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洋葱碳的制备与应用研究进展

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摘　要: 洋葱碳独特的结构，使其具有优异的物理化学性能。本文首先介绍了洋葱碳的分类和结构，对几种传统的制备方法(包括电弧放电法、等离子体、电子束辐射、化学气相沉积、纳米金刚石真空退火、热解法)的优缺点进行归纳、总结。其次，介绍了近年来发展起来的制备方法。随后，对近年来洋葱碳在锂离子二次电池负极、染料敏化太阳能电池对电极、电化学储氢电极、超级电容器电极、摩擦和磨损、催化领域的应用做一概述。最后，指出了目前洋葱碳在制备和应用方面的不足，对今后的研究做了展望。

关　键　词: 洋葱碳; 制备方法; 应用; 研究进展

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Development on the Preparation and Application of Onion-like Carbon

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Abstract: Due to unique structure, onion-like carbon has excellent physical and chemical properties that brodens the application in carbon and carbon-based composite materials. The classification and the structure of onion-like carbon were firstly introduced. Its advantages and disadvantages of traditional preparation methods, including arc discharge, plasma, electron-beam radiation, chemical vapor deposition, nanodiamond annealing in vacuum, thermolysis, were summarized. Then, some new synthetic methods developed in recent years were also presented. Subsequently, the application of onion-like carbon on anode materials of lithium ion secondary battery, counter electrode materials of dye-sensitized solar cell, electrodes materials of electrochemical hydrogen storage and super capacitor, friction and wear, and catalyst fields was summarized. Finally, deficiencies of preparation and application on onion-like carbon were pointed out and future research were put forward.

Key words: onion-like carbon; preparation methods; application; research progress

洋葱碳(Onion-like Carbon，简称 OLC)，又称为碳纳米洋葱(Carbon Nano-onions，简称 CNOs)，其尺寸大约在 3~50 nm[1]，是继 C_{60}、碳纳米管(Carbon Nano-tubes，简称 CNTs)之后，富勒烯家族的新成员。洋葱碳按其结构一般可分为两类：中空结构的洋葱碳和核壳结构的洋葱碳。理想的具有中空结构的洋葱碳是由同心的球形石墨壳层嵌套而成，如图 1(a)所示，其最内层是一个 C_{60} 分子(由 60 个碳原子组成，其直径约为 0.7 nm)。由内往外，中空结构的洋葱碳每一石墨壳层所含碳原子数为 $60n^2$ (n 代表层数)

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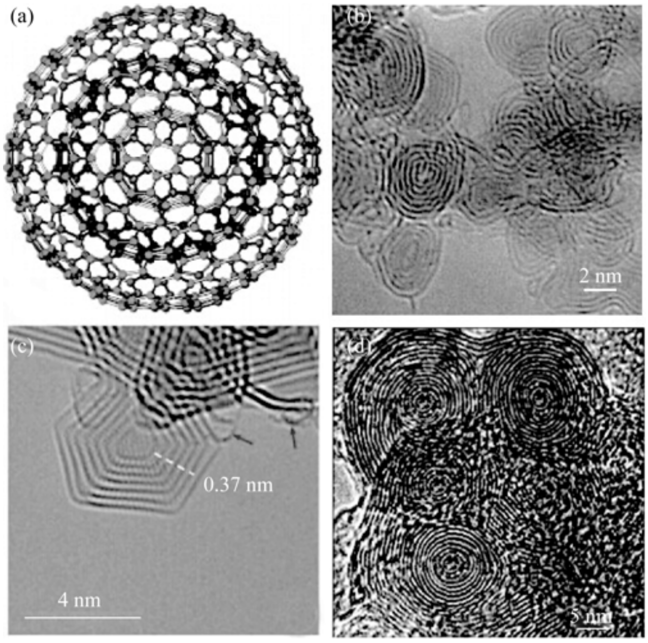

图 1 (a)理想的中空 OLC 的结构模型[7], (b)准球形结构的 OLC[8], (c)多面体结构的 OLC [9]和(d)多核结构的 OLC[10]
Fig. 1 (a) Structure model of ideal hollow OLC[7]with (b) quasi-spherical structure[8], (c) polyhedral structure[9] and (d) multi-core structure[10]

