

# 碳材料的掺杂改性及其用于燃料电池催化剂的研究

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**摘要:** 开发掺杂改性的碳材料用作燃料电池的非贵金属氧还原催化剂已成为燃料电池领域的重要研究课题, 相关研究对于降低燃料电池成本、促进燃料电池的商业化具有十分重要的意义。大量研究工作表明, 对碳材料进行掺杂改性可以实现其形貌、微观结构、组成及其他表面物理化学性质的优化, 从而得到具有较高催化活性、选择性和稳定性的氧还原催化剂。人们在这类催化剂的制备方法、性能优化和催化机理等方面进行了大量研究工作。综述了对碳纳米管、石墨烯、介孔碳、大孔碳、碳微球等碳材料进行掺杂改性的最新进展。并基于目前的研究结果, 展望了掺杂碳材料作为燃料电池非贵金属氧还原催化剂的应用前景和未来的发展趋势。

**关键词:** 掺杂; 改性; 碳材料; 催化剂; 燃料电池

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## Research Progresses on the Doping Modification of Carbon Materials and Their Application as Catalysts in Fuel Cell

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**ABSTRACT:** It is becoming one of the most important topics in the fuel cell field to develop doped/modified carbon materials as non-precious-metal catalysts for oxygen reduction, which will effectively reduce the cost of fuel cell and promote the commercialization of the fuel cells. It has been demonstrated by a lot of researches that the microstructures, compositions and other superficial physicochemical properties can be improved and optimized through the doping modification of carbon materials, thus resulting in oxygen reduction catalysts with excellent catalytic activity, selectivity and stability. A considerable amount of researches have been done in the preparation methods, performance optimization and catalytic mechanism of this type of catalysts. In this paper, the latest research progresses in the doping modification of carbon materials, such as carbon nanotube, graphene, mesoporous carbons, macroporous carbons and carbon microspheres, were reviewed. Based on the results achieved, we proposed their application prospects as catalysts in fuel cell, as well as the developing trend of the doped carbon catalyst in the future.

**KEY WORDS:** doping; modification; carbon materials; catalyst; fuel cell

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在能源需求日益增长的今天,化石能源的枯竭与环境污染的危机迫使人类加快了新能源技术的研究。其中,燃料电池技术能够将化学能直接转化成电能,具有能量转换效率较高,清洁环保,无污染物排放等突出优势。但是燃料电池所需的催化剂铂储量少,价格高,实际应用受到严重制约。由于阴极氧还原反应极其缓慢,需要的铂是阳极的 2 倍以上,开发高性能的非贵金属氧还原催化剂显得尤为必要。相比其他非贵金属电催化剂,各种碳材料,譬如碳纳米管、石墨烯、介孔碳等,由于来源广、成本低、稳定性好等特点,得到人们广泛的关注。近年来,人们通过对碳材料进行掺杂改性来实现其表面特性的优化,更使这方面的研究有了明显进展<sup>[1-3]</sup>。

1 碳纳米管的掺杂改性及其电催化应用

制备碳纳米管最初的方法是电弧法,后来发展的化学气相沉积法通常是以挥发性有机物为前驱体,即载气携带前驱体进入高温区发生热分解,得到的碳原子在催化剂纳米颗粒上生长成为碳纳米管。化学气相沉积法的设备简易,操作条件灵活可控,得到了广泛应用。2009 年,戴黎明课题组以酞菁亚铁为前驱体,采用化学气相沉积法制得垂直掺氮的碳纳米管阵列,该碳纳米管材料在碱性环境中表现出比贵金属催化剂更具有活性、更稳定及更抗一氧化碳中毒等优势。碳纳米管掺 N 后活性明显提高的机理是,N 的掺入改变了碳纳米管上各原子电荷的分布,使与 N 相邻的 C 原子上拥有了更多的正电,促进了 O<sub>2</sub> 的吸附,并且进一步弱化了 O—O 键<sup>[4-5]</sup>。从此,研究者们对掺杂碳纳米管用于 ORR 催化方面的工作开始逐渐重视起来。人们发现碳纳米管掺磷、硼等杂原子后,其氧还原催化活性也得到一定的增强<sup>[6-9]</sup>。

