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氮掺杂多壁纳米碳管的合成和定量表征

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摘要:采用化学气相沉积法制备了N掺杂多壁纳米碳管,并运用透射电子显微镜、N₂物理吸附、热重-差示扫描量热、程序升 温氧化和X射线光电子能谱等手段对样品进行了表征.结果表明,纯化处理的纳米碳管表面N含量为4.2%,其中包括吡啶、己内 酰胺、氧化吡啶、吡啶酮和吡咯等含氮官能团.研究了各种含氮官能团燃烧的动力学行为.N原子掺杂进入碳管的石墨结构中, 提高了表面碱性,有可能用于催化与能源转化领域.另外,本文提供了一种可用于场发射器件的杯状闭合结构纳米碳合成方法. 关键词: 官能团;氮掺杂;纳米碳管;X射线光电子能谱;程序升温氧化

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Preparation and Quantitative Characterization of Nitrogen-Functionalized Multiwalled Carbon Nanotubes

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Abstract: Nitrogen-doped multiwalled carbon nanotubes (MWCNTs) were produced by catalytic chemical vapor deposition. The surface and structural properties were investigated by transmission electron microscopy, nitrogen physisorption, thermogravimetry-differential scanning calorimetry, temperature-programmed oxidation (TPO) and X-ray photoelectron spectroscopy. The surface of the purified sample contained 4.2% nitrogen atoms and comprised pyridine, lactam, pyridine oxide, pyridone and pyrrol functional components. TPO results reveal the combustion kinetics of each nitrogen-containing functional group. The nitrogen atoms are incorporated within the graphitic structure to give a basic surface, which will play an important role in the investigation of catalysis and energy conversion. A convenient route to a closed cup-like carbon nanostructure applicable to field emission devices is also reported.

Key words: functional group; nitrogen doping; carbon nanotube; X-ray photoelectron spectroscopy; temperature-programmed oxidation

N掺杂材料已经成为纳米科学与技术领域研究的热点之一.在石墨结构中引入N原子,可有效控制材料的化学、机械和电子性能.传统N掺杂方法是以有机氮化物为前驱体进行化学气相沉积.与烃类类似,氮化物在金属表面发生分解,而C-N键可在一定程度上保留,进而形成N掺杂纳米结构^[1].N掺入石墨结构后使得材料具备了一定的碱性,因而其表面

活性增加.N掺杂纳米碳管(CNTs)可稳定其负载的 金属纳米颗粒,从而实现较高的金属分散度和较窄 的粒径分布.其负载的Pd,Au,Pt或Ag等金属纳米 颗粒具有较大的表面积体积比,在氧还原^[2]、醇氧 化^[3]和肼氧化^[4]等重要反应中具有良好的催化性能.

研究表明,CNTs可作为非金属催化剂活化低碳 烷烃和乙苯分子^[5-7],其中类酮结构含氧官能团作为

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活性中心促进了氧化脱氢反应的进行.反应遵循双 吸附位模式的 Langmuir-Hinshelwood 机理, 即吸附 烷烃分子的饱和 C-H 键在富电子的 C=O 位上发生 解离后,原料中的气态O2与脱离下来的H反应生成 水,暴露的活性位进而参与反应循环,类似地,含N 官能团物种本身也可以催化 Knoevenagel 缩合^[8]、甘 油三酯转化^[9]和电化学氧还原^[10]反应. 一般认为这 种非金属催化活性来自于表面碱性位,例如: Knoevenagel 缩合反应初始活性随吡啶物种的增加而增 加^[8]. 此外,裸露缺陷位置上的氮原子可以通过给电 子作用影响反应中间物种的吸附过程,进而促进了 电化学氧还原反应的进行[10]. 然而,对反应机理的清 晰描述需要建立一套完善的表面功能闭识别和定量 分析方法,本文采用电子显微学与光谱技术系统考 察了一种典型的 N 掺杂多壁纳米碳管 (MWCNTs), 所得结果可为阐明该复杂体系的化学本质提供重要 参考,同时还提供了一种可用于场发射器件的氮掺 杂杯状纳米结构碳材料的简单方法.

