is 1 : 4, the cycle stability is the best. After 50 cycles at 0.1C, the specific capacity is 593  $\text{mA h g}^{-1}$ . The cycling performances and capacities of  $\text{TiO}_2/\text{Si}$  nanocomposites is depicted in Table 7.

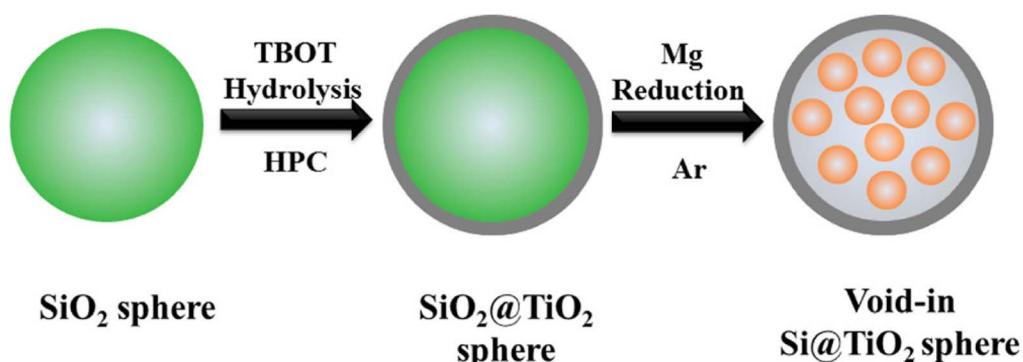


Fig. 9 Schematic diagram of the preparation process of  $\text{Si@TiO}_2$  composite.<sup>121</sup>



Table 7 Cycling performances and capacities of  $\text{TiO}_2/\text{Si}$  nanocomposites<sup>a</sup>

$C_d$	Initial coulombic efficiency	$C_n$	$R_c/\text{mA h g}^{-1}$	Areal capacities ( $\text{mA h cm}^{-2}$ )	$T_c/\text{v}$	Ref.
0.1C	53.1%	100	804	—	0.01–2.5	121
0.1C	—	100	1010.7	—	0–3	122
200 $\text{mA g}^{-1}$	61.5%	200	498.9	0.65	0.01–3	123
100 $\text{mA g}^{-1}$	67.7%	400	615.9	0.86	0.01–3	124
0.1C	69.7%	50	593	—	0–3	125

<sup>a</sup>  $C_d$ —current density,  $I_{ce}$ —initial coulombic efficiency,  $C_n$ —cycle numbers,  $R_c$ —remaining capacity,  $A_c$ —areal capacities,  $T_c$ —tested condition.

### 4.3 $\text{TiO}_2$ and metal element/metal oxide composite

Using the good electrical conductivity of metals to enhance the capacity and cycling stability of electrodes is a common modification method for  $\text{TiO}_2$ .<sup>126</sup> In recent years, there have been many reports on the compounding of  $\text{TiO}_2$  with metal materials such as Ag, Cu, Fe, etc., and metal oxides such as  $\text{SnO}_2$ ,<sup>127</sup>  $\text{Sb}_2\text{O}_3$ ,  $\text{ZnO}$ , etc. to improve the electrochemical performance of the materials.

Kacica *et al.*<sup>128</sup> prepared tin dioxide composites with a  $\text{TiO}_2$  coating using the aerosol chemical vapor deposition method, and the  $\text{SnO}_2/\text{TiO}_2$  electrode had a capacity of 497  $\text{mA h g}^{-1}$  after 100 cycles at 2C current density. Compared to pure  $\text{TiO}_2$  materials, composite  $\text{SnO}_2/\text{TiO}_2$  composites with highly oriented, nanostructured structures exhibited better performance. Fan *et al.*<sup>129</sup> synthesized Cu-doped  $\text{TiO}_2$  nano hollow spheres with a capacity of 159.06  $\text{mA h g}^{-1}$  at a high current density of 10C after 500 cycles. Ren *et al.*<sup>130</sup> synthesized  $\text{Ti}^{3+}$ -doped  $\text{TiO}_2$  nanoparticles with relatively uniform particles with an average size of 30 nm and a  $\text{Ti}^{3+}$  doping content of 4 wt%, with a capacity of 145.8  $\text{mA h g}^{-1}$  at a current density of 200  $\text{mA g}^{-1}$  after 50 cycles. Han *et al.*<sup>131</sup> prepared  $\text{Sb}_2\text{O}_3/\text{Sb}@\text{TiO}_2$  composites with  $\text{TiO}_2$  films covering the surface of  $\text{Sb}_2\text{O}_3$  and Sb elemental particles that were discontinuously distributed in the  $\text{TiO}_2$  film at a discharge capacity of 609  $\text{mA h g}^{-1}$  could be achieved at a current density of 100  $\text{mA g}^{-1}$ . Gao *et al.*<sup>132</sup> reported the preparation of porous  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO)- $\text{TiO}_2$  nanosheet arrays by hydrothermal method, which had a high initial discharge capacity of 184.6  $\text{mA h g}^{-1}$  at 200  $\text{mA g}^{-1}$  and only lost 8.3% of the specific capacity after 1000 cycles. Cao *et al.*<sup>133</sup> prepared a thin layer of titanium dioxide by calcination