相邻层的间距约为 0.34 nm。核壳结构洋葱碳的核可以是过渡金属粒子[2]、过渡金属氧化物[3-5]和纳米金刚石颗粒[6]等, 其壳由球形的石墨层嵌套而成。洋葱碳通常并不是严格的同心石墨壳层嵌套组成的球形结构, 大部分呈现出准球形结构或多面体结构, 如图 1(b)与(c)所示。在一定条件下, OLC 的外层石墨层会连接在一起, 形成具有多核结构的洋葱碳, 如图 1(d)所示。

洋葱碳和纳米石墨微粒是两个不同的概念。纳米石墨微粒包括中空结构和核壳结构的洋葱碳, 也包括那些壳层排列并不规则, 最内层常常存在尺寸不等空隙的微粒。中空的, 壳层呈不规则形状的纳米石墨微粒, 其尺寸一般大于中空的洋葱碳, 结构和稳定性更趋近于石墨。洋葱碳大的比表面积[11-12]、高的电导率[12]、高的热稳定性以及封闭稳定的结构使其具有较大的应用潜力, 在催化[13]、摩擦[14-16]、锂离子二次电池[17-18]、太阳能电池[19]、电化学储氢[20-21]、超级电容器[22-24]和电磁屏蔽[25]等领域都显示出良好的应用前景。

1 洋葱碳的制备方法

洋葱碳的制备已有 20 多年历史, 制备方法较多, 可分为物理方法和化学方法两类。物理方法主要有电弧放电[26-31]、等离子体[32]、电子束辐射[33]等; 化学方法主要有化学气相沉积法[34-37]、纳米金刚石真空热处理[38-40]、热解法[41]等, 上述制备方法的优缺点, 如表 1 所示。

表 1 OLC 的主要制备方法优缺点比较
Table 1 Advantages and disadvantages of OLC's main preparation methods

Preparation methods	Advantages	Disadvantages
Arc discharge	High crystallization，low defect density carbon onions prepared in bulk quantities using an arc in water	Containing a large amount of carbonaceous impurities such as amorphous carbon, CNTs, CNT-like structures, graphitic debris, and metallic impurities
Plasma	Low cost and prepared in bulk quantities	Containing amorphous carbon and metallic impurities
Electron-beam radiation	*In-situ* observations achieved helpful to study the growth mechanism of OLC	High cost and low yield
Chemical vapor deposition	Simple, cheap, easy to implement and to realize mass production	Purification to remove amorphous carbon, CNTs, graphite, catalyst support, *etc*
Nanodiamond annealing in vacuum	Narrow-sized distribution and produced in massive amount	Requiring nanodiamond precursor and high-temperature vacuum oven
Thermolysis	Massive amount of carbon onions produced at low cost by using simple device	Larger size CNOs and/or purification requirement

激光辐照法也是一种可以快速宏量制备洋葱碳的方法，而且它使用的碳源种类丰富，包括非晶碳化硅[42]、炭黑[43]、石墨[44]、丙酮[45]、乙烯[46]等。最近，Xiao 等[47]发现，用激光辐照纳米金刚石也可以制备出洋葱碳，并且可以实现纳米金刚石–洋葱碳的可逆转换。纳米金刚石向洋葱碳的转变是由于激光诱导的高温造成的；洋葱碳向纳米金刚石的转变是由激光诱导的高温以及高压两方面共同作用的结果。OLC 的制备方法还有碳离子注入法[48]和球磨法[49]等。

但上述制备方法都涉及到以下几个问题：高能消耗；工艺复杂、可控性低；伴有杂质相和产量低。近年来，相继出了一些新的 OLC 制备方法。Han 等[50]通过 $CuCl_2 \cdot 2H_2O$ 和 CaC_2 在 600℃反应生成了高纯度、粒度分布均匀的(大约 30 nm)OLC。Ghosh 等[51]通过先碳化木材废料，再后经浓硝酸处理，制备出水溶性的 OLC。Choucair 等[52]通过燃烧萘制备出克量级的 OLC，制备过程不需催化剂，并且产物无任何杂质。

