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The Electrocatalytic Performance of Pd Catalysts Supported on PVP Modified MWCNTs for Formic Acid Oxidation

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Pd/PVP-MWCNTs 电极对甲酸氧化的电催化性能

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摘要: 用聚乙烯吡咯烷酮(PVP)修饰的多壁碳纳米管(MWCNTs)作为 Pd 纳米粒子的载体,制得了 Pd/PVP-MWCNTs 催化剂,并研究了其对甲酸氧化的电催化性能. 红外光谱仪(FTIR)和透射电镜(TEM)观测结果表明,Pd/PVP-MWCNTs 催化剂中的 Pd 纳米粒子平均粒径小、分散性好. 因此,Pd/PVP-MWCNTs 催化剂对甲酸电氧化有很好的电催化性能.

关键词: 聚乙烯吡咯烷酮; 多壁碳纳米管; Pd 催化剂; 直接甲酸燃料电池
中图分类号: O646.542 **文献标识码:** A

近年来,直接甲酸燃料电池(Direct Formic Acid Fuel Cell,DFAFC)作为一种新型的液相质子交换膜燃料电池备受关注. 在几种常见的质子交换膜燃料(CH_3OH, HCHO, HCOOH, H_2)电池中,DFAFC 具有很多优点:具有高的理论电压(25 ℃, 1.48 V)[1-3];甲酸只有 1 个碳原子,没有 C—C 键,易于氧化;毒性很小,环境友好;燃料资源丰富;不易燃烧,存储和运输安全方便;质子交换膜的甲酸透过率很低,可采用高浓度的甲酸溶液以提高电池的比能量密度. 上述优点使 DFAFC 有望成为未来重要的便携式电源.

甲酸电催化氧化机理广泛接受的是"双途径机理"[4-7]. 第一种途径不产生毒性中间体,甲酸迅速地被氧化为 CO_2(直接途径);第二种途径可产生化学吸附的中间产物,且进一步氧化(间接途径). 直接途径反应活化能较低,在反应速率上更有优势. 某些研究[8-9]表明,甲酸在 Pd 电极上的电氧化过程主要以直接途径进行. Masel 等[10-12]报道,Pd 作为甲酸的电氧化催化剂不论是在电化学体系还是在电池中均比 Pt 有更高的活性. 目前,针对 Pd 基 DFAFC 的基础研究主要集中于甲酸在 Pd 表面的电氧化过程,尤其 Pd 电化学过程的失活机理[13-14]. 另外是制备高活性的 Pd 基催化剂[15-18]及开发新型 Pd 基催化体系,如 Pd-Pt[19-21]、Pd-Sb[22-23]和 Pd-Sn[24]等二元金属催化剂.

碳纳米管(Carbon Nanotubes, CNTs)具有独特的微观结构、优异的导电性和较高的稳定性,可作为贵金属催化剂的载体[25]. CNTs 的表面属化学惰性,通过化学修饰可增加活性位点,促进金属纳米粒子的固定. 最常用的化学修饰是强酸氧化处理[26],氧化处理后的 CNTs 表面具有丰富的含氧性官能团,同时也不可避免地产生大量缺陷,削弱了 CNTs 的导电性和抗腐蚀性. 传统的浸渍合成法简单快速,已广泛地应用于金属纳米粒子的合成. 但常规的浸渍法难于控制纳米粒子大小和粒径分布,纳米粒子在载体上会发生聚集,故需加入各种保护剂或稳定剂(如表面活性剂和高分子聚合物)以制备粒径可控和单一分散的金属纳米粒子.

聚乙烯吡咯烷酮(N-vinyl-2-pyrrolidone, PVP)作为功能性分子用于合成粒径均匀的 Pd 纳米粒子[27],可以防止纳米粒子的聚集,同时 PVP 会附着在 Pd 催化剂表面,阻碍反应物到达 Pd 的催化活性位点,所以合成催化剂之后需煅烧以除去多余的 PVP,然而煅烧过程又会促使纳米粒子聚集[28]. 为此,本文先用 PVP 功能化处理多壁碳纳米管(Multi Wall Carbon Nanotubes, MWCNTs),再

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国家高技术研究发展计划(No. 2007AA05Z159, No. 2007AA05Z143),国家自然科学基金项目(No. 20876153, No. 20703043, No. 21073180, No. 20933004, No. 21011130027)和吉林省科技研究项目(No. 20102204)资助

用浸渍还原法负载 Pd 纳米粒子制得 Pd/PVP-MWCNTs 催化剂,并研究该电极的电催化性能. 这样既能保持 CNTs 结构上的优点,又可提供活性位点促进 Pd 纳米粒子在 MWCNTs 表面的分散和固定.

