碳基纳米材料电催化氮气还原合成氨研究进展

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摘要 以可再生电能为能源, H_2O 为质子和电子源, 温和条件下将氮气(N_2)还原为氨气(NH_3)将成为替代传统高能耗合成氨工艺(Haber-Bosch方法)的有效途径之一. N_2 分子的高反应活化能和析氢反应(hydrogen evolution reaction, HER)导致的产 NH_3 速率和法拉第效率低, 是目前电催化氮气还原(nitrogen reduction reaction, NRR)合成 NH_3 面临的主要挑战. 过渡金属基催化剂可通过反馈 π 电子过程吸附、活化 N_2 分子, 然而d轨道电子同样有利于质子吸附, 进而促进HER竞争反应, 导致合成 NH_3 法拉第效率降低. 碳基纳米材料因其出色的电导率、优异的化学稳定性以及可调的电子结构、形貌特征, 成为当前电催化NRR合成 NH_3 领域的研究热点. 结合上述研究工作, 本文从电催化NRR合成 NH_3 机理出发, 介绍了碳基纳米材料的种类和结构, 重点综述了碳基纳米材料电催化NRR合成 NH_3 活性提高策略, 包括杂原子掺杂、单原子活性中心设计、缺陷工程. 最后总结了该领域目前存在的问题与挑战以及未来发展趋势.

关键词 电催化, 氮气还原, 氨合成, 碳基纳米催化剂, 结构缺陷设计

NH_3 作为全球第二大无机化工产品, 是氮肥、尼龙、胺等工业品生产的基本原料, 在国民经济中占有重要地位. 此外, NH_3 作为一种无碳氢能载体, 具有高能量密度(4.32 kWh L^{-1})、高氢密度、低液化压力、易存储运输等优点. 目前, 全球 NH_3 产量约为1.7亿吨/年, 其生产主要采用Haber-Bosch方法: 即在高温、高压($400\sim 500^\circ\text{C}$, $10\sim 30 \text{ MPa}$)条件下利用铁基催化剂将高纯度的氮气和氢气转化为氨气($\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$). 该方法首先需要利用天然气水蒸气重整制备纯氢气, 这一过程消耗的天然气约占全球天然气总消耗量的3%~5%, 生成的 CO_2 副产物约占全球 CO_2 排放量的0.5%. 其次, 作为一个放热反应, 低温($<200^\circ\text{C}$)有利于促进该反应的热力学平衡, 但非极性 $\text{N}\equiv\text{N}$ 三键的活化、断裂又需要高能量输入($400\sim 500^\circ\text{C}$ 高温)来提高反

应动力学. 为了平衡反应热力学和动力学, Haber-Bosch方法一般在 $10\sim 30 \text{ MPa}$ 的高压下, 通过多次反应来提升反应转化率, 由此带来的能量消耗约占全球总能耗的2%^[1~3]. 因此, 寻求一种环境友好、条件温和、原料丰富的合成 NH_3 方法对人类社会的可持续性发展显得极为迫切^[4,5].

电催化 N_2 还原合成 NH_3 是以可再生的风电、太阳能发电或富余核电等洁净电能为能源, 在常温、常压条件下, 以 N_2 为氮源, H_2O 为质子和电子源, 将 N_2 直接还原为 NH_3 ^[6]. 假设反应在标准条件(25°C , 100 kPa)下进行, 反应中 N_2 分压等于1 atm ($1 \text{ atm} = 101325 \text{ Pa}$), 溶液中 NH_3 浓度为 0.1 mg L^{-1} , 可计算得到反应起始电位为 0.23 V (vs. 可逆氢电极(RHE), 下同)^[7]. 但实际反应中由于需要活化反应物、存在电能损耗等原因, 电催

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化氮气还原(nitrogen reduction reaction, NRR)存在较大的过电位, NRR电催化剂的工作电位一般在 $-0.1 \sim -0.5$ V. 此外, 当在水系电解液中进行电催化NRR合成 NH_3 时, 该还原过程与析氢反应(hydrogen evolution reaction, HER)电位相似, 使得催化剂表面不可避免地发生HER竞争反应, 导致NRR反应的产 NH_3 速率和法拉第效率下降^[8,9]. 因此, 反应过程中较大的过电位和HER竞争反应导致的低法拉第效率, 成为电催化NRR合成 NH_3 反应面临的主要问题, 也是该领域亟待解决的主要科学难题之一.

