

# SnO<sub>2</sub>基锂离子电池负极材料研究进展

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**摘要** 作为一种N型半导体, 二氧化锡基负极材料由于其拥有较高的理论比容量(782 mA·h·g<sup>-1</sup>)、高能量密度等优势受到了广泛关注。然而, 由于二氧化锡负极材料在充放电过程中的体积效应和本身导电性较差等导致的其循环性能和倍率性能较差, 从而制约了其作为锂离子电池负极材料的应用。本文从二氧化锡的纳米化及复合化(包括其与金属氧化物、无定型碳、碳纳米管和石墨烯等复合)2方面综述了二氧化锡基锂离子电池负极材料的研究进展, 同时对SnO<sub>2</sub>基锂离子电池负极材料的发展方向进行了展望。

**关键词** 锂离子电池; 二氧化锡; 负极材料; 纳米结构

近年来, 随着传统的化石能源逐渐消耗, 人类对能源需求量的不断增加, 新能源的发展受到了人们的广泛关注, 可持续发展成为了人们的普遍共识<sup>[1]</sup>。锂离子电池(lithium ion battery, LIBs)由于其比容量高、开路电压高、循环性能好、无记忆效应、对环境污染小、快速充电和自放电率低等优点, 在许多领域得到了广泛关注和应用<sup>[2]</sup>。尤其是在各类便携式移动设备等方面应用较多, 然而, 新技术的发展给储能设备提出了新的要求, 如混合动力汽车的发展, 其储能设备所需的能量密度是常用一般设备的2~5倍, 这便需要进一步对锂离子电池进行改进和创新, 提高锂离子电池的性能, 以满足新技术发展的要求<sup>[3]</sup>。

锂离子电池的负极材料是其重要组成部分, 作为储锂的主体, 实现了锂离子电池在充放电过程中锂离子的嵌入和脱出。传统锂离子电池的负极材料为石墨, 但其作为锂离子电池负极材料也存在一定的缺陷和问题。首先, 石墨材料的理论嵌锂容量仅为372 mA·h·g<sup>-1</sup>(实际嵌锂容量仅达到330 mA·h·g<sup>-1</sup>左右), 已不能满足大型动力电池的应用要求。其次, 在充放电过程中, 锂的析出电位与碳材料电位处在相近的位置, 在超过电池容量继续充电的情况下, 在碳材料的表面很容易有锂枝晶的析出造成电池的短路; 此外, 在较高温度下, 碳负极材料易与电解液发生放热反应生成可燃气体, 使电池燃烧; 石墨类负极材料还存在明显的电压滞后现象。因此, 石墨类负极材料已不能满足新型设备的发展要求, 研究者们发展了许多新型负极材料用于代替石墨, 如钛基化合物、氧化锡、硅-氧化硅、氧化钴和过渡金属氮化物等<sup>[4]</sup>。

在众多氧化物中, 氧化锡(SnO<sub>2</sub>)具有很高的理论储锂容量(782 mA·h·g<sup>-1</sup>), 作为锂离子电池负极材料可有效提高锂离子电池的能量密度, 同时其安全性好、资源储备量丰富, 是最具发展潜力的可代替石墨的锂离子电池负极材料之一<sup>[5]</sup>。然而目前阻碍其实际应用的主要问题是其在循环充放电过程中会有较大的体积变化(300%), 负极材料容易粉化, 导致循环性能较差, 此外, 这类金属氧化物还存在导电性差的普遍问题, 这也是影响其实际应用的一个重要因素<sup>[5-6]</sup>。本文主要针对氧化锡作为锂离子电池负极材料时的这些问题, 从结构、尺寸控制、到复合化, 再到综合调控, 对氧化锡基新型锂离子电池负极材料的制备和电化学性能进行了系统的概述。

## 1 二氧化锡负极材料的纳米化

与普通材料相比, 纳米材料具有较大的比表面积, 可以缓解负极材料在充放电时的体积效应, 并且纳米材料表面的多级孔通道可以有效提升锂离子在嵌入脱出的速度和电极材料的导电性, 从而提升负极材料的电化学性能<sup>[7]</sup>。近年来, 国内外研究人员通过不同工艺合成了诸如零维纳米颗粒、二维纳米片、三维纳米中空球、核壳结构等不同纳米结构的二氧化锡负极材料<sup>[8-16]</sup>。尤其是三维的纳米空心结构, 在进行电化学性能测试后表现出了优良的电化学性能<sup>[17]</sup>。

所有构成纳米二氧化锡材料的单元都由溶剂化学法合成的, 即将前驱体和添加剂加入溶剂中, 通过控制前驱体浓度和溶液pH值, 利用水热法可以合成各种尺寸的纳米单元并通过自组装形成不同形貌的纳米二氧化锡材料。

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表1 不同纳米结构二氧化锡材料的制备工艺及其负极循环性能  
Table 1 Synthesis strategy and anode cycling performance of different nanostructure tin dioxide materials

纳米颗粒	合成方法	前驱体和添加剂	容量/ (mA·h·g <sup>-1</sup> )	文献
0D 颗粒	水热	SnCl <sub>4</sub> D, 葡萄糖	700 (30 cycles)	[18]
0D 颗粒	水热	K <sub>2</sub> SnO <sub>3</sub>	600 (40 cycles)	[19]
1D 纳米棒	自组装	SnCl <sub>2</sub> , H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	700 (20 cycles)	[20]
1D 纳米线	水热	SnCl <sub>4</sub> , NaF	400 (50 cycles)	[21]
2D 纳米片	水热	尿素, NaOH, SnCl <sub>2</sub>	372 (50 cycles)	[22]
2D 纳米片	无模板	SnSO <sub>4</sub>	545 (50 cycles)	[23]

Jiang 等<sup>[20]</sup>利用 SnCl<sub>2</sub> 为前驱体, 在溶剂中添加乙二酸, 通过溶剂热方法合成了二维的纳米棒, 并利用基团的自组装效应合成了三维结构的纳米花, 见图 1。所得的纳米花作为负极材料在 20 个循环后依旧有 700 mA·h/g 的比容量, 见图 2。

Wu 等<sup>[22]</sup>利用 SnCl<sub>2</sub>·H<sub>2</sub>O 作为前驱体, 通过加入尿素及 NaOH 调节体系 pH 值得到了不同直径的多级孔纳米 SnO<sub>2</sub> 结构, 见图 3。在 50 次充放电循环后, 材料基本形貌变化不大, 可逆容量可以达到 400 mA·h/g, 见图 4。

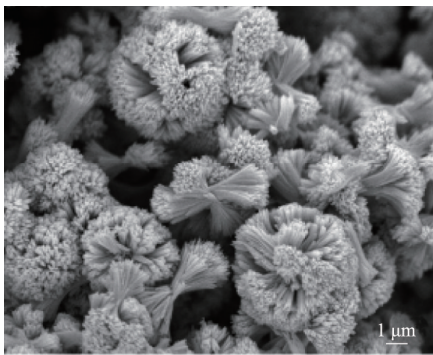


图1 SnO<sub>2</sub> 纳米花电镜

Fig. 1 SEM image of SnO<sub>2</sub> Nanoflower

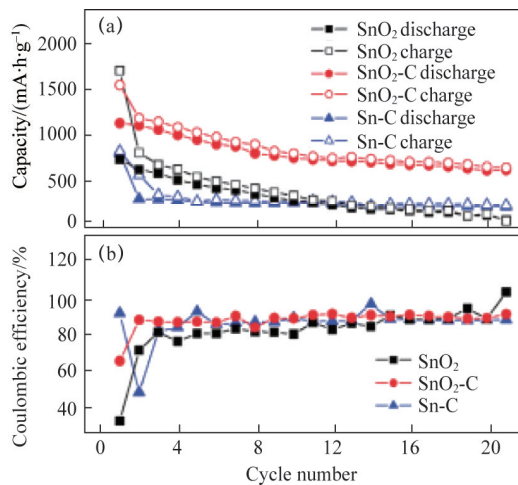


图2 SnO<sub>2</sub> 纳米花 (a) 与 SnO<sub>2</sub>@C 负极材料 (b) 循环性能  
Fig. 2 Cycling performance of SnO<sub>2</sub> Nanoflower (a) and SnO<sub>2</sub>@C anode materials (b)