2　洋葱碳的应用

2.1　OLC 在锂离子二次电池负极材料方面的应用

石墨类碳材料作为锂离子电池的负极材料，目前已实现商业化。但是石墨的理论比容量低(372 mAh/g)，限制了锂离子电池比能量的进一步提高。由于金属氧化物具有高的理论比容量(如表 2)，一些环境友好、制造成本低的金属氧化物已引起研究者的兴趣。在充放电循环过程中负极材料由于体积变化大，电极活性物质会发生破裂和粉碎，导致电池容量衰减，循环性能变差。另外，金属氧化物负极由于电导率低，还存在高倍率下充放电容量低等缺点，限制了其广泛应用。通常采用两种方法解决上述问题[53]：一种方法是合成纳米结构的金属氧化物，包括不同的形貌，如纳米粒子、纳米片、纳米线、纳米棒、纳米管和空心纳米结构。纳米材料可以提供更短的电子和锂离子传输路径，从而提高了电导率和充放电速率。另与块体材料相比，纳米材料能够更好的调节由于嵌锂/脱锂造成的机械应变，从而提高循环稳定性，延长循环寿命；另一种方法就是制备由金属氧化物/碳纳米材料构成的复合材料电极。该复合材料电极能够提供足够的空间调节电极体积在充放电过程中的变化，并保持电极的机械完整性，提高循环的稳定性。Han 等[50]发现 CNOs 的比容量(60 个循环后，其可逆容量为 391 mAh/g)高于传统石墨材料的比容量，并把原因归结为三点：第一，纳米级的洋葱碳能够提供大的电极–电解液接触面积，缩短电子和锂离子的传输路径；第二，洋葱碳的多层结构提供了更多的锂存储位；第三、洋葱碳周围的非晶碳也对提高比容量有贡献，因为无序碳比石墨具有更高的比容量。具有核壳结构的洋葱碳(核为金属氧化物)是一种良好的负极材料，主要是因为金属氧化物被包覆后提高了电极材料的电导率，并且洋葱碳的石墨壳层能够缓冲充放电过程中负极体积的变化。表 3 为几种金属氧化物在有无石墨层包覆情况下的性能比较，可以看出，包覆后的过渡金属氧化物电极的高倍率容量和循环性能大大提高。

表 2　不同金属氧化物的理论比容量

Table 2　Theoretical capacities of various metal oxides

Metal oxides	Theoretical capacity/(mAh • g^{-1})	Ref
SnO_2	782	[54]
CuO	674	[4]
CdO	1046	[55]
Cr_2O_3	1058	[56]
MoO_2	838	[57]
NiO	718	[3]
MnO	755	[58]
MnO_2	1233	[59]
Mn_2O_3	1019	[60]
Fe_2O_3	1007	[60]
Fe_3O_4	926	[61]
CoO	715	[62]
Co_3O_4	890	[5]

2.2　OLC 在染料敏化太阳能电池方面的应用

染料敏化太阳能电池(dye-sensitized solar cell，即 DSSC)具有制作工艺简单、制作成本低、无污染、光电转换效率高等优点，有望替代硅太阳能电池。自 1991，Oregan 制作了第一块染料敏化纳米晶太阳能电池以来，20 多年来广大研究者的研究热情从未间断。

DSSC 中对电极有两个作用：收集从光阳极传输过来的电子，并将 I_3^-还原成 I^-。DSSC 对电极材料必须满足高的导电性、高的比表面积、高的电催化活性和高化学稳定性等要求，因此最常用的对电极材料为铂和碳基材料。铂对电极的转化效率较高，但其价格昂贵，增加了制造成本。OLC 作为碳基材料之一，也是性能良好的对电极材料。图 2 为在同等测试条件下，分别以铂和 CNOs 为对电极的相同结构 DSSC 的光电流–光电压曲线图，可以看出 CNOs 对电极的性能与 Pt 对电极相当。二者的光电

表 3　金属氧化物负极材料性能比较

Table 3 Performance comparison of metal oxides used as anode materials

Anode materials	OLC encapsulation	Initial discharge ability of nanoparticles electrode at different rates	Cycle performance	Ref
NiO	No	NiO, 2*C*, 558.8 mAh/g	0.5*C*, 1150 mAh/g (initial discharge) and 383.5 mAh/g (after 50 cycles)	[3]
	Yes	NiO/C, 2*C*, 1105.6 mAh/g	0.5*C*, 1689.4 mAh/g (initial discharge) and 1157.7 mAh/g (after 50 cycles)	
CuO	No	CuO, 1.2*C*, 178.9 mAh/g	100 mA/g , 270.2 mAh/g (after 50 cycles)	[4]
	Yes	CuO/C, 1.2*C*, 535.6 mAh/g	100 mA/g, 628.7 mAh/g (after 50 cycles) with a high Coulombic efficiency of 98.6%	
Co_3O_4	No	Co_3O_4, 2*C*, 459 mAh/g	1248.8 mAh/g (initial discharge) and 471.5 mAh/g (after 50 cycles)	[5]
	Yes	Co_3O_4/C, 2*C*, 925 mAh/g	0.5*C*, 1467.6 mAh/g (initial discharge) and 1026.9 mAh/g (after 50 cycles)	
SnO_2	No	/	0.2 mA/cm^2, 849 mAh/g (initial discharge) to 123 mAh/g (after 50 cycles)	[63]
	Yes	/	0.2 mA/cm^2, 755 mAh/g(initial discharge) and 446 mAh/g (after 50 cycles)	