除了非金属元素掺杂外,进一步掺杂过渡金属物种(如铁和钴)也被认为可以改善碳基材料的催化活性。2012 年,戴宏杰课题组使用简单的两步方法合成钴氧化物/掺氮碳纳米管杂合物,轻微氧化的碳纳米管外壁提供促进纳米晶成核的基团,同时内壁保留完整的高度导电网络促进电荷传输。这种催化剂在碱性条件下有很好的氧还原活性和稳定性<sup>[10]</sup>。2013 年,包信和课题组以二茂铁和叠氮化钠为前驱体,在氮气保护的高压釜中反应得到催化剂,其铁或钴包裹在掺 N 的碳纳米管内部(如图 1 所示),该催化剂在酸性环境中的稳定性得到了提高<sup>[11]</sup>。Zelenay 课题组

以氰氨为掺氮碳前驱体,以醋酸铁为铁源,再加入氧化的碳粉搅拌过夜,经过热处理、酸洗、二次碳化,合成的掺氮碳催化剂中碳相由碳纳米管/碳纳米颗粒复合物组成(如图 2 所示)。这种催化剂合成方法简单,可大规模应用,其中使用的铁不仅诱导氧还原活性,而且催化 CNT 增长。因为碳纳米管有自团聚的倾向,通过化学处理进行表面功能化常常是需要的,但它不可避免会导致额外的处理步骤和高成本。不同于常用的方法,该催化剂的合成可以一步实现高度分散,无需进行额外处理,并且其氧还原活性在碱性条件下胜过铂基催化剂<sup>[12]</sup>。

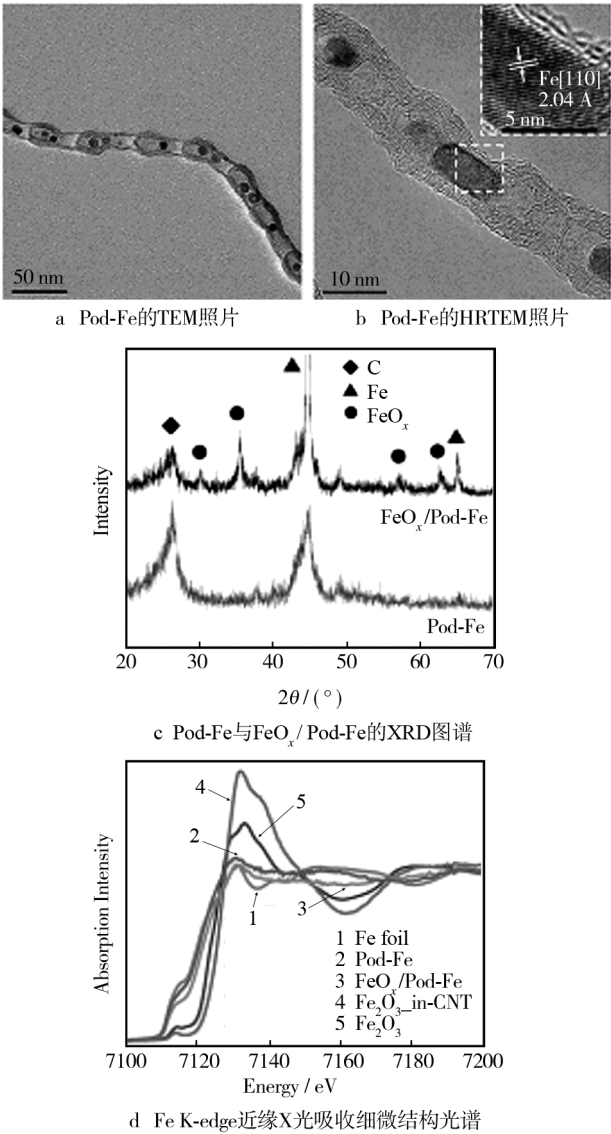
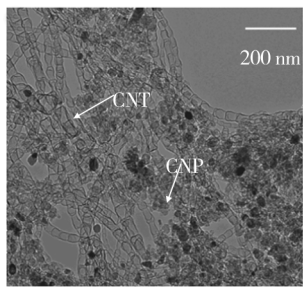
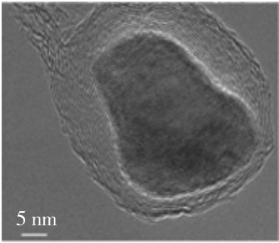