取一定量的 Fe(NO₃)₃·9H₂O, Al(NO₃)₃·9H₂O, (NH₄)Mo₇O₂₄·4H₂O 和柠檬酸 (C₆H₈O₇) (摩尔比 Fe: Mo:Al₂O₃:C₆H₈O₇ = 8:1:4.6:30) 溶于 50 ml 去离子水 中,室温搅拌 2 h,然后在空气中 110°C 干燥 12 h,400 °C 焙烧 3 h,800°C 焙烧 1 h,将所得固体研磨成粉末, 即得 Fe-Mo/Al₂O₃催化剂.在常压 Ar (35 ml/min) 中 将装有 Fe-Mo/Al₂O₃催化剂的石英反应器升温至 800°C,用注射泵将 10 ml 液态苯胺 (2.5 ml/h) 注入反 应器内,注射完成后在 Ar 中恒温 30 min 后自然冷却 至室温,即得N掺杂MWCNTs粗品.将1.0g粗品浸入100ml浓盐酸溶液中,搅拌4h后抽滤,依次用200ml去离子水、乙醇和丙酮清洗滤饼3次,在空气中110℃干燥12h,即得到黑色的纯化样品.

透射电镜 (TEM) 实验在荷兰 FEI Tecnai F20型 电子显微镜上进行,加速电压为200 kV. N₂吸附实验 在美国 Micromeritics ASAP 2020 型吸附仪上进行, 实验前样品在140°C脱气4h.分别由BET和BJH方 法计算样品的比表面积和孔体积.程序升温氧化 (TPO)实验在德国 Netzsch STA 449 F3 型热分析仪上 进行,使用瑞士 AVI Omnistar 200 型质谱仪监测尾气 组成.在50 ml/min的20% O₂-80% N₂中分别以2,5, 10,15 和 20°C/min的升温速率进行 TPO 实验. MWCNTs 的X射线光电子能谱(XPS)分析在美国 Thermo ESCA LAB 250 型表面分析系统上进行,射线 源为A1*K_a*(1489.6 eV),纯Cu标定能量.样品的总含 氮量由美国 LECO TCH-600 型元素分析仪测定.

图 1 为 MWCNTs 粗品和纯化样品的 TEM 照片. 由图可见,所得样品几乎不含有无定形碳,碳管外径 在 12~45 nm.碳管腔体内具有典型的竹节状结构并 由弯曲石墨层隔开,与文献中的 N 掺杂 CNTs 结 构^[11]相似.管壁石墨结构的晶格间距(*d*₀₀₂)为0.348 nm,大于纯石墨的(0.335 nm).这是因为随机分布的 N原子引起六角形对称性的局部畸变和石墨片曲率 增加.还可以看出, MWCNTs 上含有丰富的结构缺 陷,石墨晶格条纹发生一定弯曲,这与大量 N 原子掺 入石墨晶格有关.



图 1 含有金属纳米粒子的 MWCNTs 粗品和纯化样品的 TEM 照片 Fig. 1. TEM images of the as-synthesized MWCNTs containing metal nanoparticles (a-d) and the purified MWCNTs after acid washing (e-h).

采用浓盐酸可以有效地去除粗品中残留的金属 纳米粒子. XPS测得样品表面 Fe 含量仅为 0.15%,也 未检测到 Mo. 纯化处理后,样品石墨结构的变化较 大,在缺陷位置上的强酸刻蚀使得 CNTs 的长度变 短. 令人惊奇的是,酸洗后内层的石墨结构仍保留完 好,所得杯状纳米结构碳材料可用于能源和 DNA 核 苷酸检测中^[12,13]. 此外,这种结构规整、多壁且完全 封闭的杯状尖端亦可用于场发射器件上,可稳定地 提供较低的电压^[14]. 尤其是掺杂 N 原子之后,小半径 的纳米尖具有较高的场增强因子和优越的发射性 能^[15]. 需要指出的是,改变气相沉积合成和酸处理条 件将有可能调控尖端的结构参数(管径、长度、管层 数等).