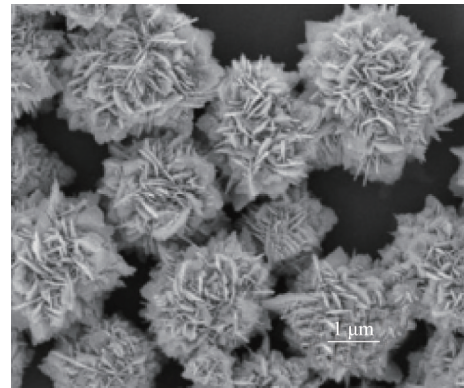


图3 多级孔 SnO<sub>2</sub> 纳米结构电镜

Fig. 3 SEM image of SnO<sub>2</sub> hierarchically porous nanostructure

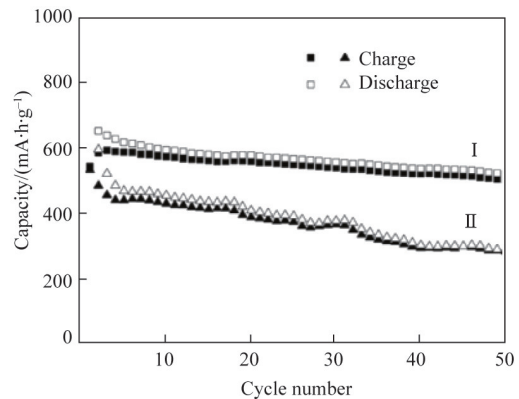


图4 多级孔 SnO<sub>2</sub> 纳米结构负极材料循环性能

Fig. 4 Cycling performance of SnO<sub>2</sub> hierarchically porous nanostructure

其次, 中空结构的二氧化锡纳米结构因其比表面积大, 并能有效缓解二氧化锡负极材料在充放电时的体积效应受到了极大地关注。现阶段主要有 2 种方法合成纳米空心结构, 一种为硬模板法<sup>[21,24-30]</sup>。例如, Wang 等<sup>[24]</sup>利用碳球作为模板, 通过控制碳球大小, 煅烧时间和包覆时间合成了单层的核壳结构以及多层的核壳结构, 如图 5 所示。双层核壳结构的第一次放电比容量可以达到 1803 mA·h/g, 单层核壳结构的第一次放电比容量为 1595 mA·h/g。在 30 次充放电循环后双层核壳结构与单层核壳结构的比容量分别降低到 157 和

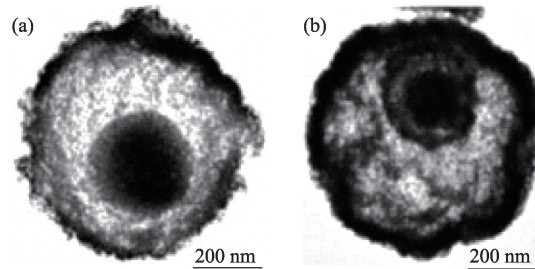


图5 单层 (a) 与双层 (b) 核壳 SnO<sub>2</sub> 纳米结构的 TEM

Fig. 5 TEM image of core-shell SnO<sub>2</sub> nanostructure (a) and core-in-double shell SnO<sub>2</sub> nanostructure (b)

281 mA·h/g(图6)。

另外一种合成空心结构二氧化锡材料是利用水热法,通过奥斯瓦尔德熟化效应和柯肯达尔效应来得到相应的产物<sup>[28,31-36]</sup>。例如, Lou 等<sup>[36]</sup>利用奥斯瓦尔德效应得到了直径在 200 nm 左右的空心纳米二氧化锡微球。根据奥斯瓦尔德熟化效应,一开始处于中心部分的晶粒溶解并重新在表面聚集并长大,从而得到了中空的结构。在 65 个充放电循环后依然有 645 mA·h/g 的比容量,且首次放电库伦效率高达 75%,显著高于早前合成的空心结构二氧化锡负极材料。Wang 等<sup>[36]</sup>利用 SnCl<sub>4</sub> 作为前驱体,通过加入 NaF 与 NH<sub>4</sub>F 一步水热法制备了空心的二氧化锡纳米微球,如图 7。在 100 mA/g 的电流密度下,在 50 个循环后,二氧化锡纳米空心球比实心球的比容量要高出 187 mA·h/g,见图 8 所示。

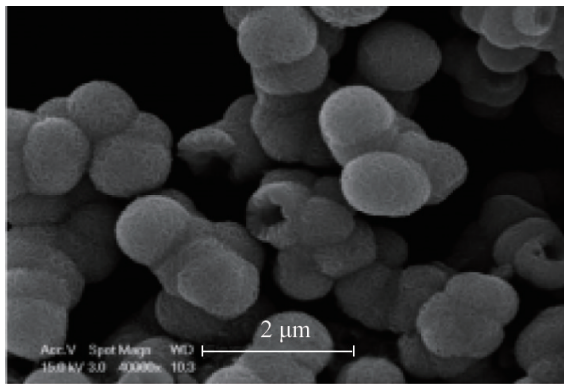


图 7 SnO<sub>2</sub> 空心纳米球电镜

Fig. 7 SEM image of SnO<sub>2</sub> hollow sphere

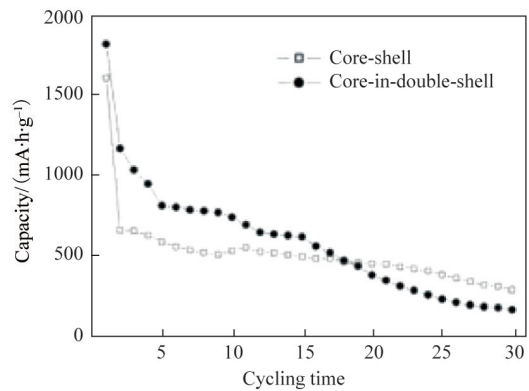


图 6 单层与双层核壳 SnO<sub>2</sub> 负极材料循环性能

Fig. 6 Cycling performance of Core-shell and Core-in-double shell SnO<sub>2</sub> Nanostructure

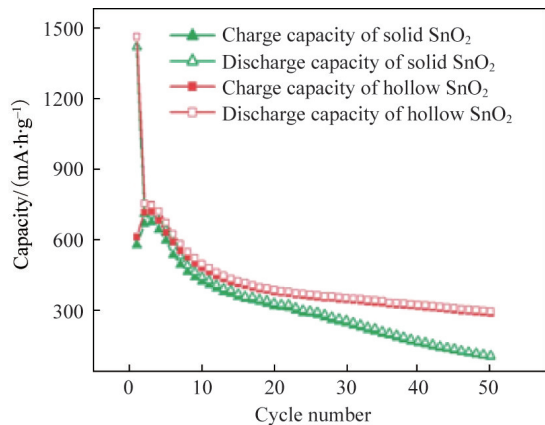


图 8 SnO<sub>2</sub> 空心与实心纳米球的负极材料循环性能

Fig. 8 Cycling performance of SnO<sub>2</sub> hollow sphere and solid sphere

## 2 二氧化锡负极材料的复合化

对二氧化锡负极材料进行复合也是获得理想性能的一种主要方法。主要有金属氧化物与二氧化锡的复合,例如, TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub><sup>[37-43]</sup>等,由于各种金属氧化物有各自的优异性能,通过多种氧化物的协同作用可以得到性能综合的复合二氧化锡负极材料。其次,是与碳的复合。主要包括与无定型碳,碳纳米管,石墨烯等。

### 2.1 二氧化锡纳米材料与金属氧化物的复合

二氧化钛作为另外一种被广泛研究的负极材料有成本低,污染小,循环性能高等特点<sup>[44,45]</sup>。而二氧化钛作为负极材料的理论比容量(335 mA·h/g)小于二氧化锡(782 mA·h/g),甚至小于多孔石墨(372 mA·h/g)<sup>[46-47]</sup>。但是二氧化钛具有优良的导电性,同时也有较小的体积效应<sup>[48-51]</sup>。因此,为了同时综合二氧化钛与二氧化锡的优点,制备 Ti 掺杂二氧化锡的材料成为一种理想的方法<sup>[52-60]</sup>。Wang 等<sup>[61]</sup>制备出了二维结构的二氧化钛复合二氧化锡纳米筛,如图 9 所示。在 250 mA/g 的电流密度下,20 个充放电循环后,依旧有 74% 的容量,能达到约 500 mA·h/g<sup>[61]</sup>。同时,在 20 个充放电循环后, Ti<sup>4+</sup> 掺杂二氧