碳基纳米催化剂因其出色的电导率、优异的化学稳定性、可调的电子结构、形貌特征, 成为当前电催化NRR合成 NH_3 领域的研究热点^[10-14]. 与传统催化剂不同, 纳米碳材料本身即为催化剂, 而非人们普遍认知的酸碱催化中心、金属、金属氧化物基催化中心或活性位^[13,14]. 但近年新兴的碳基纳米材料(例如碳纳米管、石墨烯、三维纳米多孔碳)其碳原子主要以 sp^2 方式杂化, 因此通常情况下, 该类碳材料表面化学惰性强、反应活性低. 为了提高该类碳基纳米材料的催化活性, 首先需要在碳骨架内构建缺陷位点, 使 sp^2 电子体系受到破坏, 出现局部电子局域化, 从而调变材料表面催化反应中间体的吸附自由能, 优化反应路径, 进而增加催化活性, 使其电催化性能可与商业贵金属催化剂媲美^[15,16]. 结合上述研究工作, 本文将从电催化NRR合成 NH_3 反应机理出发, 介绍碳基纳米材料的种类和活性位分类, 重点综述碳基纳米材料电催化NRR合成 NH_3 活性提高策略, 包括杂原子掺杂、单原子活性中心设计、缺陷工程, 最后对碳基纳米催化剂面临的问题及未来催化剂的设计方法作探讨和展望.

1 电催化还原氮气合成氨反应机理

氮气分子是由两个氮原子以 $\text{N}\equiv\text{N}$ 三键组成的非极性线性分子. $\text{N}\equiv\text{N}$ 解离能高达 964 kJ mol^{-1} , 因此不易发生活化断裂. 氮气分子最高占据轨道($\text{s}2\text{p}$ 和 $\text{p}2\text{p}$)和最低空轨道($\text{p}2\text{p}^*$)之间的能量差分别为 23.66 和 24.90 eV , 大能带间隙不利于电子得失, 导致了氮气分子反应性差、化学惰性强. 此外, 氮气分子的负电子亲和能(-1.9 eV)以及高电离势(15.85 eV)进一步提高了氮气分子活化难度^[17-20]. 因此, NH_3 合成过程需要采用催化剂弱化氮气分子键能、降低反应过程中的活化能, 从而实现低能耗、高效的固定 N_2 合成 NH_3 .

电催化NRR合成 NH_3 反应机理主要有解离机制和

缔合机制两类(图1)^[21-23]. 在解离机制中, 氮气分子与催化剂表面的两个活性位点进行化学吸附, 使 $\text{N}\equiv\text{N}$ 三键完全断裂; 随后两个被活化的氮原子在催化剂表面不断地进行质子化, 逐步生成 $-\text{NH}$ 、 $-\text{NH}_2$ 和 $-\text{NH}_3$, 最后氨气分子从催化剂表面脱附, 形成气态氨(路径i). 解离机制需要预先破坏 $\text{N}\equiv\text{N}$ 三键, 因此该过程能量消耗极大, 且对催化剂性能要求也较高. Haber-Bosch方法通常遵循该反应路径.

缔合机制中, 首先氮气分子通过物理吸附与催化剂表面的一个活性位点结合, 然后催化剂将从外电路接收的电子注入到氮的最高空轨道中, 对氮气分子进行活化, 随后氮气分子不断接收质子发生加氢反应, 最终 $\text{N}\equiv\text{N}$ 三键断裂, 氨分子从催化剂表面脱附, 形成气态氨. 缔合机制中的加氢过程可以通过交替机制和远端机制两种途径进行. 其中, 缔合交替机制中, 两个氮原子交替加氢发生质子化, 使得氮原子间的键全部断裂. 当第一个氨分子从催化剂表面释放后, 第二个氨分子也随之释放(路径ii交替机制, “Alternating”). 缔合末端机制中离催化剂表面最远的末端氮原子先发生质子化, 形成氨分子从催化剂表面释放, 随后剩余的氮原子继续加氢, 形成第二个氨分子并随之脱附(路径ii远端机制, “Distal”). 缔合机制是先进行加氢再断裂氮-氮键, 因此可减少能量消耗并提高催化效率. 此外, 还有另外一种途径, 即酶途径(路径iii), 其反应过程与缔合机制基本相同. 区别是氮气分子通过物理吸附与催化剂表面的两个活性位点结合, 然后氮原子再依次进行加氢形成 NH_3 完成脱附^[24-26].