纯化样品的 N₂吸附等温线见图 2(a).可以看出,
N₂吸附等温线为 IV 型,表明样品孔道主要为中孔.
吸附曲线中含有 H3 型滞后环,主要是因为吸附质在

中孔内充填过程中发生了毛细凝聚现象,这与样品 相互连通的复杂孔结构有关. 样品孔径集中于 3.8 nm,其比表面积和孔体积较低,分别为45.5 m²/g和 0.155 cm³/g,这主要是因为制备的 MWCNTs 为封闭 的竹节结构,使用 XPS 可估算样品的表面化学组成, 如图 2(b) 所示, C 1s 峰位于 284.4 eV 处, 而 N 1s 在 398.4 和 400.5 eV 处均有峰, 这表明氮原子已掺入石 墨骨架中.不对称的N1s峰至少包含四种N物种.分 峰结果如图 2(d) 所示, 分别在 398.4, 400.4, 401.1 和 403.5 eV 处存在 4 个基元峰, 依次对应于吡啶 (1.53%)、吡咯和吡啶酮(1.08%)、四价N(1.08%)和 氮氧化物(0.45%)^[16].在所有的含氮物种中,吡啶结 构的N在接近费米能级处具有尖峰,被认为是导致 纳米碳管具有化学活性的主要因素[17].而本文合成 的样品含有大量的吡啶物种,因而必将会广泛用于 催化领域中[5~10].





由 C 1s, N 1s, O 1s 和 Fe 2p 峰强度算得表面含氮 量为 4.2 mol%, 与文献中其他掺氮体系相比处于中 间位置^[18].使用氮元素分析仪测得体相中总氮量约 为 4.3 mol%,表明 N 原子在碳纳米管中分布均匀.这 可能与前驱体苯胺分子的独特结构有关.苯胺中 C-N 键以及苯环中 C-C 键的键能分别为 429 kJ/mol 和 518 kJ/mol, 二者差距不大, 且二者键长大致相同, 约为 0.139 3~0.140 4 nm^[19].这可能是大量 N 原子得 以保存并掺杂到石墨结构中的原因.

图 3 为纯化样品的 TG-DSC 和 TPO 实验中逸出的 H₂O, CO₂和 NO₂谱图.可以看出,样品失重区间为 400~650°C,氧化的起始温度和最高温度随升温速率的增加而升高.每种逸出气体在不同升温速率实验中的总释放量大致相同,相对误差仅为±7%.DSC 峰温 ($T_{\rm m}$)与升温速率 (β)遵循 Kissinger-Akahira-Sunose 公式,即 ln($\beta/T_{\rm m}^2$) = ln($AR/E_{\rm a}$) – $E_{\rm a}/RT_{\rm m}$,其中 $E_{\rm a}$ (kJ/mol)为燃烧反应的活化能^[20].用 ln($\beta/T_{\rm m}^2$)对 $T_{\rm m}^{-1}$ 作图,由所得斜率即可算得 N 掺杂 MWCNTs 燃烧活化能为 165 kJ/mol,远低于高定向热解石墨 (197~222 kJ/mol)的^[21],但略高于一般的 MWCNTs (~150

kJ/mol)^[22]和纳米碳纤维 (126~158 kJ/mol) 的^[23].表观活化能与材料结构和石墨化程度密切相关,较高的 *E*a值表明掺 N 的 MWCNTs 可用于某些高温过程.

样品中H,C和N物种燃烧后分别产生H₂O,CO₂和NO₂气体.由图3可见,CO₂和NO₂曲线十分类似,这表明C原子和N原子密切结合,同时发生氧化反应.CO₂和H₂O曲线在344~375°C处有一个相对较弱的低温峰,与气相生长过程中残留的烷烃碎片有关.对CO₂谱图进行大致估算可知,无定形碳含量低于0.5%.需要指出的是,图3以质谱强度的对数值为纵坐标,主要是为了突出曲线的细微变化.上述谱图中的不对称峰形表明每个重叠峰至少包含两个物种,这与XPS结果一致.深入分析和关联要求对谱图进行数学处理并结合系统的原位综合表征^[16].