图 1 Pod-Fe 的形貌及组成分析<sup>[11]</sup>  
Fig.1 Morphology and composition analysis of Pod-Fe

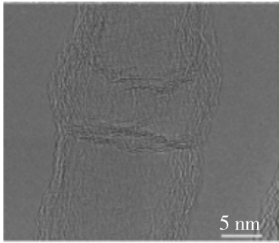
另外,大环化合物对碳纳米管的表面改性研究也得到了重视。2014 年,Campidelli 课题组研究了在多



a N-Fe-CN/CNP复合催化剂HRTEM



b 铁封装在石墨烯的纳米壳层中



c 典型竹节状缺陷石墨烯堆叠

图 2 碳纳米管/纳米粒子复合材料的显微形貌<sup>[12]</sup>

Fig. 2 Micrographs of carbon nanotube/nanoparticle composite

壁碳纳米管侧壁上吸附四乙基钴卟啉,接着通过三键发生二聚作用,以纳米管作为模板,在多壁碳纳米管表面形成卟啉聚合物层。卟啉和碳纳米管之间的多重  $\pi$  堆积相互作用和卟啉之间的共价链接使得这种材料显示了较强的稳定性。这种碳基催化剂在酸性条件下进行电化学测量时,显示出优异的氧还原催化性能,平均电子转移数接近于 4<sup>[13]</sup>。Liu 课题将轴向咪唑配位的卟啉共价地系在多壁碳纳米管上,与目前商业化的铂碳催化剂相比,这种仿生的电催化剂在酸性和碱性条件下都显示出很高的氧还原催化活性和稳定性<sup>[14]</sup>。

2 石墨烯的掺杂改性及其电催化应用

近年来,石墨烯因其巨大的比表面积和优异的电

导率,成为了备受关注的新一代碳纳米材料。随着研究的深入,研究者们将石墨烯的研究从原始二维结构拓宽到了零维石墨烯量子点、一维石墨烯丝带、三维石墨烯泡沫结构,不仅如此,石墨烯的物理和化学性质也可以通过原子级或分子级的掺杂而实现显著改变。

石墨烯的掺杂方法分为原位法和后处理法两类<sup>[15]</sup>。原位法可同时实现石墨烯的合成及杂原子的掺入,包括化学气相沉积法、自下到上合成法等。例如,Qu 等先用溅射法将镍膜镀在 SiO<sub>2</sub>/Si 基底上,然后在管式电炉中于 1000 °C 通入 NH<sub>3</sub>/CH<sub>4</sub>/H<sub>2</sub>/Ar 混合气,将镍膜用酸溶解掉后便可获得化学气相沉积法制备的掺氮石墨烯<sup>[16]</sup>;魏子栋课题组以层状蒙脱石为平面的纳米反应器聚合苯胺(如图 3 所示),这种空间限域法引导合成的掺氮石墨烯富含吡啶型和吡咯型氮<sup>[17]</sup>。后处理法则包括湿化学法、氧化石墨与杂原子前驱体热解法等。例如,Zhang 等将双氰胺和氧化石墨溶液超声后,在 180 °C 水热反应 24 h,低温条件下合成了掺氮石墨烯<sup>[18]</sup>;Sheng 等以三聚氰胺为氮源,与氧化石墨粉一起置于管式电炉中,在 Ar 气保护下高温热处理,制得了掺氮石墨烯<sup>[19]</sup>。