2 电催化NRR合成 NH_3 的碳基纳米催化剂设计方法

过渡金属基催化剂可通过反馈 π 电子过程吸附、活化 N_2 分子, 然而 d -轨道电子同样有利于质子吸附, 进而促进HER竞争反应, 导致合成 NH_3 法拉第效率降低. 碳基纳米材料因其出色的电导率、优异的化学稳定性以及可调的电子结构、形貌特征, 成为当前电催化NRR合成 NH_3 领域的研究热点.

2.1 碳基纳米材料种类和结构性质

碳基纳米材料是指在三维空间中至少有一维处于纳米尺寸范围内($1 \sim 100 \text{ nm}$)或由它们作为基础单元构成的碳材料, 其主要存在形式包括零维富勒烯、一维碳纳米管、二维石墨烯以及三维纳米金刚石和纳米多

图1 电催化NRR合成 NH_3 催化反应机理示意图^[21]: 解离机制(a)和缔合机制(b, c)

Figure 1 Schematic illustrations of the reaction mechanism for NRR^[21]: Dissociative (a) and associative (b, c) pathways

孔碳材料等(图2)^[27]。近年来, 随着纳米技术的发展, 纳米碳家族也涌现出多种多样的纳米碳结晶, 例如纳米碳纤维、洋葱状纳米碳、碳纳米角等。如按结构划分, 碳基材料分为非晶态及结晶态。非晶态炭包括炭黑、活性炭、微-介孔炭分子筛等; 结晶态碳材料中主要包括富勒烯、碳纳米管、石墨烯、纳米金刚石、纳米碳纤维等。其中, 碳纳米管和石墨烯中的碳原子以 sp^2 杂化方式存在, 每个碳原子贡献一个p轨道上的剩余未成对电子, 形成大 π 键, π 电子可以自由移动, 赋予该类材料优良的导电性, 因此该类材料也是碳基电催化剂研究的热点。

尽管碳基纳米材料的尺寸、形貌、结构各有差异, 但其合成方法(例如气相沉积、弧光放电、化学强氧)一般都涉及高温、剧烈的过程, 因此其结构中不可避免地含有各种类型的缺陷。这些缺陷结构的存在将改变碳基纳米材料的物理和化学性质, 从而影响碳基纳米材料作为电催化剂的性能表现。作为电催化剂时, 纳米碳材料的活性位点主要分为以下几类: (1) 掺杂的异质原子。是指取代碳原子进入 sp^2 晶格的原子, 例如非金属原子N、B、P、O等, 金属原子Ru、Mo、Fe、Ni、Cu等。(2) 缺陷位和边缘原子。通常指碳结构的边界、空穴位、非六元环结构缺陷, 这些缺陷目前可以通过高分辨电子显微镜观察到。(3) 表面官能团。主要是含氧官能团, 此外还有含氮或含硫官能团。在电催化NRR合成 NH_3 领域, 目前常用的碳基催化剂活性提高策略主要包括异质原子掺杂和缺陷工程^[28-30]。

图2 (网络版彩色)不同维度的碳基纳米材料^[27]

Figure 2 (Color online) Classification of carbon nanoallotropes^[27]

2.2 异质原子掺杂

近年来, 通过异质原子掺杂调控碳基纳米材料理化性质(如导电性、热稳定性、碱性、电荷转移、带隙、局域电子态、自旋分布等), 进而提高碳基纳米材料催化活性, 已成为电催化活化小分子领域的研究热点(图3)。在诸多异质原子中, 与C原子序数相近的非金属原子(如N、B、P、O等)常被优先考虑, 因为相近的原子尺寸有利于异质原子与C原子形成强化学作用, 进而提高催化稳定性^[31]。相反, 由于金属原子与C原子的