综上所述,选择合适的 C 和 N 前驱体可实现 N 原子在 MWCNTs 表面和体相与石墨结构高度掺杂. 掺杂表面的吡啶 N 物种约为 1.53%,可作为碱性催化 剂而用于某些反应中.样品经强酸处理后形成了一 种特殊的杯状纳米结构,具有多壁、小半径、结构稳 定和全封闭特性,具有潜在的场发射性能.



Fig. 3. Mass loss, DSC, and released gas profiles during the TG-MS experiments of purified samples at various heating ramps.

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英译文 English Text

Nitrogen-doped carbon is one of the hottest topics in nanoscience and nanotechnology. The presence of nitrogen atoms in a graphitic framework allows for the control of chemical, mechanistic, and electronic properties of carbon

materials. Chemical vapor deposition (CVD) has traditionally been used for nitrogen doping using nitrogen-containing chemicals as starting materials. As for hydrocarbons, nitrogen-containing molecules initially decompose on metal surfaces and carbon-nitrogen bonds remain to some extent upon which the growth of nitrogen-doped carbon nanostructures occurs [1]. The doping of nitrogen into a graphitic structure introduces basic properties to carbon and gives rise to surface reactivity. The major role of N-doped CNTs in catalysis is to anchor metal nanoparticles in a stable manner, which promotes high metal dispersion and narrow particle size distributions. The large surface-to-volume ratio of supported Pd, Au, Pt, and Ag nanoparticles leads to excellent performance for these catalysts in many important reactions such as oxygen reduction [2], alcohol oxidation [3], and hydrazine oxidation [4].

Metal-free catalysis by carbon nanotubes has recently been used to activate light alkanes and ethylbenzene [5–7]. Ketone-like oxygen functionalities were found to coordinate the reaction turnover of oxidative dehydrogenation reactions. Fundamental research has revealed that the reaction follows a dual-site Langmuir-Hinshelwood mechanism. In this reaction the adsorbed saturated C-H bonds are dissociated by electron- rich C=O sites and gaseous oxygen molecules are responsible for the renewal of active sites by reacting with adsorbed H to form water. Similarly, the nitrogen functionalities can catalyze the Knoevenagel condensation [8], triglycerides transesterification [9], and electrocatalytic oxygen reduction reaction [10]. The metal-free application is believed to originate at the basic sites on the surface. The initial activity in the Knoevenagel condensation was found to increase with the amount of pyridine components [8]. Electron-donating nitrogen atoms at the exposed defects can affect the adsorption of reactive intermediates and thus improve the electrocatalysis of oxygen reduction [10]. However, a clear understanding of the reaction mechanism requires a well-established methodology to determine and quantify each surface functional group. We thus report on our attempts to characterize one typical nitrogen- doped MWCNT using microscopic and spectroscopic techniques. We investigated the chemical environment on a complicated surface. This study also demonstrates a facile route to a nitrogen-doped cup-like nanostructure, which is valuable for field emission. We believe that it will attract considerable interest in the nanoscience and nanotechnology research fields.

Specific quantities of Fe(NO₃)₃·9H₂O, Al(NO₃)₃·9H₂O, (NH₄)Mo₇O₂₄·4H₂O, and citric acid (C₆H₈O₇) (molar ratio Fe:Mo:Al₂O₃:C₆H₈O₇ = 8:1:4.6:30) were dissolved in 50 ml of deionized water and stirred for 2 h at room temperature. The aqueous solution was dried at 110 °C for 12 h, 400 °C for 3 h, and 800 °C for 1 h consecutively. The obtained solid was

then ground to a fine powder forming an Al_2O_3 -supported bimetallic catalyst. MWCNT growth was carried out in a tubular furnace system at atmospheric pressure using the CCVD method. The horizontal quartz tube was refreshed at 800 °C using an argon flow of 35 ml/min. Liquid aniline (10 ml) as the C and N source was then injected into the quartz tube at a rate of 2.5 ml/h using a pump. The system was then kept under these conditions for 30 min and finally cooled to room temperature in argon. For the purification of the MWCNTs, 1.0 g of the mixture was then immersed into 100 ml hydrochloric acid for 4 h. The filter cake was thoroughly washed three times each with 200 ml deionized water, alcohol, and acetone to remove residual chlorine. After drying in an oven at 110 °C for 12 h, a purified black sample was obtained.