研究表明,石墨烯中掺入氮、硫、磷、硼元素时,能表现出一定的氧还原催化活性,因此也被认为是一类比较有应用前景的非铂催化剂。掺杂石墨烯在碱性电解液中具有比传统 Pt/C 催化剂更高的氧还原催化活性、稳定性、抗甲醇中毒和抗一氧化碳中毒的能力。虽然催化剂的氧还原机制等细节尚未被完全了解,但人们普遍认为掺杂物种能够通过促进缺陷在六边形碳原子排列中的形成,增加石墨烯边缘存在,引起石墨烯结构破裂,在石墨烯堆叠中引入不规则曲率,导致氧还原活性的增强。也有研究者将两元素同时掺入石墨烯,合成了二元掺杂的石墨烯,结果发现它具有比单元素掺杂的石墨烯更好的氧还原催化活性。

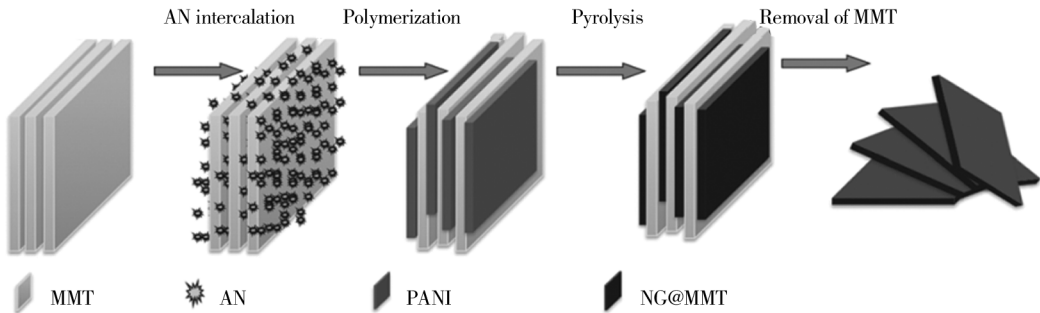


图 3 掺氮石墨烯 NG@ MMT 的制备流程<sup>[17]</sup>

Fig. 3 Schematic representation of the synthesis of NG@ MMT



氧还原催化活性的提高得益于两掺杂元素的协同作用导致自旋密度与电荷密度的重新分配,从而产生了更多的碳原子活性点位<sup>[20-23]</sup>。

此外,掺杂过渡金属物种(如铁和钴)也可以改善石墨烯材料的氧还原催化活性。戴黎明课题组报道了一种  $\text{Co}_3\text{O}_4$  纳米晶生长在还原的氧化石墨烯上的杂合材料,这种新材料是基于两步法合成的:首先水解氧化醋酸钴,通过调节乙醇/水的比例和反应温度来减缓醋酸钴的水解速度,从而实现  $\text{Co}_3\text{O}_4$  纳米粒子在轻度氧化的石墨烯上的可控成核;然后进行水热反应,实现  $\text{Co}_3\text{O}_4$  的结晶和氧化石墨烯的还原。这种  $\text{Co}_3\text{O}_4/\text{rGO}$  杂合材料在碱性电解质中的氧还原催化性能与  $\text{Pt}/\text{C}$  催化剂相当,而且稳定性比  $\text{Pt}/\text{C}$  催化剂更高,他们认为这种优异的性能源于  $\text{Co}_3\text{O}_4$  纳米晶与石墨烯中间的协调化学耦合作用<sup>[24]</sup>。Klaus Müllen 课题组以水热自组装后冻干热处理的方法合成了一种负载  $\text{Fe}_3\text{O}_4$  纳米颗粒的三维氮掺杂石墨烯气凝胶,石墨烯构成的相互贯通的大孔框架里均匀分散着  $\text{Fe}_3\text{O}_4$  纳米颗粒,大孔隙和高比表面积有利于改善氧还原性(如图4所示)。该材料用作燃料电池阴极氧还原催化剂时,在碱性介质中性能优异,过氧化氢产量低,此外,它还显示出比商业  $\text{Pt}/\text{C}$  催化剂更好的耐久性<sup>[25]</sup>。