图3 (网络版彩色)异质原子掺杂碳基催化剂的活性位点示意图
Figure 3 (Color online) Schematic diagram of active sites of heteroatom-doped carbon-based catalysts

结合能较低,当金属原子负载在碳纳米材料表面时,则会发生团聚的趋势.为了稳定客体金属原子,通常需要在碳主体中增加杂原子、官能团或孔洞缺陷等作为锚定位点,通过形成杂原子-金属配位键的方式,将金属原子固定在碳晶格中,形成单原子催化剂^[32].单金属原子掺杂的碳基材料作为一种新兴催化剂,不仅能够降低金属负载量,提高金属原子的利用率,同时能够调控碳催化剂活性中心对反应分子和不同反应中间体的吸脱附性能,从而改变反应活化能,优化反应途径,因此,在多相催化领域具有广阔的应用前景^[33-37].

2.2.1 非金属原子掺杂

由于非金属原子与C原子(C的电负 $\chi_C=2.55$)之间存在电负性差异,当非金属原子掺杂到碳晶格后,会引起掺杂原子和邻近C原子间的电荷极化,从而改变碳材料的能带结构,引起电子态的变化,提高催化活性^[38,39].例如,N掺杂的碳是典型的n型半导体材料,这是因为氮掺杂后,在碳纳米管的导带引入新的电子能态,其中包括接近导带最小值的电子供态;而B在碳纳米管晶格的掺杂会在价带的最大值附近产生电子接受态,从而形成p型掺杂材料.此外,密度泛函理论(density functional theory, DFT)计算表明,其带隙打开程度常与掺杂量呈正相关关系,因此,可通过改变掺杂原子种类和浓度调节碳基催化剂的电子态^[29].

N作为一种富电原子($\chi_N=3.04$),常用作杂原子掺杂提高碳催化剂的催化活性^[40-45].Liu等人^[40]以ZIF-8为前体,通过调节炭化温度(750~950°C),制备了一系列N种类(吡啶氮、吡咯氮、石墨氮)和N含量(13.6at%~2.1at%, at%为原子百分含量)可调的掺N多孔碳(NPC)(图4(a), (b)).当用于电催化NRR时,在-0.9 V电位下NH₃的最大法拉第效率为1.42%, NH₃生

成速率为23.8 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ (图4(c)和表S1). DFT计算结合实验研究表明,吡啶氮和吡咯氮是N₂分子吸附和N≡N断裂的关键位点. NH₃合成路径为 $*\text{N}\equiv\text{N} \rightarrow *\text{NH}=\text{NH} \rightarrow *\text{NH}_2-\text{NH}_2 \rightarrow 2\text{NH}_3$.类似地, Mukherjee等人^[45]和Zhao等人^[41]的研究也表明,N掺杂的多孔碳催化剂中吡啶氮是NRR的主要活性位点.有意思的是, Mukherjee等人^[45]研究发现当N掺杂多孔碳中出现杂原子Fe时,催化NRR产NH₃速率将降低, HER反应活性增强.这是因为Fe原子与碳骨架中的吡啶氮配位,从而减少了NRR合成NH₃的活性位点.

不同于N, B原子比C少一个电子, B电负性($\chi_B=2.04$)小于C原子.当B掺杂到碳晶格后, B显正电性,可以作为Lewis酸为N₂分子提供空轨道,活化N₂分子,促进N≡N断裂.同时,带正电的活性位点B可有效减少H⁺吸附,从而抑制HER竞争反应,提高反应选择性^[46-49].例如, Yu等人^[46]以硼酸为B源,通过调节硼酸与石墨烯质量比,制备了一系列B种类(B₄C、BC₃、BC₂O和BCO₂)和B浓度(3.0at%~6.4at%)可调的B掺杂石墨烯(BG, 图4(d), (e)).电化学测试研究表明, BG催化NRR活性与B掺杂浓度和种类密切相关(图4(f)). DFT计算表明,掺杂的B浓度越高,碳催化剂表面可提供更多的Lewis酸位,从而有利于N₂分子吸附; BC₃结构可以有效降低NRR决速步骤NH₂*的形成能垒(图4(g)~(i)). B掺杂浓度为6.2at%、BC₃结构比例为60%时,催化剂活性达到峰值, NH₃生成速率为9.8 $\mu\text{g h}^{-1} \text{cm}^{-2}$ 、法拉第效率为10.8%.