化锡复合材料的比容量就已经高于二氧化锡纳米花,有效减轻了电极比容量在充放电过程中的衰减,见图 10<sup>[61]</sup>。

### 2.2 二氧化锡纳米材料与无定型碳的复合

在二氧化锡与无定型碳的复合中,一方面由于无定型碳的存在起到了稳定结构的作用,可以有效缓解负极材料在充放电过程中的体积效应,降低负极的粉化<sup>[16]</sup>。另一方面,由于碳的优良导电性,可以提高电极材料的导电性和锂离子在纳米材料表面的传输速度,从而相应的提升负极材料的循环性能<sup>[14,62-64]</sup>。

刘瑞平等使用碳球作为模板合成了直径 200 nm 的二氧化锡空心球。利用聚合物多巴胺包覆的方式得到了碳包覆的二氧化锡空心球<sup>[65]</sup>。在煅烧过程中,部分碳将二氧化锡还原成了金属单质锡,从而获得了碳包覆的 SnO<sub>2</sub>/Sn 微球,如图 11~图 12 所示<sup>[65]</sup>。此种结构的优点就是在二氧化锡电极反应的第一个阶段减少锂离子的消耗,减小电极的不可逆容量。经过优化后的二氧化锡复合材料电极在 50 个充放电循环以后还剩余 500 mA·h/g 的比容量首次循环的库伦效率为 82.3%,见图 13<sup>[65]</sup>。

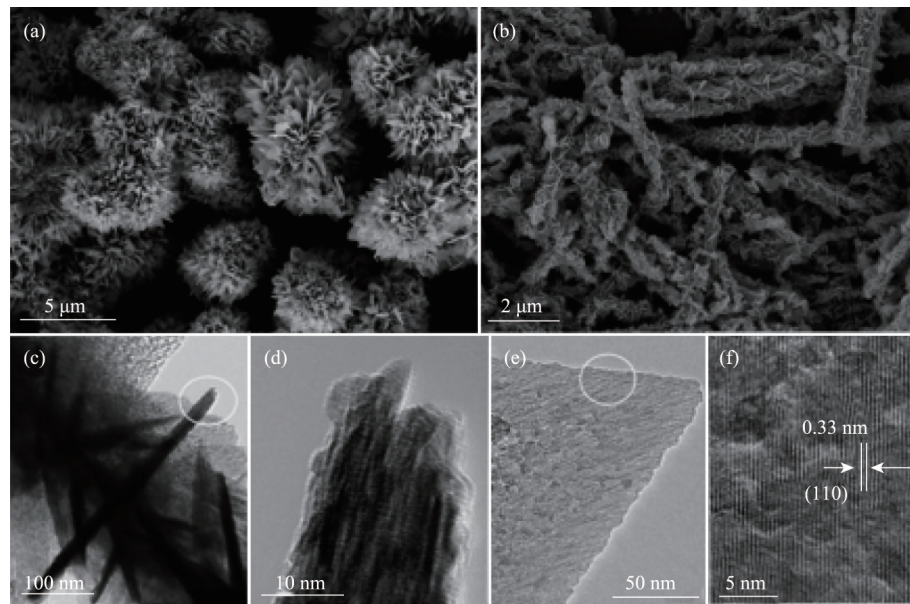


图9 二氧化钛复合二氧化锡纳米筛的微观形貌  
Fig. 9 SEM and TEM images of TiO<sub>2</sub>/SnO<sub>2</sub> hybrids nanostructures

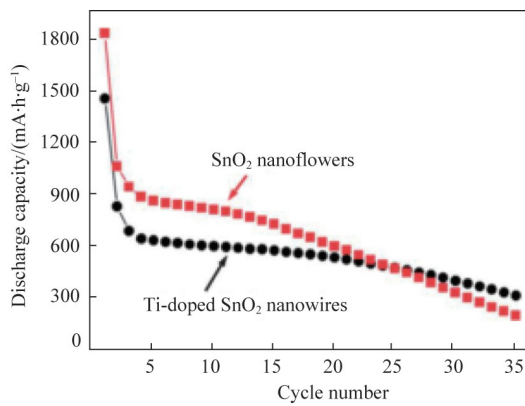


图10 Ti<sup>4+</sup>和Sn<sup>2+</sup>掺杂SnO<sub>2</sub>纳米结构负极材料与SnO<sub>2</sub>纳米花的循环性能  
Fig. 10 Cycling performance of Ti<sup>4+</sup>/Sn<sup>2+</sup> co-doped SnO<sub>2</sub> nanostructures and SnO<sub>2</sub> nanoflowers

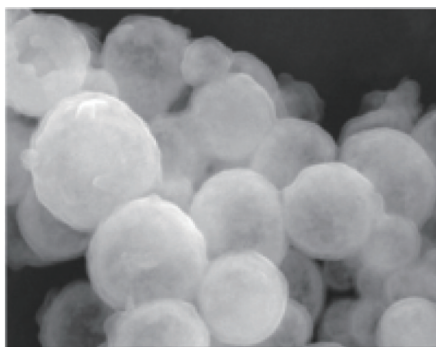


图11 碳包覆的SnO<sub>2</sub>/Sn微球电镜  
Fig. 11 SEM image of SnO<sub>2</sub>/Sn hollow sphere

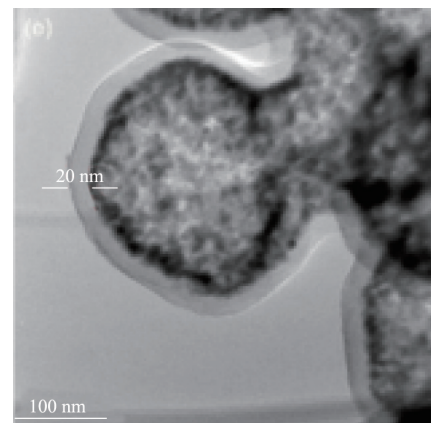


图12 碳包覆的SnO<sub>2</sub>/Sn微球的透射电镜  
Fig. 12 TEM image of SnO<sub>2</sub>/Sn hollow sphere

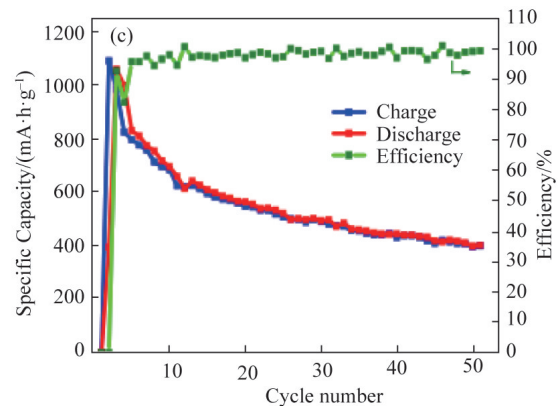


图13 碳包覆的SnO<sub>2</sub>/Sn微球的循环性能  
Fig. 13 Cycling performance of SnO<sub>2</sub>/Sn hollow sphere

Wang等<sup>[61]</sup>利用碳纳米管作为模板,使用真空灌注成型工艺将SnO<sub>2</sub>纳米颗粒灌注进碳纳米管,接着通过煅烧的方式除去碳纳米管最后得到空心的SnO<sub>2</sub>纳米管。最后,将乙炔和氮气通入管式炉煅烧3 h后得到SnO<sub>2</sub>和无定型碳复合的SnO<sub>2</sub>纳米管,如图14所示<sup>[66]</sup>。碳包覆的SnO<sub>2</sub>纳米管有很好的循环稳定性,在0.5 C的电流密度下起始比容量为586 mA·h/g,在200个循环以后依然有542 mA·h/g的比容量。平均每个循环的容量衰减只有0.0375%,其首次充放电循环的库伦效率更是接近92.5%远远高于同类材料<sup>[65-71]</sup>。