1　实　验

1.1　试剂和仪器

聚乙烯吡咯烷酮(PVP),H_2PdCl_4 溶液(5.0 mg Pd · mL^{-1}),Nafion 溶液(5%,by mass,DuPont 公司),多壁碳纳米管(MWCNTs,20 ~ 40 nm).

美国 Model 273A 电化学工作站(Princeton Applied Research),傅里叶变换红外(FTIR)光谱仪. 透射电子显微镜(TEM),操作电压 200 kV.

1.2　碳纳米管功能化处理

100 mg MWCNTs 浸泡于 200 mL 0.5% (by mass) PVP 水溶液中,超声分散 1 h,搅拌 12 h 后过滤、干燥,即得 PVP-MWCNTs.

1.3　催化剂制备

Pd/PVP-MWCNTs:将 30 mg PVP-MWCNTs 加入 100 mL 去离子水中,超声搅拌 0.5 h,加入 1.5 mL H_2PdCl_4 溶液,用氨水调节 pH 值为 9,机械搅拌 2 h,再滴加 20 mL 硼氢化钠水溶液(1 mg · mL^{-1}),使 H_2PdCl_4 还原为 Pd 纳米粒子. 再继续搅拌 1 h,过滤,洗涤,在干燥箱中 80 ℃烘干即得 Pd/PVP-MWCNTs(20%,by mass).

Pd/MWCNTs:将未处理的 MWCNTs 载体按上述方法制得.

1.4　电化学测试

玻碳基底(ϕ = 3 cm)依次用 0.5 和 0.03 μm 的 Al_2O_3 粉末抛光至镜面,蒸馏水超声洗涤. 将 5 mg 催化剂、950 μL 乙醇和 50 μL Nafion 溶液混合,超声分散 30 min. 然后将 5 μL 该悬浊液滴于玻碳基底上,室温下干燥 30 min 即得工作电极. 由工作电极、光滑 Pt 片对电极、Ag/AgCl 参比电极和电解液组成三电极体系. 通过循环伏安法(扫速 20 mV · s^{-1})和计时电流法(恒定电位 0.2 V,时间 3600 s)考察电极的电催化活性和稳定性,测试前体系通高纯 N_2 气 20 min 除氧.

2　结果与讨论

2.1　红外光谱分析

图 1 示出未处理 MWCNTs、PVP 功能化 MWCNTs 和 PVP 样品的 FTIR 谱图. 从红外谱图中可以看出,PVP-MWCNTs 样品在 1651、1419 和 1279 cm^{-1} 处呈现 PVP 的红外特征峰. PVP 包裹 MWCNTs 后,其相应的红外特征峰较纯 PVP 的红外吸收峰位有微小红移,表明碳管与 PVP 不是简单的物理共混,与文献报道一致[29-30]. 通常,PVP 和碳纳米管结合是用聚合物包裹(Polymer Wrapping). Smalley 认为其热力学驱动力源于消除碳纳米管与水媒介间的疏水界面[29],MWCNTs 与 PVP 相互作用方式可能是疏水相互作用. 未处理的 MWCNTs 未呈现 PVP 特征峰及酸处理后的羟基和羰基峰,由此证明 PVP 处理确实能够有效地功能化 MWCNTs. 另外,合成过程发现,PVP 处理的 MWCNTs 可均匀分散于去离子水中,而未处理的 MWCNTs 分散性较差. 这也表明 PVP 已功能化 MWCNTs,使其在极性溶剂中不易聚集.