除了N、B, 第VI主族非金属元素(O、S、Se、Te)也常被用作掺杂杂原子合成碳基NRR催化剂^[50-53]. Wang等人^[50]以葡萄糖酸钠为前驱体,通过高温热分解合成了O掺杂石墨烯.电化学活性研究表明,该材料催化NH₃生成速率为21.3 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$, 法拉第效率为12.6%. DFT计算表明,含氧官能团降低了NRR决速步骤能垒,提高催化活性及选择性.相似地, S掺杂的石墨烯同样表现出优异的NRR选择性^[51,52],这归因于S原子的引入,使S周围C原子的电子云密度重排,产生非电中性活性位点,进而提高催化活性. Yang等人^[53]以金属有机框架(metal-organic framework, MOF)作为前驱体,通过高温热分解得到多孔碳,以该多孔碳为基底,系统研究了O、S、Se、Te掺杂对NRR性能的影响.理论计算显示,低电负性杂原子($\chi_S=2.5$, $\chi_{\text{Se}}=2.4$, $\chi_{\text{Te}}=2.1$)通过诱导效应使相邻C原子的电子云密度升高,促进N₂吸附;杂原子与骨架C原子电负性差异引起的自旋极化促进

图 4 (网络版彩色)非金属掺杂碳材料结构、性能示意图。(a) N掺杂多孔碳(NPC)示意图。(b) NPC-x样品的N含量和种类。(c) NPC样品NH₃生成速率^[40]。(d) B掺杂石墨烯(BG)材料的氮气升温脱附曲线。(e) BG系列材料的B含量和种类。(f) BG材料的NH₃生成速率。(g) BG材料电子分布图。(h) BG电催化NRR生成NH₃示意图。(i) BG和石墨烯上N₂还原步骤的自由能变火山图^[46]

Figure 4 (Color online) The structures and catalytic performance of heteroatom-doped carbon materials. (a) Schematic illustration for NPCs synthesis. (b) Contents of different N species in NPCs. (c) NH₃ formation rates of NPC samples^[40]. N₂ TPD curves (d), contents of various B types (e), and NH₃ formation rates (f) of BG and G samples. (g) Electron density of BG. (h) Schematic illustration of BG for electrochemical NRR. (i) Free-energy diagrams of BG and graphene samples for NRR^[46]

了NRR催化决速步骤 $\ast\text{NNH}$ 的形成;诱导与自旋极化协同效应使掺杂碳材料有高NRR活性,其中Se和Te电负性低,诱导和极化效应更明显.性能测试表明,Se和Te掺杂的碳材料催化NRR合成 NH_3 法拉第效率分别为4.67%和3.92%,明显高于O(1.16%)和S(1.48%)掺杂碳材料性能.

2.2.2 单金属原子掺杂

由于金属原子与C原子的结合能低,在捕获金属原子之前,首先需要在碳骨架上建立锚定位点.最常见的锚定位点为吡啶型及石墨型N原子,它们分别与2或3个 sp^2 杂化的C原子相连,并在 π 系统中分别提供1或2个电子.局部较高的电子云密度及表面能差异可提高碳表

面对金属原子的锚定能力,从而促进形成金属-氮配位键,增加活性位点稳定性. Geng等人^[54]以含Ru ZIF-8作为前驱体,通过高温碳化将Ru原子锚定在N掺杂的碳骨架上,合成Ru基单原子催化剂(Ru SAs/N-C, 图5(a)).球差校正扫描透射电子显微镜(AC-STEM, 图5(b))和X射线衍射图(XRD, 图5(c))表明Ru以单原子形式均匀分布在碳骨架上,不存在Ru纳米颗粒. X射线近边吸收谱(XANES)和扩展边X射线吸收精细结构谱(EXAFS)研究表明,催化剂中仅存在Ru-N键,不含Ru-Ru键,进一步证明Ru的单原子分布状态(图5(d)-(f)).电感耦合等离子体原子发射光谱(ICP-AES)测试表明催化剂中Ru的含量为0.18wt%. N_2 -TPD曲线证实Ru SAs/N-C对 N_2 分子