of  $\text{MnCO}_3$  microspheres and thermal decomposition of tetrabutyl titanate, and prepared a layered structure  $\text{MnO}_2/\text{TiO}_2$  composite (nano- $\text{MnO}_2@\text{TiO}_2$ ). After 200 cycles at 300  $\text{mA g}^{-1}$ , its capacity is 938  $\text{mA h g}^{-1}$ . Opra *et al.*<sup>134</sup> synthesized vanadium-doped  $\text{TiO}_2$ -B/anatase nanotubes by a simple one-step hydrothermal reaction. The material has a mesoporous structure with a specific surface area of 179.1  $\text{m}^2 \text{ g}^{-1}$ . After 100 cycles at 3000  $\text{mA g}^{-1}$ , the specific capacity is 133  $\text{mA h}^{-1}$ , which has good cyclability. The cycling performances and capacities of  $\text{TiO}_2$ /metal and  $\text{TiO}_2$ /metal oxide nanocomposites is depicted in Table 8.

## 5 Summary and outlook

$\text{TiO}_2$  is a promising anode material for LIBs, but its large-scale application is limited due to its poor electrical conductivity and low  $\text{Li}^+$  diffusion coefficient. In view of these problems, this paper reviews the research achievements of researchers to improve the electrochemical performance of  $\text{TiO}_2$  and promote their practical applications, including the preparation of nanomaterials with different morphologies and the preparation of composite materials with other materials. Although considerable progress has been made in improving the lithium storage performance of  $\text{TiO}_2$ , there are still some fundamental issues that need to be addressed. For example, nanomaterials usually have a larger surface area, which leads to more pronounced side reactions, resulting in low coulombic efficiencies. In addition,  $\text{TiO}_2$  nanomaterials combining with other materials is the development direction of  $\text{TiO}_2$  anode materials, but the current preparation methods are complicated. As a result, low yields and high costs limit its commercial application. It is necessary

Table 8 Cycling performances and capacities of  $\text{TiO}_2$ /metal and  $\text{TiO}_2$ /metal oxide nanocomposites<sup>a</sup>

$T_m$	$C_d$	Initial coulombic efficiency	$C_n$	$R_c/\text{mA h g}^{-1}$	Areal capacities ( $\text{mA h cm}^{-2}$ )	$T_c/\text{v}$	Ref.
$\text{SnO}_2/\text{TiO}_2$	2C	—	100	497	—	0.05–1.5	128
$\text{Cu}/\text{TiO}_2$	10C	90%	500	159.06	—	0.01–3	129
$\text{Ti}^{3+}/\text{TiO}_2$	200 $\text{mA g}^{-1}$	—	50	145.8	0.15	1–3	130
$\text{Sb}_2\text{O}_3/\text{Sb}@\text{TiO}_2$	100 $\text{mA g}^{-1}$	68.4%	500	485	—	0.01–3	131
$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$	200 $\text{mA g}^{-1}$	—	100	172.4	—	1–3	132
$\text{MnO}_2@\text{TiO}_2$	300 $\text{mA g}^{-1}$	86%	200	938	—	0.01–3	133
V-doped $\text{TiO}_2$ -B/anatase	3 A $\text{g}^{-1}$	75%	100	133	0.33	1–3	134

<sup>a</sup>  $T_m$ —typical materials,  $C_d$ —current density,  $I_{ce}$ —initial coulombic efficiency,  $C_n$ —cycle numbers,  $R_c$ —remaining capacity,  $A_c$ —areal capacities,  $T_c$ —tested condition.



to develop efficient and low-cost preparation methods. In conclusion, the exploration of  $\text{TiO}_2$  anode materials with the advantages of low cost, large capacity and good cycling performance will be the focus of future research.

## Conflicts of interest

There are no conflicts to declare.

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