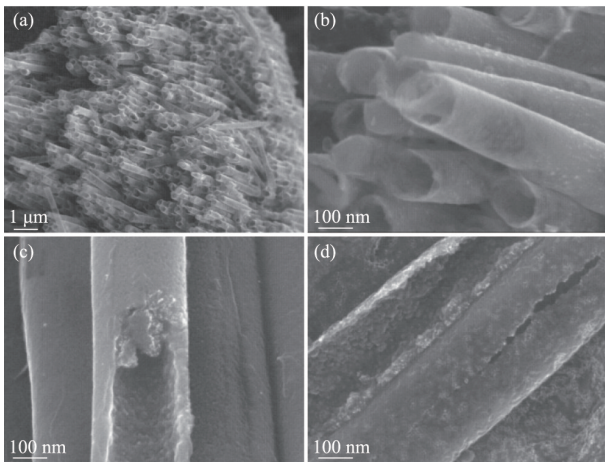


图14 碳包覆的SnO<sub>2</sub>纳米管显微形貌

Fig. 14 FESEM images of SnO<sub>2</sub>-core/carbon-shell nanotubes

### 2.3 二氧化锡纳米材料与碳纳米管的复合

碳纳米管作为一种新型的纳米材料,由于其优异的力学性能和电学性能在锂离子电池负极材料的复合中显示了广阔的应用前景。碳纳米管在与二氧化锡负极材料的复合中可以有效的解决二氧化锡导电性差的缺点,提高离子和电子在负极材料中的传递效率<sup>[72-76]</sup>。同时,碳纳米管可以起到骨架的作用,缓解体积效应造成的粉化<sup>[77-83]</sup>。

Ma等<sup>[84]</sup>利用一步水热法,制备出了无定型碳包覆碳纳米管与二氧化锡颗粒的复合结构,见图15。相比较于之前大部分人所做的碳纳米管与二氧化锡复合材料多了一层无定型的碳,从而合成了一种多级孔结构。这种结构在充放电循环

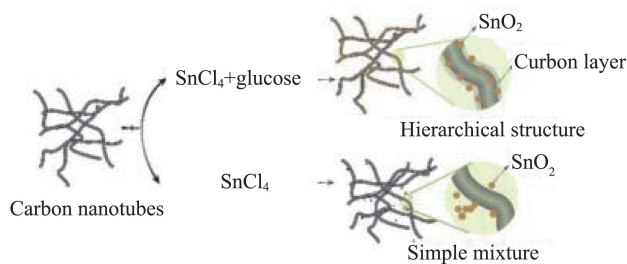


图15 C-SnO<sub>2</sub>/CNT纳米结构

Fig. 15 Schematic diagram of the material synthesis processes

时可以避免二氧化锡活性物质的破坏和脱落。在1000 mA/g的电流密度下首次充放电循环的充放电容量分别为1684 mA·h·g<sup>-1</sup>和791 mA·h·g<sup>-1</sup>,见图16<sup>[84]</sup>。

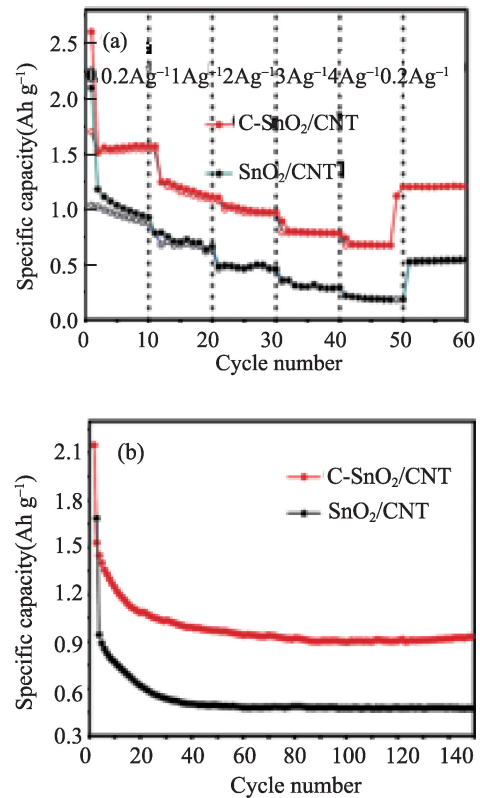


图16 C-SnO<sub>2</sub>/CNT纳米复合材料倍率(a)及循环(b)性能  
Fig. 16 Rate capability (a) and cycling performance (b) of C-SnO<sub>2</sub>/CNT

Chen等<sup>[85]</sup>利用NaBr和锡的前驱体与多壁碳纳米管共水热合成了树枝状的二氧化锡结构。二氧化锡结晶成一种纳米棒的形式复合在碳纳米管的表面,并在纳米管表面包覆无定型的碳来提高电极材料的循环性能,如图17所示<sup>[85]</sup>。这种

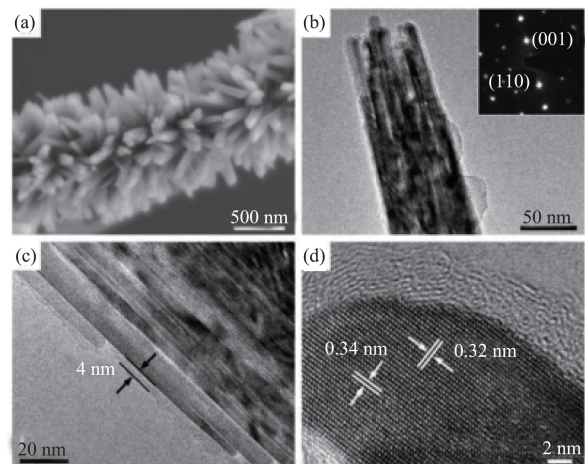


图17 树枝状CNT@SnO<sub>2</sub>@C纳米结构示意图

Fig. 17 SEM image of a branched CNT@SnO<sub>2</sub>@C hierarchical heterostructure.

结构提供了更为有效的锂离子传输路径,从而提升了负极材料的表现。在0.2 C的电流密度下40个循环后的比容量仍然留有720 mA·h/g,见图18。

### 2.4 二氧化锡纳米材料与石墨烯的复合

石墨烯是一种新型的二维碳材料,是一种和纳米结构复合的理想材料。石墨烯具有单原子层,优良的导电性,良好的化学稳定性和高比表面积等特点。这些优点可以有效的缓解二氧化锡材料的体积效应和内应力,从而提升负极材料的循环性能<sup>[86-89]</sup>。

现阶段有很多种将金属氧化物纳米颗粒复合在氧化石墨烯表面的方法,例如原子沉积的方法<sup>[87-92]</sup>。但是这种方法

因为相互作用力不够的缘故很难将金属氧化物晶粒复合在氧化石墨烯的表面。Zhang等<sup>[86]</sup>利用氧化石墨烯和二氧化锡合成了两面都有二氧化锡的平面材料,具有良好的电化学性能以及柔韧性。Chen等利用一步水热法,合成出了颗粒大小为5 nm的二氧化锡复合氧化石墨烯材料,如图19所示<sup>[93]</sup>。这种结构的比表面积大,可以缩短离子传输的距离,增加了反应位点,从而获得了很高的可逆容量。在0.1 A/g的电流密度下首次充放电的可逆容量有1239 mA·h/g,在10 A/g的电流密度下首次充放电容量为574 mA·h/g。在1000个充放电循环后,依然有1813 mA·h/g的可逆容量,见图20<sup>[93]</sup>。

在上述过程中,虽然通过改进将氧化锡颗粒附着在了石

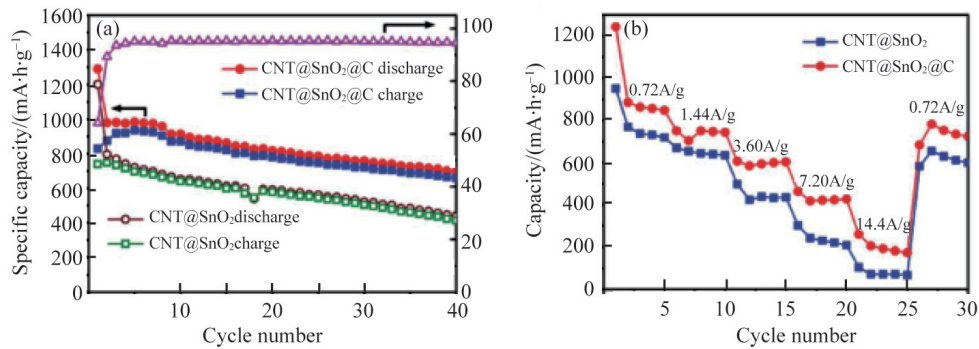


图18 树枝状CNT@SnO<sub>2</sub>@C纳米复合材料倍率(a)及循环(b)性能  
Fig.18 Cycling (a) and rate capability performance(b) of CNT@SnO<sub>2</sub>@C