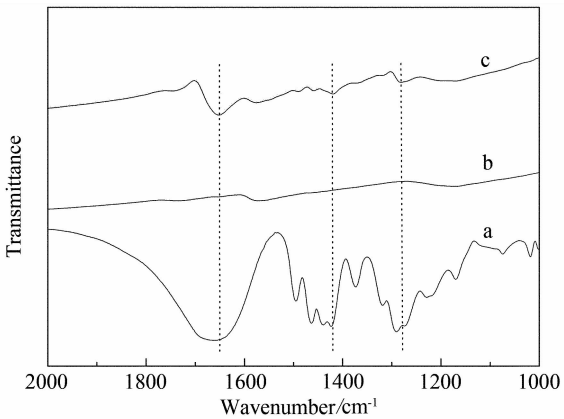

图 1　PVP(a)、MWCNTs(b)和 PVP-MWCNTs(c)样品的 FTIR 谱图

Fig. 1　FTIR spectra of PVP(a), MWCNTs(b) and PVP-MWCNTs(c)

2.2　TEM 分析

图 2 为 Pd/PVP-MWCNTs 和 Pd/MWCNTs 样品的 TEM 照片. 从图可以看出,Pd/PVP-MWCNTs 样品的 Pd 纳米粒子均匀地分散于 MWCNTs 表面,且粒径较均一. 而 Pd/MWCNTs 样品的 Pd 纳米粒子发生聚集,粒径增大. PVP 修饰的 MWCNTs 不仅促进了 MWCNTs 在去离子水中的分散,同时在 MWCNTs 上可引入锚定位点以促进 Pd 纳米粒子的吸附与固定[28],使 Pd 纳米粒子能以很小的粒径均匀分散于 MWCNTs 表面.

2.3　电化学测试

图3给出Pd/MWCNTs和Pd/PVP-MWCNTs电

极在 0.5 mol · L^{-1} H_2SO_4 溶液中的氢吸脱附曲线. 从图 3 看出,两电极都显示出 Pd 的典型氢吸脱附行为,在 -0.2 ~ 0.1 V 电位区有两对氢吸脱峰,分别对应于氢的强吸附和弱吸附. 但两个电极氢吸脱附峰的面积和电位却有差异. 与 Pd/MWCNTs 相比,Pd/PVP-MWCNTs 有着更大的氢吸脱附峰面积,即有更大的电化学活性[16,28]. 这与其 TEM 结果一致,均一、细小粒径的 Pd/PVP-MWCNTs 电极有更大的比表面积,使得氢脱附电位负移,这可归因于尺寸效应所产生的不同表面电子状态[31-32].

图 4 给出 Pd/PVP-MWCNTs 和 Pd/MWCNTs 电极在 0.5 mol · L^{-1} H_2SO_4 + 0.5 mol · L^{-1} HCOOH 溶液中的循环伏安曲线. 从图 4 可以看出,甲酸在 Pd/PVP-MWCNTs 电极上氧化峰电位为 0.263 V,较Pd/MWCNTs电极氧化峰值(0.306 V)负. 这表明甲酸在 Pd/PVP-MWCNTs 电极上更易氧化. 两电极的峰电流密度分别为 1517 和 968 mA · mg^{-1}(Pd). 在 0.2 V 的电位下,Pd/PVP-MWCNTs 电极的甲酸氧化电流密度是 Pd/MWCNTs 电极的 1.5 倍.

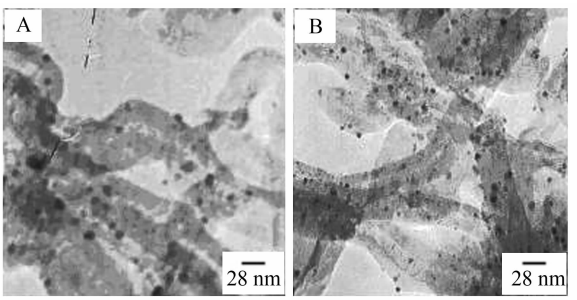

图 2 Pd/MWCNTs 样品(A)和 Pd/PVP-MWCNTs 样品(B)的 TEM 照片

Fig. 2 TEM images of Pd/MWCNTs (A) and Pd/PVP-MWCNTs (B)

