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Electrochemical Applications of Single-walled Carbon Nanohorns

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单壁碳纳米角电化学应用

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摘要：单壁碳纳米角具有独特的性质,如大的比表面积、良好的导电性和生物相容性等,在某些领域应用广泛. 本文结合作者课题组工作,综述了单壁碳纳米角电化学应用现状,并展望其今后的发展趋势.

关键词：单壁碳纳米角;电化学;综述

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1999 年 Iijima 研究组[1]在氩气氛围下用激光烧蚀石墨法制得一端呈封闭的锥形(锥角约 20°),而其余部分系与碳纳米管类似的石墨管状 (管内径为 2 ~ 5 nm,管长为 30 ~ 50 nm)的单壁碳纳米角(SWCNHs),约 2000 根 SWCNHs 聚集于一起形成直径约 80 ~ 100 nm 大丽花状的 SWCNHs 聚集体, 如图 1 所示. 无金属催化剂就可制得 SWCNHs,可避免金属杂质带来的干扰. 其特殊的几何构型决定了其力学、化学和电子性质,如高比表面积、热稳定性、优良的导电性质,使其在吸附和存储气体[2-3]、催化剂载体[4]、药物载体[5]、气体传感器[6]、生物传感器[7-8]和电化学储能[9]等方面具有广泛的应用.

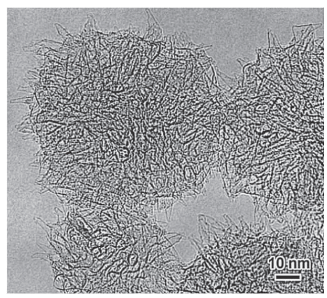

图 1 大丽花状 SWCNHs 聚集体的透射电镜照片[1]
Fig. 1 TEM image of dahlia-like SWCNHs[1]

本文结合作者课题组工作, 综述 SWCNHs 在电化学分析和电化学能源等的应用现状并展望其今后的发展趋势.

1 电化学应用

近年,SWCNHs 主要在电催化、电化学分析、锂离子电池材料、电化学电容器以及燃料电池中金属纳米颗粒的催化载体等有重要应用.

1.1 SWCNHs 糊电极

2001 年, 碳糊电极首次应用于研究有机物质在电极上的反应机理[10]. 随着研究的深入,因碳糊电极制备简单等优点[11],碳糊修饰电极已大量应用于电化学分析[12]及生物传感器领域[13]. 碳纳米管 (CNTs) 的出现拓宽了碳糊电极的应用范围. 同时 CNTs 糊电极显现了对抗坏血酸、尿酸、多巴胺、3,4-二羟基苯乙酸(DOPAC)及过氧化氢等有良好电催化活化作用[14-17].

为改善性能, 作者课题组制作 SWCNHs 糊电极[18],经活化处理提高检测 H_2O_2 的灵敏度和线性范围. 与石墨糊电极及多壁 CNTs 电极相比, 其线性范围更宽 (0.5 ~ 100 $mmol \cdot L^{-1}$). SWCNHs 的电化学活化可形成大量的缺陷, 其边缘部分的含氧官能团更利于高浓度 H_2O_2 的检测. 其大丽花状的

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聚集体提高了目标分析物接触的活性位点，呈现了良好的 H_2O_2 电化学性能，有望替代常用铂电极用于 H_2O_2 检测，特别是高浓度 H_2O_2 检测. SWCNHs 制备过程不使用金属催化剂，故 SWCNHs 不含金属杂质，对 H_2O_2 的电催化活性主要源于 SWCNHs.

1.2 SWCNHs 修饰电极

1)固相萃取吸附剂

SWCNHs 作为固相萃取吸附剂，结合电化学法可快速、灵敏检测 4-硝基苯酚. 与多壁碳纳米管(MWCNTs)修饰电极相比，该电极检测目标物 4-硝基苯酚的灵敏度提高 5.6 倍[19].