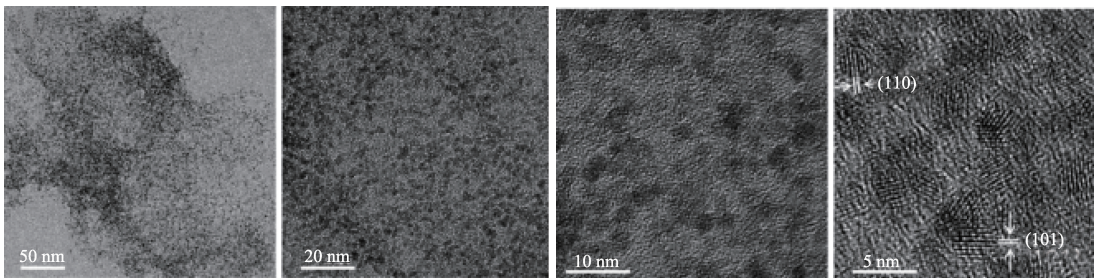


图19 不同放大倍数SnO<sub>2</sub>@GO纳米结构示意图  
Fig. 19 TEM images of SnO<sub>2</sub>/G under different magnifications

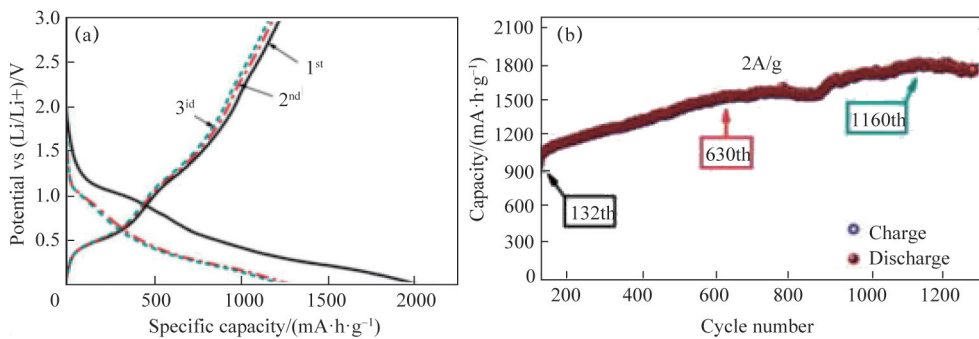


图20 SnO<sub>2</sub>@GO纳米复合材料在0.1 A/g电流密度下的充放电曲线(a)以及在2 A/g电流密度下的循环性能(b)  
Fig. 20 Electrochemical performances of SnO<sub>2</sub>/G composite cycled between 0.005 and 3 V. Charge-discharge curves of the SnO<sub>2</sub>/G composite at (a) current density of 0.1 A/g and cycling capability performance of SnO<sub>2</sub>@GO at 2 A/g (b)

石墨烯表面,但是依旧难以从根本上改变氧化锡的体积效应以及在充放电过程中的材料粉化<sup>[94-101]</sup>。另外一种思路是将石墨烯包覆在纳米空心球表面,这样石墨烯不仅能起到提高导电性的作用还能有效的抑制体积膨胀。Liu 等<sup>[94]</sup>利用硅烷偶联剂将石墨烯包覆在纳米空心二氧化锡球的表面,并通过沉积氧化铝制备得到了复合的纳米空心球,如图 21 所示。一方面,石墨烯的存在提高了导电性,提升了离子传输效率,另一方面氧化铝薄膜的存在也能保护负极材料的结构完整。因此,在 0.1 A/g 的电流密度下,60 个充放电循环后,可逆容量依旧可以达到 1176 mA·h/g。明显高于普通的二氧化锡空心球以及石墨烯包覆二氧化锡空心球材料(图 22)。

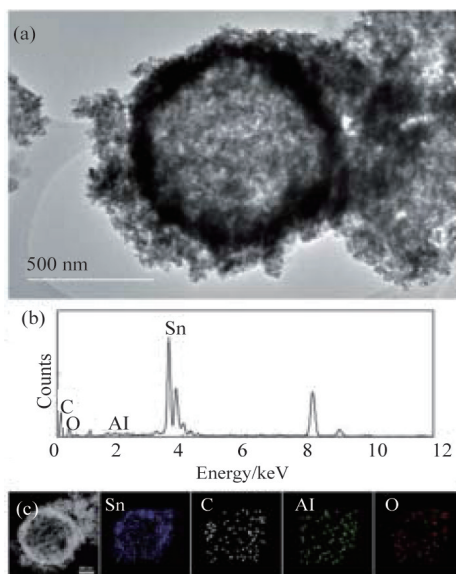


图 21 Al<sub>2</sub>O<sub>3</sub> 包覆 SnO<sub>2</sub> HS/GO 纳米结构示意图及元素分布  
Fig. 21 (a) TEM image of Al<sub>2</sub>O<sub>3</sub> coated SnO<sub>2</sub> HS/GO composite (b and c) EDX spectrum and element mapping images of Al<sub>2</sub>O<sub>3</sub> coated SnO<sub>2</sub> HS/GO composite

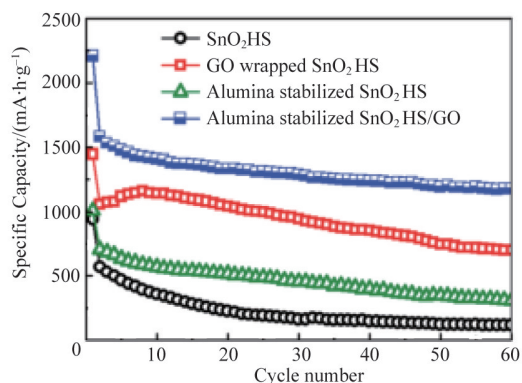


图 22 Al<sub>2</sub>O<sub>3</sub> 包覆 SnO<sub>2</sub> HS/GO 纳米材料在 0.1 A/g 电流密度下的循环性  
Fig. 22 Cycling performance of different electrodes at charge/discharge rate of 100 mA/g

### 3 结论

二氧化锡材料作为锂离子电池负极材料有广阔的前景和实际应用潜力,通过优化材料微观形貌和结构组成,可以有效的提高负极材料的循环,倍率以及可逆性能。改变微观形貌主要的方法包括,制备纳米空心球介孔材料,纳米管状材料,纳米片状材料等。改变结构组成主要是利用二氧化锡材料与纳米氧化物的复合,如氧化钛,氧化钴,氧化锰等。同时构建与碳材料的复合,例如与无定型碳,碳纳米管,石墨烯的复合。通过以上方式,可以有效的缓解二氧化锡材料作为锂离子电池负极材料导电性差以及充放电过程中体积效应明显的缺点。尽管在过去几年中,通过将上述两种方法同时使用构建二氧化锡基复合材料的报道已经有很多,并且在一定程度上改善了二氧化锡负极材料的循环性能和倍率性能,然而,在 SnO<sub>2</sub> 基负极材料实际应用之前,还有很多科学问题亟待解决。一方面,由于氧化锡与 Li 离子在充放电过程中的部分可逆反应,氧化锡基锂离子电池负极材料的首次充放电库伦效率较低。研究表明,减小氧化锡纳米颗粒尺寸可以使上述反应完全可逆。然而,减小纳米颗粒尺寸后带来的团聚以及如何保证充放电过程中氧化锡纳米颗粒的稳定性是今后的研究重点之一。另一方面,尽管与不同的材料复合可以利用两种或几种材料之间的协同作用,从而提高氧化锡基锂离子电池负极材料的电化学性能。然而,如何理解复合结构中各组元在提高电化学性能方面的作用机制是另一个需要深入研究的方向。