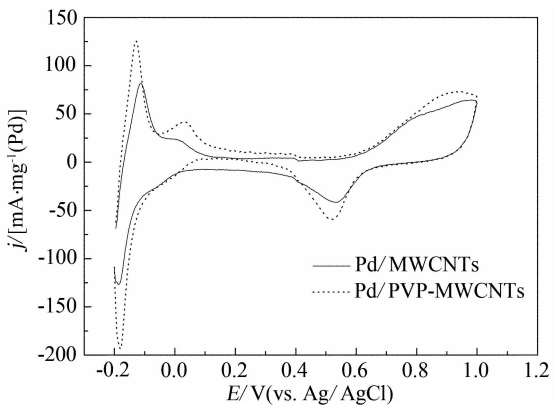

图 3 Pd/MWCNTs 和 Pd/PVP-MWCNTs 电极在 0.5 mol · L^{-1} H_2SO_4 溶液中的循环伏安曲线(扫速 20 mV · s^{-1})

Fig. 3 CV curves of Pd/MWCNTs and Pd/PVP-MWCNTs electrodes in 0.5 mol · L^{-1} H_2SO_4 solution with a scan rate of 20 mV · s^{-1}

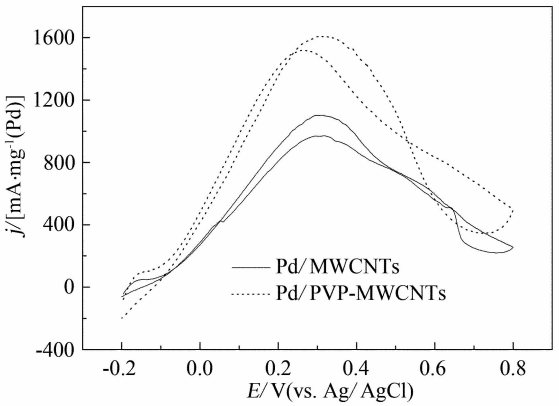

图 4 Pd/MWCNTs 和 Pd/PVP-MWCNTs 电极在 0.5 mol · L^{-1} H_2SO_4 + 0.5 mol · L^{-1} HCOOH 溶液中的循环伏安曲线(扫速 20 mV · s^{-1})

Fig. 4 CV curves of Pd/MWCNTs and Pd/PVP-MWCNTs electrodes in 0.5 mol · L^{-1} H_2SO_4 + 0.5 mol · L^{-1} HCOOH solution with a scan rate of 20 mV · s^{-1}

图 5 给出 0.2 V 恒电位下 Pd/PVP-MWCNTs 和 Pd/MWCNTs 电极在 0.5 mol · L^{-1} H_2SO_4 + 0.5 mol · L^{-1} HCOOH 溶液的计时电流曲线. 由图 5 可以看到,两条曲线均发生衰减,随之逐渐平缓. 3600 s 时,两电极的计时电流密度值分别为 127 和 60 mA · mg^{-1}(Pd),前者是后者的2倍,其活性衰减

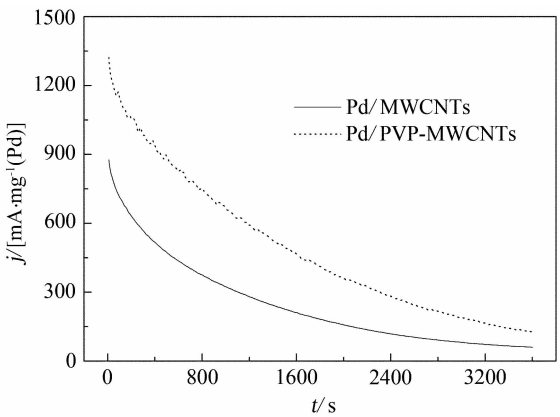

图 5 Pd/MWCNTs 和 Pd/PVP-MWCNTs 电极在 0.5 mol · L^{-1} H_2SO_4 + 0.5 mol · L^{-1} HCOOH 溶液中的计时电流曲线(恒电位 0.2 V)

Fig. 5 CA curves of Pd/MWCNTs and Pd/PVP-MWCNTs electrodes in 0.5 mol · L^{-1} H_2SO_4 + 0.5 mol · L^{-1} HCOOH solution at a constant potential of 0.2 V

速率较慢,稳定性更高. 由上可知,Pd/PVP-MWCNTs 电极对甲酸电催化性能更佳,其 Pd 利用率高、稳定性好.