2)苯二酚的异构体的检测

作者课题组应用 SWCNHs 修饰电极检测苯二酚的三种同分异构体(对苯二酚、儿茶酚和间苯二酚)[20]. 这三种苯二酚的同分异构体分布广泛，难以降解. 邻、间、对苯二酚异构体的氧化电位在 SWCNHs 修饰电极上得以分离，并可实现同时检测. 且在另两种苯二酚异构体存在下，其单一种苯二酚异构体的氧化电流仍随其浓度增加而线性增长.

3)尿酸、多巴胺及抗坏血酸的检测

作者课题组研究表明，SWCNHs 修饰电极对尿酸(UA)、多巴胺(DA)和抗坏血酸(AA)有很好的电催化活性[21]. 三者扫描伏安曲线氧化还原电位在该电极上均明显负移，氧化还原电流峰增大，且可同时检测到. 有意思的是，UA 在一般电极上的氧化是不可逆的，而在 SWCNHs 修饰电极上的氧化还原峰是可逆的. 且 SWCNHs 修饰电极对 UA 具有很高的灵敏度，检测限较文献报道值低 1～2 个数量级(图 2).

Zhu 等[22]应用类似方法，快速直接定量地检测 L-色氨酸(Trp)和 L-酪氨酸(Tyr)，SWCNHs 修饰电极对 Trp 和 Tyr 有很好的电催化氧化活性. Trp 和 Tyr 检测限分别达到 50 和 400 nmol·L^{-1}. 有望直接应用于血清实样的 Trp 和 Tyr 检测. Xu 等[23]也应用 SWCNHs 修饰电极检测双酚 A.

1.3 电化学生物传感器

SWCNHs 溶解度系亟需解决的实际问题. 文献曾报道 SWCNHs 功能化主要有共价修饰和非共价修饰法. 这两种方法均可提高 SWCNHs 溶解度，以满足不同检测需要. 作者课题组[7]采用聚苯乙烯磺酸钠非共价修饰 SWCNHs. 功能化 SWCNHs 能吸附肌红蛋白，用以构建检测 H_2O_2 电化学生物传感器，呈现出良好的电催化活性. 响应线性范围和检测限分别为 3～350 μmol·L^{-1} 和 0.5 μmol·L^{-1}. 此外，Yang 等[24]应用 SWCNHs 纳米材料信号标记三明治型双酶生物催化构建电化学免疫传感器，提高癌症生物标志物的检测灵敏度. Zhang 等[25]提出快速检测微囊藻毒素-LR 的电化学免疫传感器. Liu 等[26]还应用 SWCNHs-空心 Pt 纳米球信号标记构建了检测降钙素原的新型电化学免疫传感器. Qian 组[27]和 Dai 组[28]等亦报道了相关的研究. SWCNHs 的高比表面积及良好的电催化性能使得该类传感器表现出对目标分析物良好的灵敏度.