Transmission electron microscopy (TEM) was performed using a FEI Tecnai F20 microscope with an accelerating voltage of 200 kV. Nitrogen physisorption tests were carried out on a Micromeritics ASAP 2020 instrument. The surface area and pore volume were calculated using BET and BJH methods, respectively. The sample was degassed in vacuum at 140 °C for 4 h to remove the physically adsorbed components before the measurements. A Netzsch STA 449 F3 thermogravimetric setup containing a mass spectrometer (Omnistar 200, AVI GmbH) was used to conduct temperature-programmed oxidation (TPO) experiments using various heating ramps (2, 5, 10, 15, and 20 °C/min). A flow of synthetic air containing 20% O2 was used in these experiments. Surface properties of the doped MWCNTs were investigated using an ESCALAB 250 surface analysis system with Al K_{α} X-rays (1 489.6 eV) and the energy scale of the spectrometer was calibrated using pure Cu samples. The total amount of nitrogen was analyzed with a LECO TCH-600 element analyzer.

Morphologies of the as-synthesized and purified MWCNTs are shown in Fig. 1. The MWCNTs were free of amorphous carbon and the outer diameters ranged from 12 to 45 nm. We found that the MWCNTs have a bamboo-like structure with curved graphitic bridges that form inherent compartments similar to the N-doped carbon nanostructures reported in the literature [11]. The spacing (d_{002}) of the interlayer walls was found to be 0.348 nm, which is larger than that of pure graphite (0.335 nm). This is due to the randomly distributed nitrogen atoms causing a local distortion of the hexagonal symmetry and the corresponding curvature of the graphene sheet. As shown in Fig. 1(a-d), the produced MWCNTs are rich in structural defects and the graphitic lattice fringes have a wave-like structure over long distances, which is related to the large amount of nitrogen atoms (shown in Fig. 2(d)).

The encapsulated metal nanoparticles in the as-synthesized samples can be efficiently washed out with a

concentrated HCl solution. XPS results show that the fraction of Fe is only 0.15% while the Mo signal is absent. One important change in the graphitic structure is the decreased tube length, which arises from the cleavage of defective nanotubes by the strong acid. It is quite surprising that the inner graphitic kinks remained after this treatment. The resultant cup-like nanostructure has been reported to be desirable for energy applications and for probing DNA nucleotides [12,13]. Furthermore, well-ordered, multiwalled, and fully closed cup-like tips are preferred to provide low operating voltages as well as long lifetimes in the field of emission devices [14]. The small radius of the pointed tips also benefits a large field amplification factor and good emission performance, especially in the presence of nitrogen doping [15]. The structural parameters (radius, length, and wall number) can be altered by changing the CCVD synthesis and acid-treatment conditions.

The surface area and porosity of the purified sample were characterized by nitrogen physisorption (Fig. 2(a)). The purified sample exhibits a type IV isotherm, which is typical for a mesoporous texture. The filling and emptying of mesopores by capillary condensation/evaporation produces a H3 type hysteresis curve. This is characteristic of solids featuring a complex porosity with interconnected networks. The sample shows a monomodal pore distribution that peaks at around 3.8 nm. The measured BET surface area and pore volume are not high at 45.5 m²/g and 0.155 cm³/g, respectively. This is related to the closed nature of the purified MWCNTs as detailed above. We estimated the chemical composition of the purified sample's surface using X-ray photoelectron spectroscopy (XPS). As shown in Fig. 2(b), the C1s signal is centered at 284.4 eV while the N1s signal is centered at 398.4 and 400.5 eV indicating that substitution of nitrogen atoms occurred in the graphene sheet. The asymmetric character of the N1s peak suggests the existence of at least four components. The deconvolution in Fig. 2(d) reveals four elementary peaks at 398.4, 400.4, 401.1, and 403.5 eV, and these are attributed to pyridine (1.53%), pyrrol and pyridone (1.08%), guaternary nitrogen (1.08%), and nitrogen oxides (0.45%), respectively [16]. Of all these species, the pyridinic nitrogen giving sharp peaks close to the Fermi energy is believed to induce chemical activity in carbon nanotubes [17]. The sample contains a high amount of pyridine and thus it may be widely applied in catalytic processes [5-10].