图5 (网络版彩色)单原子催化剂结构性能图. Ru SAs/N-C样品合成示意图(a)和HAADF-STEM(b). (c) Ru SAs/N-C和Ru NPs/N-C样品XRD谱图;不同样品的Ru K-edge XANES(d)和EXAFS(e). (f) Ru SAs/N-C样品的Ru K-edge EXAFS拟合曲线. (g) Ru SAs/N-C的氮气升温脱附曲线. (h)不同活性位上氮气还原步骤的自由能变火山图^[54]

Figure 5 (Color online) The structures and catalytic performance of single atom catalysts. The synthetic process (a) and HAADF-STEM (b) of Ru SAs/N-C. (c) XRD patterns for Ru NPs/N-C and Ru SAs/N-C. Ru K-edge XANES (d) and EXAFS (e) spectra for Ru SAs/N-C and a series of control samples. (f) EXAFS fitting result of Ru SAs/N-C. (g) The N_2 -TPD curves for Ru NPs/N-C Ru and SAs/N-C. (h) Free-energy diagrams of the NRR process on different sites^[54]

有强的吸附作用(图5(g)). 当用于电催化NRR合成NH₃时, 在-0.2 V电位下NH₃生成速率为120.9 $\mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}$, 法拉第效率高达29.6%. 高NRR活性得益于均匀分布的Ru原子促进N₂吸附及活化(图5(h)). 类似地, Tao等人^[55]通过高温碳化UiO-66-NH₂合成了Ru基碳催化剂Ru@ZrO₂/NC. 由于UiO-66-NH₂中未配位NH₂可有效稳定RuCl₃前驱体, 从而抑制了Ru原子聚集, 使得88%的Ru原子以单原子状态分布在N掺杂的碳骨架上. 电化学性能研究表明, 在-0.21 V处, Ru@ZrO₂/NC催化N₂生成NH₃速率高达3.665 $\text{mg h}^{-1} \text{mg}_{\text{Ru}}^{-1}$. DFT理论计算显示拥有O空位的Ru位点有利于*NNH吸附, 是催化NRR活性中心.

作为自然界固氮酶活性位点金属之一^[56], 金属Mo用作NRR催化剂的研究吸引了科学家广泛关注^[57-60]. Han等人^[60]以N掺杂的三维(3D)多孔碳为基底, 合成了Mo基单原子催化剂SA-Mo/NPC. EXAFS表明该催化剂中Mo原子以Mo-C或Mo-N键形式存在于碳晶格中, 而且催化剂中不含Mo-Mo键. 在用于电催化NRR时, 该催化剂的N₂还原法拉第效率为14.6% $\pm$ 1.6%, NH₃生成速率为34.0 $\pm$ 3.6 $\mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}$. 除了贵金属(如Ru)、稀有金属(如Mo), 3d过渡金属(如Fe、Co、Ni等)也可被用作NRR催化剂^[61-67]. 例如, Lü等人^[66]以Fe-ZIF为前驱体, 通过高温热解合成了Fe基单原子催化剂ISAS-Fe/NC. 理论计算结果表明Fe-N₄构型有利于N₂吸附及活化. 在-0.4 V条件下, ISAS-Fe/NC催化NRR生成NH₃速率为62.9 $\pm$ 2.7 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$, 法拉第效率为18.6 $\pm$ 0.8%. 有关单原子催化剂的研究, 多以金属-氮或者金属-碳(M-N_x和M-C_x)构型为主, 最近Zhang等人^[67]设计合成了Fe-(O-C₂)₄构型的单原子Fe催化剂(Fe-SAs/LCC). 以0.1 mol L⁻¹ KOH为电解液, Fe-SAs/LCC的NRR法拉第效率为29.3%, 相应的NH₃生成速率为32.1 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$.