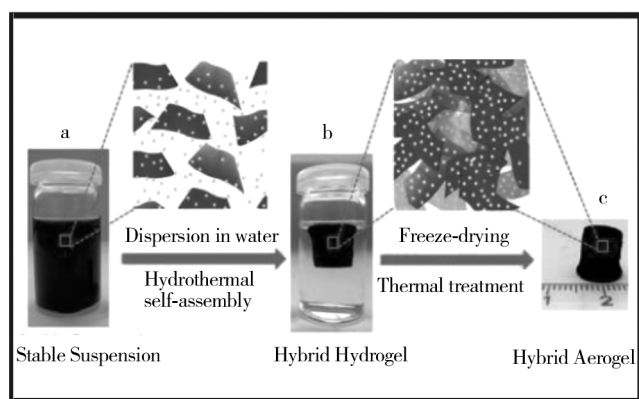


图4 掺氮石墨烯 3D  $\text{Fe}_3\text{O}_4/\text{N-GAs}$  的制备流程<sup>[25]</sup>

Fig. 4 Fabrication process for the 3D  $\text{Fe}_3\text{O}_4/\text{N-GAs}$  catalyst

在大环化合物对石墨烯的掺杂改性方面,陈卫课题组将酞菁铁分散在 DMF 溶剂中,逐滴加入到等浓度的石墨烯溶液中,搅拌并超声混匀后,过滤洗涤,得到一种非贵金属氧还原催化剂,酞菁铁通过  $\pi-\pi$  堆积相互作用固定在石墨烯片层表面上。该催化剂的氧还原性能在碱性条件下与铂碳催化剂相当,其稳定性、抗甲醇中毒和抗一氧化碳中毒的能力可超越铂碳

催化剂<sup>[26]</sup>。

### 3 其他碳材料的掺杂改性及其电催化应用

除了碳纳米管和石墨烯之外,介孔碳<sup>[27-33]</sup>、大孔碳<sup>[34]</sup>、碳微球<sup>[35-36]</sup>、活性炭<sup>[37-40]</sup>等碳材料的掺杂改性也获得了广泛研究。

乔世樟课题组采用低成本且工艺简单的纳米铸法,在具有高电导率的高度有序介孔碳(CMK-3)中掺入石墨化的氮化碳。这种氮掺杂的复合材料表现出很好的氧还原催化活性和比商业  $\text{Pt}/\text{C}$  催化剂更好的抗甲醇中毒性能<sup>[27]</sup>。

Klaus Müllen 课题组以含氮芳香染料为前驱体,以有序介孔硅 SBA-15 为模板,制备了一种氮掺杂的有序介孔石墨阵列。该工艺简单,节省成本,而且易重复。在碱性电解质中,这种完全不含金属的碳材料催化剂显示出较好的氧还原催化活性和稳定性<sup>[28]</sup>。

Sang Hoon Joo 课题组报告了一种采用纳米铸法,以介孔二氧化硅模板与金属卟啉为前体制备的碳基催化剂,它具有高比表面和可调的孔隙结构,在酸性介质中表现出优秀的氧还原活性,高于其他非贵金属催化剂<sup>[29]</sup>。

Liang 等使用纳米  $\text{SiO}_2$  为模板,以蔗糖为碳源,高温碳化成  $\text{C}@\text{SiO}_2$  型复合材料,用 HF 除去  $\text{SiO}_2$  后得到大孔碳,大孔碳与熔化的氨脒混合再碳化后,就得到了掺氮大孔碳材料。该催化剂在碱性条件下表现出良好的氧还原催化活性,起始电位达到  $-0.13 \text{ V}$  (vs.  $\text{Ag}/\text{AgCl}$ )<sup>[34]</sup>。

逯乐慧课题组以多巴胺为碳源和氮源,合成尺寸可控的单分散掺氮碳微球。他们在室温下的水/乙醇/氨水混合液中聚合多巴胺,得到亚微米级的聚多巴胺球,经过碳化即得到原位掺氮的碳球。相比酚醛树脂基的碳球,该材料富含大量具有电催化活性的含氮基团,且所含的  $\text{sp}^3$  型碳较少,因此导电性能更好<sup>[35]</sup>。