The calculated fraction of all nitrogen atoms on the surface is around 4.2 mol% on the basis of the C 1s, N 1s, O 1s, and Fe 2p intensities. This value ranks as medium compared with other N-doped systems in the literature [18]. The extent of nitrogen in the bulk was also analyzed and we obtained a similar value of 4.3 mol%. The homogeneous distribution of nitrogen atoms throughout the carbon nanostructure is therefore confirmed. This is related to the unique configuration of aniline as a precursor because the C–N bonding energy (429 kJ/mol) is close to that of C–C (518 kJ/mol) in benzene. The similar bond distances between C–N and C–C, i.e. 0.1393–0.1404 nm [19], could also benefit the incorporation and maintenance of nitrogen atoms in the graphitic structure.

To examine the stability of each nitrogen-containing component, TPO experiments were carried out using the thermogravimetric setup containing a mass spectrometer to monitor all effluent. Figure 3 shows the obtained TG-DSC and TPO spectra for H₂O, CO₂, and NO₂ from the purified sample. The weight of sample starts to decrease at around 400 °C and this ends at around 650 °C. Both the onset and maximum temperatures for oxidation increased with an increase in the heating ramp. The integration of mass intensity into time gives similar amounts of released gas at various ramps and a negligible error bar of $\pm 7\%$. The peak maximum $(T_{\rm m})$ from the DSC spectra is related to the heating ramp (β), and it follows the Kissinger-Akahira-Sunose equation, e.g. $\ln(\beta/T_m^2) = \ln(AR/E_a) - E_a/RT_m$, in which E_a (kJ/mol) represents the activation energy of the combustion reaction [20]. From the slope of $\ln(\beta/T_m^2) - T_m^{-1}$ the activation energy of the combustion of nitrogen-doped MWCNTs is 165 kJ/mol, which is far lower than that of highly oriented pyrolytic graphite (197-222 kJ/mol) [21] but a little higher than that of normal MWCNTs (~150 kJ/mol) [22] and carbon nanofibers (126-158 kJ/mol) [23]. The apparent activation energy is strongly affected by the fabrication structure and extent of carbon graphitization. Their high E_a values suggest that nitrogen-doped MWCNTs can be used in high-temperature processes.

The prevailing gases found in the effluents were H_2O , CO_2 , and NO_2 . These gases reveal that hydrogen-, carbon-,

and nitrogen-containing compounds are present in the sample. As shown in Fig. 3, the profile of CO₂ largely resembles that of NO₂ suggesting a high extent of carbon and nitrogen atom mixing to allow the simultaneous release of their oxidation products. One small low-temperature peak is centered at 344-375 °C in the CO₂ and H₂O profiles, which is related to the dangling hydrocarbon fragments that were produced during the CCVD process. As estimated from the CO₂ profiles, the amount of amorphous species is lower than 0.5%. We note that the Y axial in Fig. 3 is the logarithm of mass intensity, which explains any negligible change in the curves. The asymmetric shape of each profile suggests that there are at least two components included in the overlapping peaks, and this is in accordance with the XPS results. Detailed analysis and correlation requires a careful treatment by mathematical methods as well as comprehensive characterization using in situ techniques [16].

To summarize, we employed TEM, XPS, TG-DSC, and TPO methods to investigate a typical nitrogen-doped multiwalled type of carbon nanotube. The nitrogen atoms are tightly incorporated into the graphitic structure, both at the surface and in the bulk. This was possible because of the selection of appropriate carbon and nitrogen precursors. The amount of surface pyridinic nitrogen was around 1.53%, which allows for its application as a basic catalyst for some catalysis reactions in the future. A cup-like nanostructure was observed after treatment with strong acid and its multiwalls, small radius, stable structure and fully closed end are expected to provide outstanding performance in field emission applications.

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