### 参考文献 (References)

- [1] Scrosati B, Garche J. Lithium batteries: Status, prospects and future[J]. *Journal of Power Sources*, 2010, 195(9): 2419-2430.
- [2] Tarascon J M, Armand M. Issues and challenges facing rechargeable lithium batteries[J]. *Nature*, 2001, 414(6861): 359-367.
- [3] Li Y, Song J, Yang J. A review on structure model and energy system design of lithium-ion battery in renewable energy vehicle[J]. *Renewable and Sustainable Energy Reviews*, 2014, 37: 627-633.
- [4] Chen J S, Lou X W D. SnO<sub>2</sub>-based nanomaterials: synthesis and application in lithium-ion batteries[J]. *Small*, 2013, 9(11): 1877-1893.
- [5] Chen J. Recent progress in advanced materials for lithium ion batteries [J]. *Materials*, 2013, 6(1): 156-183.
- [6] Xiao G, Wang Y, Ning J, et al. Recent advances in IV-VI semiconductor nanocrystals: synthesis, mechanism, and applications[J]. *RSC Advances*, 2013, 3(22): 8104-8130.
- [7] Srinivasan N R, Mitra S, Bandyopadhyaya R. Improved electrochemical performance of SnO<sub>2</sub>-mesoporous carbon hybrid as a negative electrode for lithium ion battery applications[J]. *Physical Chemistry Chemical Physics*, 2014, 16(14): 6630-6640.
- [8] Yin L, Chai S, Wang F, et al. Ultrafine SnO<sub>2</sub> nanoparticles as a high performance anode material for lithium ion battery[J]. *Ceramics International*, 2016, 42(8): 9433-9437.
- [9] Wang J, Song W L, Wang Z, et al. Facile fabrication of binder-free metallic tin nanoparticle/carbon nanofiber hybrid electrodes for lithium-ion batteries[J]. *Electrochimica Acta*, 2015, 153: 468-475.
- [10] Ji X, Huang X, Liu J, et al. Carbon-coated SnO<sub>2</sub> nanorod array for lith-

- ium-ion battery anode material[J]. *Nanoscale Research Letters*, 2010, 5(3): 649–654.
- [11] Xue X Y, Chen Z H, Xing L L, et al. SnO<sub>2</sub>/α-MoO<sub>3</sub> core-shell nanobelts and their extraordinarily high reversible capacity as lithium-ion battery anodes[J]. *Chemical Communications*, 2011, 47(18): 5205–5207.
- [12] Thomas R, Rao G M. SnO<sub>2</sub> nanowire anchored graphene nanosheet matrix for the superior performance of Li-ion thin film battery anode[J]. *Journal of Materials Chemistry A*, 2015, 3(1): 274–280.
- [13] Zeng W, Zheng F, Li R, et al. Template synthesis of SnO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> nanotube array for 3D lithium ion battery anode with large areal capacity[J]. *Nanoscale*, 2012, 4(8): 2760–2765.
- [14] Zhou D, Song W L, Fan L Z. Hollow core-shell SnO<sub>2</sub>/C fibers as highly stable anodes for lithium-ion batteries[J]. *ACS Applied Materials & Interfaces*, 2015, 7(38): 21472–21478.
- [15] Zhang L, Wu H B, Lou X D W. Growth of SnO<sub>2</sub> nanosheet arrays on various conductive substrates as integrated electrodes for lithium-ion batteries[J]. *Materials Horizons*, 2014, 1(1): 133–138.
- [16] Lin Y S, Duh J G, Hung M H. Shell-by-shell synthesis and applications of carbon-coated SnO<sub>2</sub> hollow nanospheres in lithium-ion battery[J]. *The Journal of Physical Chemistry C*, 2010, 114(30): 13136–13141.
- [17] Wang J H. Synthesis of mesoporous SnO<sub>2</sub> and its application in lithium-ion battery[J]. *Acta Physico-Chimica Sinica*, 2008, 24(4): 681–685.
- [18] Deng D, Lee J Y. Hollow core-shell mesospheres of crystalline SnO<sub>2</sub> nanoparticle aggregates for high capacity Li<sup>+</sup> ion storage[J]. *Chemistry of Materials*, 2008, 20(5): 1841–1846.
- [19] Lou X W, Wang Y, Yuan C, et al. Template-free synthesis of SnO<sub>2</sub> hollow nanostructures with high lithium storage capacity[J]. *Advanced Materials*, 2006, 18(17): 2325–2329.
- [20] Jiang L Y, Wu X L, Guo Y G, et al. SnO<sub>2</sub>-based hierarchical nanostructures: facile synthesis and their applications in gas sensors and lithium-ion batteries[J]. *The Journal of Physical Chemistry C*, 2009, 113(32): 14213–14219.
- [21] Yang H X, Qian J F, Chen Z X, et al. Multilayered nanocrystalline SnO<sub>2</sub> hollow microspheres synthesized by chemically induced self-assembly in the hydrothermal environment[J]. *The Journal of Physical Chemistry C*, 2007, 111(38): 14067–14071.
- [22] Wu H B, Chen J S, Lou X W, et al. Synthesis of SnO<sub>2</sub> hierarchical structures assembled from nanosheets and their lithium storage properties[J]. *The Journal of Physical Chemistry C*, 2011, 115(50): 24605–24610.
- [23] Yin X M, Li C C, Zhang M, et al. One-step synthesis of hierarchical SnO<sub>2</sub> hollow nanostructures via self-assembly for high power lithium ion batteries[J]. *The Journal of Physical Chemistry C*, 2010, 114(17): 8084–8088.
- [24] Wang Y, Niu S, Lu S. Controlled-synthesis and lithium storage properties of SnO<sub>2</sub> porous core-shell spheres and core-in-double-shell spheres[J]. *Materials Letters*, 2015, 157: 209–211.
- [25] Ding S J, Chen J S, Qi G G, et al. Formation of SnO<sub>2</sub> hollow nanospheres inside mesoporous silica nanoreactors[J]. *Journal of the American Chemical Society*, 2010, 133(1): 21–23.
- [26] Kravchik K, Protesescu L, Bodnarchuk M I, et al. Monodisperse and inorganically capped Sn and Sn/SnO<sub>2</sub> nanocrystals for high-performance Li-ion battery anodes[J]. *Journal of the American Chemical Society*, 2013, 135(11): 4199–4202.
- [27] Du N, Zhang H, Chen J, et al. Metal oxide and sulfide hollow spheres: Layer-by-layer synthesis and their application in lithium-ion battery[J]. *The Journal of Physical Chemistry B*, 2008, 112(47): 14836–14842.
- [28] Ding S, Lou X. SnO<sub>2</sub> nanosheet hollow spheres with improved lithium storage capabilities[J]. *Nanoscale*, 2011, 3(9): 3586–3588.
- [29] Yan W W, Fang M, Tan X L, et al. Template-free fabrication of SnO<sub>2</sub> hollow spheres with photoluminescence from Sn[J]. *Materials Letters*, 2010, 64(19): 2033–2035.
- [30] Wang H Z, Liang J B, Fan H, et al. Synthesis and gas sensitivities of SnO<sub>2</sub> nanorods and hollow microspheres[J]. *Journal of Solid State Chemistry*, 2008, 181(1): 122–129.
- [31] Yec C C, Zeng H C. Synthesis of complex nanomaterials via Ostwald ripening[J]. *Journal of Materials Chemistry A*, 2014, 2(14): 4843–4851.
- [32] Lou X W, Wang Y, Yuan C, et al. Template-free synthesis of SnO<sub>2</sub> hollow nanostructures with high lithium storage capacity[J]. *Advanced Materials*, 2006, 18(17): 2325–2329.
- [33] Yin X M, Li C C, Zhang M, et al. One-step synthesis of hierarchical SnO<sub>2</sub> hollow nanostructures via self-assembly for high power lithium ion batteries[J]. *The Journal of Physical Chemistry C*, 2010, 114(17): 8084–8088.
- [34] Zeng H C. Synthesis and self-assembly of complex hollow materials[J]. *Journal of Materials Chemistry*, 2011, 21(21): 7511–7526.
- [35] Shi L, Bao K Y, Cao J, et al. Controlled fabrication of SnO<sub>2</sub> solid and hollow nanocubes with a simple hydrothermal route[J]. *Applied Physics Letters*, 2008, 93(15): 152511.
- [36] Hong K, Wang F F. Hydrothermal synthesis of hierarchical SnO<sub>2</sub> microspheres for gas sensing and lithium-ion batteries applications: Fluoride-mediated formation of solid and hollow structures[J]. *Journal of Materials Chemistry*, 2012, 22(5): 2140–2148.
- [37] Dou X, Sabba D, Mathews N, et al. Hydrothermal synthesis of high electron mobility Zn-doped SnO<sub>2</sub> nanoflowers as photoanode material for efficient dye-sensitized solar cells[J]. *Chemistry of Materials*, 2011, 23(17): 3938–3945.
- [38] Li Z, Zhou Y, Yu T, et al. Unique Zn-doped SnO<sub>2</sub> nano-echinus with excellent electron transport and light harvesting properties as photoanode materials for high performance dye-sensitized solar cell[J]. *CrystEngComm*, 2012, 14(20): 6462–6468.
- [39] Sun P, You L, Sun Y, et al. Novel Zn-doped SnO<sub>2</sub> hierarchical architectures: synthesis, characterization, and gas sensing properties[J]. *CrystEngComm*, 2012, 14(5): 1701–1708.
- [40] Drake C, Seal S. Band gap energy modifications observed in trivalent In substituted nanocrystalline SnO<sub>2</sub>[J]. *Applied Physics Letters*, 2007, 90(23): 233117.
- [41] Ara M, Wadumesthrige K, Meng T, et al. Effect of microstructure and Sn/C ratio in SnO<sub>2</sub>-graphene nanocomposites for lithium-ion battery performance[J]. *RSC Advances*, 2014, 4(39): 20540–20547.
- [42] Chai X, Shi C, Liu E, et al. Hierarchically structured carbon-coated SnO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> microparticles with enhanced lithium storage performance[J]. *Applied Surface Science*, 2016, 361: 1–10.
- [43] Lian P, Wang J, Cai D, et al. Porous SnO<sub>2</sub>@C/graphene nanocomposite with 3D carbon conductive network as a superior anode material for lithium-ion batteries[J]. *Electrochimica Acta*, 2014, 116: 103–110.
- [44] Xin X, Zhou X, Wu J, et al. Scalable synthesis of TiO<sub>2</sub>/graphene nanostructured composite with high-rate performance for lithium ion batteries[J]. *ACS Nano*, 2012, 6(12): 11035–11043.
- [45] Myung S T, Takahashi N, Komaba S, et al. Nanostructured TiO<sub>2</sub> and