转换效率接近，并且以 CNOs 为对电极的 DSSC 的填充因子大于 Pt 对电极电池。

2.3　OLC 在电化学储氢方面的应用

OLC 具有高的比表面积和电导率，是碳质储氢材料的重要成员之一。碳质储氢材料的储氢容量与比表面积有关，理论储氢容量可以通过公式 mads≈*S*spec×2.27×10^{-3}wt%估算求得[64]。Zhang 等[20]在 850℃下，以铁镍合金为催化剂，用 CVD 方法制备 OLC，再经过 1100℃高温退火，制备了中空的 OLC，然后制作成电极，在室温下进行电化学储氢性能测试，发现 OLC 电极具有优异的电化学活性和放电容量。在 500 mA/g 的电流密度下，首次充放电循环达到最大放电容量约 590 mAh/g；经过 10 次充放电循环，放电容量保持在 481.6 mAh/g 以上(对应储氢容量为 1.76wt%)；经过 55 次循环，电极仍然保持稳定，容量保持率仍超过 80%。在高温退火过程中，金属颗粒从具有核壳结构的 OLC 中游离出来，导致 OLC 表面形成开口缺陷，所以中空 OLC 具有较高放电容量。氢分子可以通过这些开口缺陷扩散到 OLC 的内部中空部分，大大增加了吸附氢分子的表面积。Zhang 等[21]还利用 CVD 方法制备了三种核壳结构的 CNOs，即 Ni@CNOs、$Fe_{0.64}Ni_{0.36}$@CNOs 和 Fe_3C@CNOs，并在室温下进行了电化学储氢性能测试(如图 3 所示)。结果表明：Ni@CNOs 的储氢容量最大(1.42wt%)，这主要是由于 Ni@CNOs 中存在大量的缺陷，且 Ni 粒子具有高的电导率和电催化活

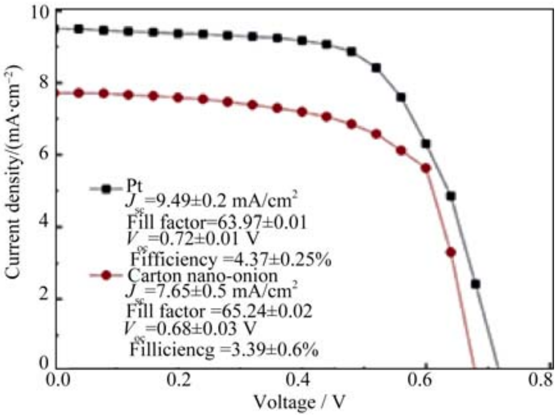

图 2　用 Pt 和 CNOs 做对电极的 DSSCs 的光电流密度-光电压曲线[19]

Fig. 2　Photocurrent density-photovoltage of the fabricated DSSCs using Pt and CNOs counter electrodes[19]

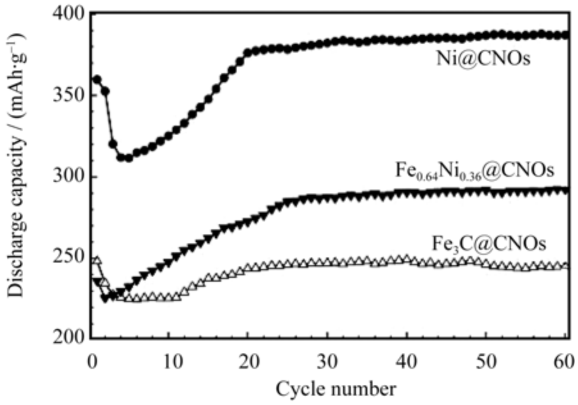

图 3　室温下，充放电电流密度为 500 mA/g 时三种电极的放电容量随循环次数的变化[21]

Fig. 3　Discharge capcity of the three types of CNOs versus cycle number at a charge-discharge current density of 500 mA/g at room temperature[21]