2.3 缺陷工程

根据热力学第二定律, 晶体材料中的缺陷是无法完全消除的. 同样, 纳米碳材料在实际制备过程中, 也存在各种类型缺陷. 本文的缺陷工程主要针对纳米碳材料的本征缺陷, 它是指纯碳晶格中存在的缺陷位, 主要包括边缘、空位、孔洞以及拓扑结构缺陷等^[68]. 例如, Stone-Wales缺陷, 它是通过六元环的C-C键旋转90°, 4个六元环变为2个五元环和2个七元环, 形成5-5-7-7结构. 此外, 还有因不同数量原子缺失导致的缺陷,

例如由1个碳原子缺失引起的单缺陷, 2、4、6或8个碳原子缺失引起的缺陷等. 由于纳米碳材料表面缺陷位的局域化电子特性, 其反应活性较高, 因此缺陷位极易被氧化生成稳态或亚稳态的含氧官能团, 这些官能团同样可作为催化反应的活性中心^[69-71]. Zhang等人^[72]以还原的氧化石墨烯(DrGO)为催化剂, 研究了缺陷类型对电催化NRR反应活性的影响. 首先通过DFT计算分别模拟了含有单缺陷位点(SV)、双缺陷位点(DV)以及含羧基官能团位点(-COOH)的DrGO(图6(a)-(c))对N₂化学吸附能力. 研究表明, DrGO-DV吸附N₂的吉布斯自由能为-3.91 eV, 远远低于H吸附自由能(0.52 eV), 因此该材料更有利于N₂吸附及活化. 类似地, DrGO-SV对N₂的吸附选择性超过H, 而DrGO-COOH对二者的吸附差异不明显(图6(d)-(f)). 此外, DFT计算表明, DrGO-COOH和DrGO-DV活化N₂的理论过电位与目前报道的过渡金属基催化剂相当^[73,74], 说明富含该类缺陷位的石墨烯具有高NRR潜力. 为了验证理论推测, Zhang等人^[72]通过在不同温度下高温淬火合成了一系列DrGO材料. 并研究其催化NRR活性. 性能测试表明, 富含缺陷石墨烯样品电催化NRR过电位仅为0.126 V, 远低于相同条件下N掺杂多孔碳(0.38 V), 法拉第效率为10.8%, 与DFT计算结果基本相同.

3 总结与展望

本文从电催化NRR合成NH₃反应机理出发, 介绍了碳基纳米材料的种类和结构, 重点综述了电催化NRR合成NH₃碳基纳米催化剂活性提高策略. 对于杂原子掺杂碳材料, 碳骨架中与杂原子相邻碳的电子云密度和自旋密度将发生极化, 为N₂提供非电中性吸附及活化位点, 从而提高电催化NRR活性及选择性. 对于单原子催化剂, 原子分散的金属中心与N, 或者其他杂原子如O、C等配位, 形成不饱和配位中心, 为N₂吸附及活化提供位点. 对于缺陷工程合成的碳基催化剂, 缺陷位点附近的碳原子都处于不饱和状态, 可以吸附及活化N₂.

目前, 碳基纳米材料作为电催化还原N₂合成NH₃催化剂已极大地提高了该反应的选择性和催化电流密度, 降低了反应过电位. 为了实现工业水平应用, 以下方面仍需进一步探索: (1) NH₃的定性和定量分析. 目前大多数催化剂的产NH₃量与外源性污染NH₃在同一数量级上, 很难确定检测到的NH₃是电催化NRR产物还是源于外源性污染, 因此标准化操作对于排除电催化NRR实

图6 (网络版彩色)富含缺陷位碳材料结构及能级图。(a~c) DrGO上不同缺陷位示意图。(d~f) 不同缺陷位上氮气还原步骤的自由能变火山图^[72]
Figure 6 (Color online) The structures and free energy diagrams of defective carbon materials. (a~c) Atomic configurations with various defect structures for theoretical calculations. (d~f) The free-energy diagrams of NRR on different defect sites^[72]