3　结　论

以 PVP 功能化的 MWCNTs 作 Pd 催化剂的载体,其颗粒可稳定分散且粒径较小. Pd/PVP-MWCNTs 电极对甲酸的电氧化具有较高的电催化活性和稳定性,有望作为一种高效阳极催化剂应用于直接甲酸燃料电池.

参考文献(References):

[1] Rice C, Ha S, Masel R I, et al. Direct formic acid fuel cell[J]. Journal of Power Sources, 2002, 111(1): 83-89.

[2] Ha S, Adams B, Masel R I. A miniature air breathing direct formic acid fuel cell[J]. Journal of Power Sources, 2004, 128(2): 119-124.

[3] Zhu Y M, Ha S Y, Masel R I. High power density direct formic fuel cells[J]. Journal of Power Sources, 2004, 130(1/2): 8-14.

[4] Capon A, Parsons R. The oxidation of formic acid at noble metal electrodes: Part III. Intermediates and mechanism on platinum electrodes[J]. Journal of Electroanalytical Chemistry, 1973, 45(2): 205-231.

[5] Capon A, Parsons R. The oxidation of formic acid on noble metal electrodes II. A comparison of the behaviour of pure electrodes[J]. Journal of Electroanalytical Chemistry, 1973, 44(2): 239-254.

[6] Adzic R R, Simic D N, Despic A R, et al. Electrocatalysis by foreign metalmonolayers-oxidationof formic-acid on platinum[J]. Journal of Electroanalytical Chemistry, 1975, 65(2): 587-601.

[7] Clavilier J, Parsons R, Durand R, et al. Formic acid oxidation on single crystal platinum electrodes—comparison with polycrystalline platinum[J]. Journal of Electroanalytical Chemistry, 1981, 124(1/2): 321-326.

[8] Arenz M, Stamenkovic V, Wandelt K, et al. The electrooxidation of formic acid on Pt-Pd single crystal bimetallic surfaces[J]. Physical Chemistry Chemical Physics, 2003, 5(19): 4242-4251.

[9] Miyake H, Okada T, Samjeske G, et al. Formic acid electrooxidation on Pd in acidic solutions studied by surface-enhanced infrared absorption spectroscopy[J]. Physical Chemistry Chemical Physics, 2008, 10(25): 3662-3669.

[10] Larsen R, Ha S, Zakzeski J, et al. Unusually active palladium-based catalysts for the electrooxidation of formic acid[J]. Journal of Power Sources, 2006, 157(1): 78-84.

[11] Ha S, Larsen R, Masel R I. Performance characterization of Pd/C nanocatalyst for direct formic acid fuel cells[J]. Journal of Power Sources, 2005, 144(1): 28-34.

[12] Ha S, Dunbar Z, Masel R I. Characterization of a high performing passive direct formic acid fuel cell[J]. Journal of Power Sources, 2006, 158(1): 129-136.

[13] Yu X W, Pickup P G. Deactivation/reactivation of a Pd/C catalyst in a direct formic acid fuel cell (DFAFC): Use of array membrane electrode assemblies[J]. Journal of Power Sources, 2009, 187(2): 493-499.

[14] Pan Y H, Zhang R M, Blair S L. Anode poisoning study in direct formic acid fuel cells[J]. Electrochemistry Solid State Letters, 2009, 12(3): B23-B26.

[15] Zhang L L, Lu T H, Bao J C, et al. Preparation method of an ultrafine carbon supported Pd catalyst as an anodic catalyst in a direct formic acid fuel cell[J]. Electrochemistry Communications, 2006, 8(10): 1625-1627.

[16] Huang Y J, Zhou X C, Liao J H, et al. Preparation of Pd/C catalyst for formic acid oxidation using a novel colloid method[J]. Electrochemistry Communications, 2008, 10(4): 621-624.

[17] Ge J J, Zhang Y W, Liu C P, et al. Hydrogen vanadate as an effective stabilizer of Pd nanocatalysts for formic acid electroxidation[J]. Journal of Physical Chemistry C, 2008, 112(44): 17214-17218.

[18] Ge J, Xing W, Xue X, et al. Controllable synthesis of Pd nanocatalysts for direct formic acid fuel cell (DFAFC) application: From Pd hollow nanospheres to Pd nanoparticles[J]. Journal of Physical Chemistry C, 2007, 111(46): 17305-17310.