性；Fe_3C@CNOs 的储氢容量最小(0.91wt%))，这主要是由于 Fe_3C 电导率低导致 Fe_3C@CNOs 电化学性能较差。

2.4　OLC 在超级电容器电极材料方面的应用

碳材料超级电容器电极的比电容低、能量密度低，如何提高碳材料的比电容、能量密度，是解决问题的关键。作为碳材料的一员，OLC 电极比电容也较低，约 30~40 F/g。提高 OLC 比电容主要有两条途径。第一条途径是提高 OLC 的比表面积，可以通过在制备过程中控制温度[65]或后期的化学活化作用实现。Gao 等[66]通过 KOH 化学活化作用，得到多孔 OLC，提高了比电容和能量密度。同等测试条件下，未活化 OLC 电极的比电容、功率密度、能量密度分别为 25.8 F/g、123 kW/kg、1.5 Wh/kg；活化后多孔 OLC 电极的比电容、功率密度、能量密度分别为 122 F/g、153 kW/kg、8.5 Wh/kg。性能提高主要是由于化学活化提高了 OLC 的比表面积，但活化后的 OLC 在后期的冲洗、超声和过滤过程中，会损失大量原材料。第二条途径是制备 OLC 基复合材料电极，包括过 OLC/过渡金属氧化物电极和 OLC/导电聚合物电极等。Anjos 等[67]测试了 PQ/OLC 复合材料电极性能，发现其能量密度最高可以达到 4.5 Wh/kg，大约是 OLC 电极的 9 倍；比电容最高可以达到 264 F/g，在恒电流密度 1.3 A/g 下，经过 10000 次充放电循环，比电容保持率仍较高。表 3 为不同方法活化的 OLC 电极和 CNOs 复合材料电极的比电容。

表 3　CNOs 电极和 CNOs 基复合材料电极的比电容

Table 3　Specific capacitances of various CNOs and CNOs-based composite electrode

Types of materials	Specific capacitances/(F・g^{-1})	Ref
CNOs	30	[67]
CNOs/KOH activation	<122	[66]
CNOs/H_2SO_4 activation	20–40	[68]
CNOs/RuO_2・xH_2O	96–334	[69]
CNOs/NiO	218.2–290.6	[70]
CNOs/Ni(OH)2	727.4–1225.2	[70]
CNOs/MnO2	177.5	[71]
CNOs/PDDA	20–30	[72]
CNOs/chit	20–30	[72]
CNOs/PANI	<525	[73]
CNOs/PQ	267	[67]
CNOs/NQ	91	[67]
CNOs/PY	130	[67]

2.5　OLC 在磨擦磨损领域的研究与应用

碳基润滑剂(石墨、石墨烯、碳纳米管、类金刚石等)表现出优异的耐磨擦磨损性能，OLC 有望成为性能更加优异的固体润滑剂，这是由于 OLC 约 10 nm 的准球形结构，有可能在纳米尺寸范围内起“微轴承”作用；碳原子排列完美，表面没有悬挂键，OLC 和偶件材料只可能存在弱的分子间键合；稳定的封闭结构使其具有高的机械强度。

Hirata 等[74]通过用钢球和硅片做球盘摩擦磨损试验，测试了 OLC 的固体润滑性能，研究表明：(1) 室温下，OLC 在空气和真空中都显示出较稳定的低摩擦系数(<0.1)，摩擦系数低于同等测试条件下石墨、$C_{60/70}$ 和金刚石团簇的摩擦系数。(2)小尺寸的 OLC 比大尺寸的 OLC 具有更加优异的耐摩擦性能，这主要是由于大尺寸的 OLC 最外层有更多的缺陷，会与偶件材料发生键合，从而造成较大的摩擦系数和较多的磨损量。

Bucholz 等[75]通过原子分子动力学仿真研究了 OLC 的摩擦机理。结果表明，摩擦性能主要由 OLC 纳米颗粒滚动和滑动所占的比例决定。滚动摩擦变为滑动摩擦时，摩擦系数会有一个数量级的增长(由 0.024 增大到 0.151)，而在摩擦过程中，OLC 滚动和滑动的相对比例与界面键的形成有关。