- its application in lithium-ion storage[J]. *Advanced Functional Materials*, 2011, 21(17): 3231-3241.
- [46] Sun P, Sun L Y Y. Novel Zn-doped SnO<sub>2</sub> hierarchical architectures: synthesis, characterization, and gas sensing properties[J]. *CrystEngComm*, 2012, 14(5): 1701-1708.
- [47] Ding S, Chen J S, Qi G, et al. Formation of SnO<sub>2</sub> hollow nanospheres inside mesoporous silica nanoreactors[J]. *Journal of the American Chemical Society*, 2010, 133(1): 21-23.
- [48] Chen J S, Archer L A, Lou X W D. SnO<sub>2</sub> hollow structures and TiO<sub>2</sub> nanosheets for lithium-ion batteries[J]. *Journal of Materials Chemistry*, 2011, 21(27): 9912-9924.
- [49] Wang Z, Luan D, Boey F Y C, et al. Fast formation of SnO<sub>2</sub> nanoboxes with enhanced lithium storage capability[J]. *Journal of the American Chemical Society*, 2011, 133(13): 4738-4741.
- [50] Wang C, Zhou Y, Ge M, et al. Large-scale synthesis of SnO<sub>2</sub> nanosheets with high lithium storage capacity[J]. *Journal of the American Chemical Society*, 2009, 132(1): 46-47.
- [51] Li Z, Zhou Y, Yu T, et al. Unique Zn-doped SnO<sub>2</sub> nano-echinus with excellent electron transport and light harvesting properties as photoanode materials for high performance dye-sensitized solar cell[J]. *CrystEngComm*, 2012, 14(20): 6462-6468.
- [52] Pan Z W, Dai Z R, Wang Z L. Nanobelts of semiconducting oxides[J]. *Science*, 2001, 291(5510): 1947-1949.
- [53] Tian N, Zhou Z Y, Sun S G, et al. Synthesis of tetrahedral platinum nanocrystals with high-index facets and high electro-oxidation activity[J]. *Science*, 2007, 316(5825): 732-735.
- [54] Yang H G, Sun C H, Qiao S Z, et al. Anatase TiO<sub>2</sub> single crystals with a large percentage of reactive facets[J]. *Nature*, 2008, 453(7195): 638-641.
- [55] Han X, Jin M, Xie S, et al. Synthesis of tin dioxide octahedral nanoparticles with exposed high-energy {221} facets and enhanced gas-sensing properties[J]. *Angewandte Chemie*, 2009, 121(48): 9344-9347.
- [56] Chen X, Liu L, Peter Y Y, et al. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals[J]. *Science*, 2011, 331(6018): 746-750.
- [57] Sun Y, Xia Y. Shape-controlled synthesis of gold and silver nanoparticles[J]. *Science*, 2002, 298(5601): 2176-2179.
- [58] Ariga K, Ji Q, McShane M J, et al. Inorganic nanoarchitectonics for biological applications[J]. *Chemistry of Materials*, 2011, 24(5): 728-737.
- [59] Drake C, Seal S. Band gap energy modifications observed in trivalent In substituted nanocrystalline SnO<sub>2</sub>[J]. *Applied Physics Letters*, 2007, 90(23): 233117.
- [60] Dou X, Sabba D, Mathews N. Hydrothermal synthesis of high electron mobility Zn-doped SnO<sub>2</sub> nanoflowers as photoanode material for efficient dye-sensitized solar cells[J]. *Chemistry of Materials*, 2011, 23(17): 3938-3945.
- [61] Wang H, Xi L, Tucek J, et al. Hierarchical assembly of Ti(IV)/Sn(II) co-doped SnO<sub>2</sub> nanosheets along sacrificial titanate nanowires: synthesis, characterization and electrochemical properties[J]. *Nanoscale*, 2013, 5(19): 9101-9109.
- [62] Han S, Jang B, Kim T, et al. Simple synthesis of hollow tin dioxide microspheres and their application to lithium-ion battery anodes[J]. *Advanced Functional Materials*, 2005, 15(11): 1845-1850.
- [63] Lou X W, Wang Y, Yuan C L, et al. Template-free synthesis of SnO<sub>2</sub> hollow nanostructures with high lithium storage capacity[J]. *Advanced Materials*, 2006, 18(17): 2325-2329.
- [64] Yang H G, Zeng H C. Self-construction of hollow SnO<sub>2</sub> octahedra based on two-dimensional aggregation of nanocrystallites[J]. *Angewandte Chemie*, 2004, 116(44): 6056-6059.
- [65] Liu R, Su W, He P, et al. Synthesis of SnO<sub>2</sub>/Sn hybrid hollow spheres as high performance anode materials for lithium ion battery[J]. *Journal of Alloys and Compounds*, 2016, 688: 908-913.
- [66] Zhang D F, Sun L D, Yin J L, et al. Low-temperature fabrication of highly crystalline SnO<sub>2</sub> nanorods[J]. *Advanced Materials*, 2003, 15(12): 1022-1025.
- [67] Maiti A, Rodriguez J A, Law M, et al. SnO<sub>2</sub> nanoribbons as NO<sub>2</sub> sensors: insights from first principles calculations[J]. *Nano Letters*, 2003, 3(8): 1025-1028.
- [68] Göpel W, Schierbaum K D. SnO<sub>2</sub> sensors: current status and future prospects[J]. *Sensors and Actuators B: Chemical*, 1995, 26(1-3): 1-12.
- [69] Xu J Q, Wang D, Qin L P, et al. SnO<sub>2</sub> nanorods and hollow spheres: Controlled synthesis and gas sensing properties[J]. *Sensors and Actuators B: Chemical*, 2009, 137(2): 490-495.
- [70] Prasittichai C, Hupp J T. Surface modification of SnO<sub>2</sub> photoelectrodes in dye-sensitized solar cells: significant improvements in photovoltage via Al<sub>2</sub>O<sub>3</sub> atomic layer deposition[J]. *The Journal of Physical Chemistry Letters*, 2010, 1(10): 1611-1615.
- [71] Snaith H J, Stavrinadis A, Docampo P, et al. Lead-sulphide quantum-dot sensitization of tin oxide based hybrid solar cells[J]. *Solar Energy*, 2011, 85(6): 1283-1290.
- [72] Wada T, Ichitsubo T, Yubuta K, et al. Bulk-nanoporous-silicon negative electrode with extremely high cyclability for lithium-ion batteries prepared using a top-down process[J]. *Nano Letters*, 2014, 14(8): 4505-4510.
- [73] Taberna P L, Mitra S, Poizat P, et al. High rate capabilities Fe<sub>3</sub>O<sub>4</sub>-based Cu nano-architected electrodes for lithium-ion battery applications[J]. *Nature Materials*, 2006, 5(7): 567-573.
- [74] Guo Q, Sun Z, Gao M. Porous V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub>/CNTs composites as high performance cathode materials for lithium-ion batteries[J]. *Journal of Energy Chemistry*, 2013, 22(2): 347-355.
- [75] Du N, Zhang H, Chen J, et al. Metal oxide and sulfide hollow spheres: Layer-by-layer synthesis and their application in lithium-ion battery[J]. *The Journal of Physical Chemistry B*, 2008, 112(47): 14836-14842.
- [76] Haruyama J, Sodeyama K, Han L. Space-charge layer effect at interface between oxide cathode and sulfide electrolyte in all-solid-state lithium-ion battery[J]. *Chemistry of Materials*, 2014, 26(14): 4248-4255.
- [77] Armand M, Tarascon J M. Building better batteries[J]. *Nature*, 2008, 451(7179): 652-657.
- [78] Tarascon J M, Armand M. Issues and challenges facing rechargeable lithium batteries[J]. *Nature*, 2001, 414(6861): 359-367.
- [79] Yue H, Wang S, Yang Z, et al. Ultra-thick porous films of graphene-encapsulated silicon nanoparticles as flexible anodes for lithium ion batteries[J]. *Electrochimica Acta*, 2015, 174: 688-695.
- [80] Liu Y, Liu P, Wu D. Boron-doped, carbon-coated SnO<sub>2</sub>/graphene nanosheets for enhanced lithium storage[J]. *Chemistry - A European Journal*, 2015, 21(14): 5617-5622.
- [81] Li Y, Zhu S, Liu Q, et al. Carbon-coated SnO<sub>2</sub>@C with hierarchically porous structures and graphite layers inside for a high-performance lithium-ion battery[J]. *Journal of Materials Chemistry*, 2012, 22(6): 2766-2773.