[19] Zhang H X, Wang C, Wang J Y, et al. Carbon-supported Pd-Pt nanoalloy with low Pt content and superior catalysis for formic acid electro-oxidation[J]. Journal of Physical Chemistry C, 2010, 114(14): 6446-6451.

[20] Li X G, Hsing I M. Electrooxidation of formic acid on carbon supported Pt_xPd_{1-x} ($x = 0 \sim 1$) nanocatalysts[J]. Electrochimica Acta, 2006, 51(17): 3477-3483.

[21] Yuan Q, Zhou Z Y, Zhuang J, et al. Pd-Pt random alloy nanocubes with tunable compositions and their enhanced electrocatalytic activities[J]. Chemistry Com-

munications, 2010, 46(9): 1491-1493.
[22] Yu X W, Pickup P G. Deactivation resistant PdSb/C catalysts for direct formic acid fuel cells[J]. Electrochemistry Communications, 2010, 12(6): 800-803.
[23] Haan J L, Stafford K M, Morgan R D, et al. Performance of the direct formic acid fuel cell with electrochemically modified palladium-antimony anode catalyst [J]. Electrochimica Acta, 2010, 55(7): 2477-2481.
[24] Zhang Z H, Ge J J, Ma L A, et al. Highly active carbon-supported PdSn catalysts for formic acid electrooxidation[J]. Fuel Cells, 2009, 9(2): 114-120.
[25] ShaoY Y, Liu J, Wang Y, et al. Novel catalyst support materials for PEM fuel cells: Current status and future prospects[J]. Journal of Material Chemistry, 2009, 19(1): 46-59.
[26] Cui Z M, Liu C P, Liao J H, et al. Highly active PtRu catalysts supported on carbon nanotubes prepared by modified impregnation method for methanol electro-oxidation[J]. Electrochimica Acta, 2008, 53(27): 7807-7811.
[27] Teranishi T, Miyake M. Size control of palladium nanoparticles and their crystal structures[J]. Chemical Materials, 1998, 10(2): 594-600.
[28] Li H Q, Sun G Q, Jiang Q A, et al. Synthesis of highly dispersed Pd/C electro-catalyst with high activity for formic acid oxidation[J]. Electrochemistry Communications, 2007, 9(6): 1410-1415.
[29] Smalley R E, O'Connell M J, Boul P, et al. Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping[J]. Chemical Physics Letters, 2001, 342 (3/4): 265-271.
[30] Dong S J, Guo S J, Wang E. Gold/platinum hybrid nanoparticles supported on multiwalled carbon nanotube/silica coaxial nanocables: Preparation and application as electrocatalysts for oxygen reduction[J]. Journal of Physical Chemistry C, 2008, 112 (7): 2389-2393.
[31] Zhou W P, Lewera A, Larsen R, et al. Size effects in electronic and catalytic properties of unsupported palladium nanoparticles in electrooxidation of formic acid [J]. Journal of Physical Chemistry B, 2006, 110(27): 13393-13398.
[32] Zhou W, Lee J Y. Particle size effects in Pd-catalyzed electrooxidation of formic acid[J]. Journal of Physical Chemistry C, 2008, 112(10): 3789-3793.

The Electrocatalytic Performance of Pd Catalysts Supported on PVP Modified MWCNTs for Formic Acid Oxidation

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Abstract: In this paper the MWCNTs were modified by poly (N-vinyl-2-pyrrolidone) (PVP) to support Pd nanoparticles, which were used as the catalysts for formic acid electrooxidation. And the performance of Pd/PVP-MWCNTs catalysts was studied by electrochemical measurements. The observations from Fourier transforms infrared spectroscopy(FTIR) and transmission electron microscopy (TEM) illustrated that the Pd nanoparticles with a small size and narrow size distribution were highly dispersed on PVP-MWCNTs support. Therefore, the Pd/PVP-MWCNTs catalysts showed excellent ctalytic activity for formic acid electrooxidation.

Key words: poly(N-vinyl-2-pyrrolidone); multi wall carbon nanotubes; Pd catalyst; direct formic acid fuel cell