2.6　OLC 在催化方面的应用

阴极氧还原反应动力学缓慢严重制约了燃料电池性能的提高。纳米结构的原子掺杂碳材料能够提高电催化活性和降低成本，有望取代传统的 Pt 或 Pt 基电极。常见的掺杂原子有 N、S、P 和 B 等。比表面积大，且具有多孔结构的共掺杂碳材料在氧还原反应中具有高的活性。Han 等[76]通过一步法合成了氮、硫共掺杂介孔洋葱碳(NS-MCV)，证实其在氧还原反应中具有较高的电催化活性，和商用 Pt/C 催化剂相比，NS-MCV 具有更好的稳定性和耐受性。

Lin 等[8]研究发现氮掺杂的洋葱碳(N-OLC)在苯乙烯的环氧化反应中显示出良好的催化性能，其催化性能优于未掺杂的洋葱碳和一些金属催化剂。N-OLC 制备方法如图 4 所示，纳米金刚石在氩气氛围中经 1300℃退火 4 h 得到洋葱碳；然后将 OLC 放入 120℃的硝酸中，持续搅拌 2 h，所得产物经过过滤、清洗和烘干，得到氧掺杂的 OLC(O-OLC)；最后，在氨气氛中，O-OLC 在不同温度下退火 4h 得到 N-OLC。

OLC 除了在上述领域有着广泛应用外，还可作为制备纳米栾晶金刚石和聚晶金刚石的前驱物。

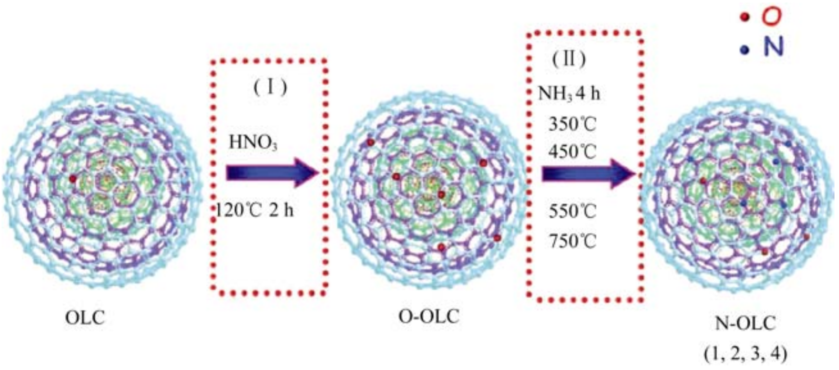

图 4 N-OLC 制备示意图[24]

Fig. 4 Schematic illustration for fabrication N-OLC[24]

Huang 等[77]以 OLC 为前驱物，在高温高压下制备出纳米栾晶金刚石，其硬度高达 200 GPa，超过了天然金刚石。Gong[78]和 Yu[79]以洋葱碳为前驱物，在高温高压下制备出了无添加剂的聚晶金刚石，其硬度最高可达 55.9 GPa。

3 结束语

经过多年的研究，人们已经掌握了多种 OLC 的制备方法并对其生长机理有了一定的认识，并且在应用方面有了一定尝试，显示出其优异的性能，但是仍然存在一些不足:

1) 目前比较成熟的 OLC 的制备方法都存在成本高、产量低和含有杂质等缺点。快速、简单、低成本和宏量制备 OLC 以及 OLC 的纯化仍然是以后的研究重点。

2) OLC 的曲率半径、比表面积、晶化程度与制备方法、制备条件密切相关，而曲率半径、比表面积、晶化程度等因素又影响着 OLC 的理化性能，所以在微观上实现 OLC 的可控生长，精确控制 OLC 的石墨壳层数、比表面积和晶化程度，具有重要意义。

3) OLC 的应用研究才刚刚起步，仍需要开展大量的基础研究。优化过渡金属氧化物/OLC 复合材料电极的制备参数，进一步提高锂离子二次电池的比容量、高倍率性能以及循环稳定性能；研究 OLC 比表面积、多孔结构、晶化程度对 OLC 对电极性能的影响，进一步提高 OLC 对电极的性能；研究 OLC 比表面积、多孔结构对储氢容量的影响，通过在 OLC 的表面引入官能团或者掺杂提高氢气和 OLC 的表面结合能，从而提高储氢容量；优化 OLC 基复合材料电极的性能，提高超级电容器的比电容和能量密度；研究不同的元素掺杂以及共掺杂对 OLC 催化性能的影响等。

OLC 的结构、表面功能化以及掺杂对其性能有重要影响，理清它们之间的关系，优化 OLC 基器件的性能，可以推进 OLC 在能源等诸多领域的应用。

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