- [82] Wang D, Li X, Wang J, et al. Defect-rich crystalline SnO<sub>2</sub> immobilized on graphene nanosheets with enhanced cycle performance for Li ion batteries[J]. *The Journal of Physical Chemistry C*, 2012, 116(42): 22149–22156.
- [83] Zhang X, Zhu H, Guo Z. Design and preparation of CNT@SnO<sub>2</sub> core-shell composites with thin shell and its application for ethanol oxidation[J]. *International Journal of Hydrogen Energy*, 2010, 35(17): 8841–8847.
- [84] Ma C, Weimin Z. Carbon coated SnO<sub>2</sub> nanoparticles anchored on CNT as a superior anode material for lithium-ion batteries[J]. *Nanoscale*, 2016, 8(7): 4121–4126.
- [85] Shuai Chen Y, Yi X, Zhou Y. Branched CNT@SnO<sub>2</sub> nanorods@carbon hierarchical heterostructures for lithium ion batteries with high reversibility and rate capability[J]. *Journal Materials Chemistry A*, 2014, 2(37): 15582–15589.
- [86] Zhang L, Jiang L, Yan H. Mono dispersed SnO<sub>2</sub> nanoparticles on both sides of single layer graphene sheets as anode materials in Li-ion batteries[J]. *Journal of Materials Chemistry*, 2010, 20(26): 5462–5467.
- [87] Wang D, Choi D, Li J, et al. Self-assembled TiO<sub>2</sub>-graphene hybrid nanostructures for enhanced Li-ion insertion[J]. *ACS Nano*, 2009, 3(4): 907–914.
- [88] Yoo E J, Kim J, Hosono E, et al. Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries [J]. *Nano Letters*, 2008, 8(8): 2277–2282.
- [89] Rao C N R, Sood A K, Subrahmanyam K S, et al. Graphene: The new two-dimensional nanomaterial[J]. *Angewandte Chemie International Edition*, 2009, 48(42): 7752–7777.
- [90] Paek S M, Yoo E J, Honma I. Enhanced cyclic performance and lithium storage capacity of SnO<sub>2</sub>/graphene nanoporous electrodes with three-dimensionally delaminated flexible structure[J]. *Nano Letters*, 2008, 9(1): 72–75.
- [91] Wang X, Tabakman S M, Dai H. Atomic layer deposition of metal oxides on pristine and functionalized graphene[J]. *Journal of the American Chemical Society*, 2008, 130(26): 8152–8153.
- [92] Williams G, Seger B, Kamat P V. TiO<sub>2</sub>-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide[J]. *ACS Nano*, 2008, 2(7): 1487–1491.
- [93] Chen Y, Song B, Chen R M, et al. A study of the superior electrochemical performance of 3 nm SnO<sub>2</sub> nanoparticles supported by graphene[J]. *Journal of Materials Chemistry A*, 2014, 2(16): 5688–5695.
- [94] Liu X, Sun Q. An alumina stabilized graphene oxide wrapped SnO<sub>2</sub> hollow sphere LIB anode with improved lithium storage[J]. *RSC Advances*, 2015, 5(122): 100783–100789.
- [95] Bhaskar A, Deepa M. Size-controlled SnO<sub>2</sub> hollow spheres via a template free approach as anodes for lithium ion batteries[J]. *Nanoscale*, 2014, 6(18): 10762–10771.
- [96] Liang J, Yu X Y, Zhou H, et al. Bowl-like SnO<sub>2</sub>@ carbon hollow particles as an advanced anode material for lithium-ion batteries[J]. *Angewandte Chemie International Edition*, 2014, 53(47): 12803–12807.
- [97] Zhu Z, Wang S, Du J, et al. Ultrasmall Sn nanoparticles embedded in nitrogen-doped porous carbon as high-performance anode for lithium-ion batteries[J]. *Nano Letters*, 2013, 14(1): 153–157.
- [98] Dong Y, Zhao Z, Wang Z, et al. Dually fixed SnO<sub>2</sub> nanoparticles on graphene nanosheets by polyaniline coating for superior lithium storage [J]. *ACS Applied Materials & Interfaces*, 2015, 7(4): 2444–2451.
- [99] Li Y, Meng Q, Ma J, et al. Bioinspired Carbon/SnO<sub>2</sub> Composite Anodes Prepared from a Photonic Hierarchical Structure for Lithium Batteries[J]. *ACS Applied Materials & Interfaces*, 2015, 7(21): 11146–11154.
- [100] Wu P, Wang H, Tang Y W, et al. Three-dimensional interconnected network of graphene-wrapped porous silicon spheres: In situ magnetothermal-reduction synthesis and enhanced lithium-storage capabilities[J]. *ACS Applied Materials & Interfaces*, 2014, 6(5): 3546–3552.
- [101] Zhu J, Zhang G H. Graphene double protection strategy to improve the SnO<sub>2</sub> electrode performance anodes for lithium-ion batteries[J]. *Nano Energy*, 2014, 3: 80–87.

## Progress of tin oxide-based anode materials for lithium-ion batteries

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**Abstract** As an N-type semi-conductor, the tin dioxide (SnO<sub>2</sub>) based anode materials have received a great attention due to its high theoretical capacity (782 mA·h/g) and high energy density. However, the poor cycling performance resulting from the electrode pulverization and the electrical disconnection caused by large volume changes (about 300%) during the charge and discharge process and the poor rate properties resulting from the low electrical conductivity of SnO<sub>2</sub> have limited its development. To address these problems, one strategy is to construct various nanostructures, including the nanoparticles, the nanowires, the nanofibers, the nanotubes, the nanosheets and the nanospheres. In addition to the nanosizing SnO<sub>2</sub> particles, the SnO<sub>2</sub> based hybrids as the anode materials for the LIBs have been also studied intensively to enhance the reaction reversibility. This paper mainly reviews the research progress of tin dioxide based anode materials based on the two aspects of nanosizing and preparing SnO<sub>2</sub> based hybrids, including the hybrids with other metal oxides, the amorphous carbon, the carbon nanotubes and the graphene. Finally, we also discuss the existing issues and challenges in the development of SnO<sub>2</sub>-based anode materials for lithium ion batteries.

**Keywords** lithium-ion battery; tin dioxide; anode materials; nanostructure

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