作者课题组还首次构建了 SWCNHs 的葡萄糖电化学生物传感器[29]. 将葡萄糖氧化酶固定于

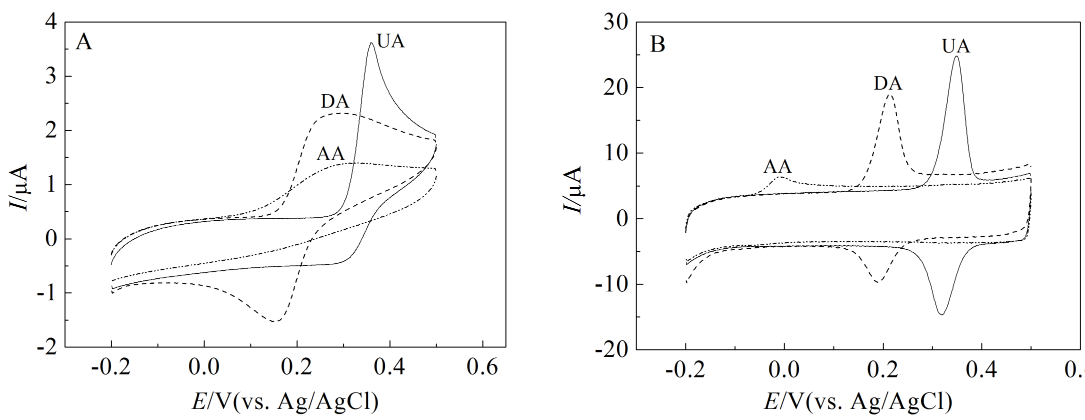

图 2 玻碳电极(A)和 SWCNHs 修饰电极(B)在 0.1 mol·L^{-1} 磷酸缓冲 pH 7.0 溶液中尿酸(UA，100 μmol·L^{-1})、多巴胺(DA，100 μmol·L^{-1})和抗坏血酸(AA，100 μmol·L^{-1})的循环伏安曲线，扫速 50 mV·s^{-1}[21]

Fig. 2 CVs of uric acid (UA, 100 μmol·L^{-1}), dopamine (DA, 100 μmol·L^{-1}), and ascorbic acid (AA, 100 μmol·L^{-1}) at bare GCE (A) and SWCNHs-modified GCE (B) in 0.1 mol·L^{-1} pH 7.0 PBS, scan rate: 50 mV·s^{-1}[21]

Nafion-SWCNHs 复合材料中,在缓冲溶液条件下,其呈现良好的电催化活性. 另外,还可将大豆过氧化物酶固定于 SWCNHs,实现大豆过氧化物酶的直接电子转移,构建了无媒介体的 H_2O_2 生物传感器[8].

1.4 新能源电池

Xu 等[30]构建纳米介孔锐钛矿 TiO_2/SWCNHs 复合材料,应用于锂离子电池. Zhao 等[31]通过简单水热合成锂离子电池 Fe_2O_3/SWCNHs 复合材料,该材料在高电流密度下显示出良好的循环稳定性. 另外,他们还合成了锂离子电池 SnO_2/SWCNHs 复合材料[32]. Aissa 等[33]应用 SWCNHs 包覆微纤维构筑电化学电源独立电极.

SWCNHs 还可应用于燃料电池中的电催化载体[34-37]或基底材料[38],用于增强聚合物电解质膜燃料电池的性能. SWCNHs 作为金属纳米颗粒催化载体[39],较传统炭黑性能更佳. Dong 组应用 SWCNHs 作为氧化还原中介及电催化载体构建生物燃料电池[40],该葡萄糖/O_2 生物燃料电池在生理条件下具有良好的性能.

1.5 电化学电容器

Yuge 等构建了电化学电容电极[41-42],该电极的比电容达到 100 $F·g^{-1}$. Izadi-Najafabadi 等[43]合成 SWCNHs/SWCNTs(80%/20%,by mass)复合材料用于高功率超级电容器电极. 该新型复合电极具有较高的中-大孔体积,可容纳更多电解液,确保离子传输,从而实现更高的功率.

2 展 望

单壁碳纳米角特殊的结构决定了该材料具有独特的性能,使其广泛应用于电化学的诸多领域如电化学分析、生物传感器、锂离子电池、燃料电池和太阳能电池[44]等. 但单壁碳纳米角在电化学领域的应用仍处于起步阶段,今后还需不断地探索和拓宽.

SWCNHs 在电化学领域的研究和应用可能在以下几个方面展开:①开发 SWCNHs 自身的催化性能,拓宽其在电催化和电化学分析的应用范围;②发挥 SWCNHs 吸附能力强的优点,通过富集提高分析的灵敏度或作为新型载体;③制备各种 SWCNHs 复合材料,开发 SWCNHs 复合材料电化学新应用.

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Electrochemical Applications of Single-walled Carbon Nanohorns

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Abstract: Single-wall carbon nanohorns (SWCNHs) have unique properties, such as a large specific surface area, good electrical conductivity and biocompatibility. It has been widely utilized in many fields. In the present review, the progress in electrochemistry study of SWCNHs electrochemistry study has been summarized and the future research trends have been proposed.

Key words: single-walled carbon nanohorns; electrochemistry; review