廖世军课题组使用硫和聚丙烯腈作为前体,制备了平均直径大约 200 nm 的氮硫共掺杂纳米碳球。催化剂在碱性介质中表现出较强的氧还原催化活性和稳定性。硫的掺入在提高材料的催化性能上起着至关重要的作用,它不仅防止纳米碳球的团聚,在热处理中构建多孔结构,增大材料的比表面,而且参与氧还原活性中心的形成<sup>[36]</sup>。

Dodelet 研究小组以氰胺、菲啰啉、铁盐为前驱物,以各种活性碳和具有高氮含量、高孔隙率及高比表面积 of 的金属有机框架为载体,采用浸渍法和行星式球磨法混匀,再经两次热处理研制,最后制得的氧还原活性最好的催化剂,扣除内阻影响后,在 0.8 V 条件下其体积电流达到  $230 \text{ A/cm}^3$ ,单电池测试中表现的功率密度也达到领先水准,实现了很大的突破。若其稳定性能进一步提高,它将会是一种很有前途的非贵金属催化剂<sup>[37-38]</sup>。

Zelenay 课题组在活性碳颗粒表面包覆聚苯胺并进行金属铁钴掺杂,再在惰性气体中热处理,之后在 80 °C 用硫酸回流浸洗 8 h,除去不稳定及 ORR 惰性的物种,最后进行第二次热处理,得到催化剂(如图 5 所示)。该催化剂的氧还原催化性能很不错,运行 100 h,在 0.4 V 下电流没有明显的衰减<sup>[39-40]</sup>。

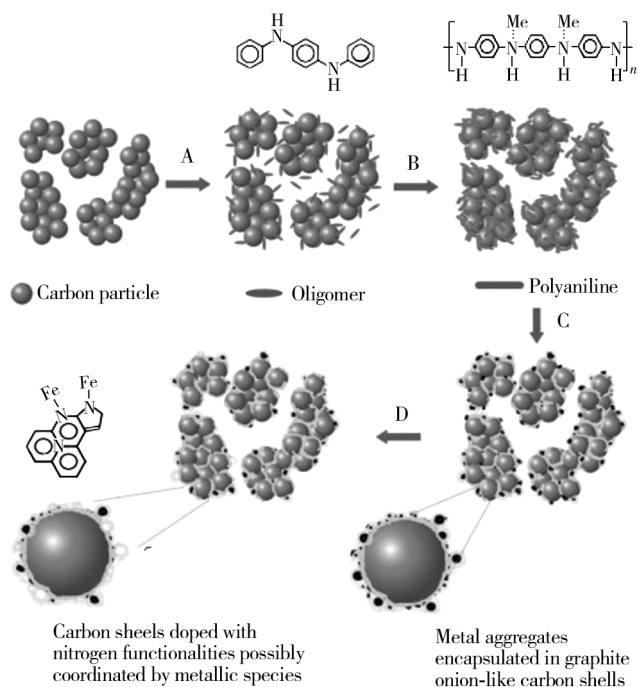


图 5 PANI-M-C 催化剂制备流程图<sup>[40]</sup>

Fig. 5 Schematic diagram of the synthesis of PANI-M-C catalysts

## 4 结语

掺杂改性的碳材料是目前研究中,催化活性与稳定性都比较突出的一类燃料电池阴极非铂催化剂,对该类材料的制备及催化机理的研究是目前非铂催化剂研究的热点。大多数碳基催化剂在碱性电解液中氧还原反应的催化活性可以与 Pt/C 催化剂相当,有的甚至在 Pt/C 催化剂之上,然而在酸性电解质中,它

们的氧还原活性仍逊于传统的 Pt/C 催化剂。要使燃料电池非贵金属催化剂能真正推广应用,还需要尽可能增大材料的比表面积,对材料的孔结构进行合理设计和调控,提高其活性位点的密度,增强非贵金属催化剂的活性,提高稳定性。对该类非贵金属的研究,还需科研工作者们更加艰苦卓绝的努力,以实现燃料电池阴极催化剂的非铂化。

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