验中 NH_3 的外源性污染至关重要^[75-77]。首先, 由于 NH_3 极性较强和水溶性高, 导致水溶液中、空气中、实验装置及耗材表面、Nafion膜、含氮催化剂, 甚至实验手套表面都存在 NH_3 污染, 因此在整个电催化合成 NH_3 测试实验中应严格控制实验条件, 降低外源性污染。其次, 如果实验中检测到 NH_3 , 应立即进行两个空白对照实验: 在相同条件下通氩气, 看是否产 NH_3 ; 在相同条件下通氮气但是不施加电位, 如果产生 NH_3 , 证明 NH_3 不是由氮气还原产生的, 是由污染物产生的, 这就是假阳性结果, 要检查可能的污染源。如果对比实验的产 NH_3 浓度远远小于通氩气、加电压时的产 NH_3 浓度, 接下来进行同位素实验, 通入含有 $^{15}\text{N}_2$ 的气体, 比较相同条件下 $^{15}\text{NH}_3$ 与 $^{14}\text{NH}_3$ 生成效率, 进一步检测 NH_3 的法拉第效率及实验的重复性。(2) NH_3 产生速率和法拉第效率。目前催化剂的产 NH_3 量大多停留在 $10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ 量级, 法拉第效率低于10%, 这远低于工业水平的要求值(产 NH_3 量在 $10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ 量级, 法拉第效率高于50%)。因此, 需要开发常温常压条件下可高效地电催化NRR

合成 NH_3 催化剂仍是未来研究的重点之一。(3) 催化活性中心设计和反应机理探究。未来催化剂设计需要依赖多种活性提高策略, 例如对杂原子掺杂材料进一步进行形貌调控, 以暴露更多的活性位点, 促进电子迁移, 并增强反应物和中间体与催化剂结合力。理论模拟和计算是研究反应机理的有效途径和方法, 促进了高效催化剂设计。理论探索可以有效地揭示催化剂活性位点、速控步骤自由能变以及确定可能的反应路径。但是当前的计算研究仍然具有局限性。例如, 电催化NRR还原过程极其复杂, 这将增加模拟结果的不确定性。开发先进的表征手段, 特别是原位表征手段, 对于监测反应中间体的转化和催化剂表面结构的变化至关重要。考虑到反应条件下局部环境、电子性质和催化剂结构信息的潜在变化, 需要使用原位表征技术(如原位XRD和XAS)揭示NRR关键活性相的形成和转变过程。理论计算结合实验数据, 可以对反应过程和结构与性能之间的关系有更深入的了解, 有助于高效催化剂的精准设计。

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补充材料

图S1 不同碳基纳米材料电催化NRR合成NH₃性能

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Summary for “碳基纳米材料电催化氮气还原合成氨研究进展”

The development of carbon-based catalysts for selective electrochemical nitrogen-to-ammonia conversion

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Ammonia (NH₃) has been widely utilized as fertilizer in agriculture and synthetic building blocks for a couple of industrial products. It also works as a carbon-free fuel in internal combustion engines. Therefore, NH₃ is of considerable significance for modern human community with over 160 million tons synthesized every year. However, NH₃ synthesis was commonly carried out by the energy-intensive and fossil fuel-dependent Haber-Bosch process where the high-cost of clean and pure H₂ produced from fossil fuel resources and huge energy inputs are needed. In addition, only 10%–15% NH₃ conversion efficiency can be achieved by single reaction even at the pressures as high as 40 MPa. The harsh reaction conditions and relatively low conversion efficiency as well as the valuable and fossil fuel-dependent reactant of H₂ cause the Haber-Bosch process to be currently one of the largest global energy consumers and greenhouse gas emitters, contributed to 1.2% of the global anthropogenic CO₂ emissions. In this regard, it is of great importance to develop alternative sustainable approaches for NH₃ synthesis with cheap and abundant H resources (e.g., H₂O) under mild conditions.

Electrochemical nitrogen reduction reaction (NRR) to NH₃ under mild conditions powered by renewable electricity is a potential alternative to the energy-intensive and fossil fuel-dependent Haber-Bosch process. The intrinsic inertness of N₂ molecule and competition of hydrogen evolution reaction (HER) in aqueous solutions are the major challenges for electrochemical NRR. In order to overcome obstacles and facilitate this sluggish reaction, extensive attentions have been given to explore efficient and robust electrocatalysts. Although transition metal-based catalysts can solve the kinetic limitation of N≡N activation through the π -back donation process, the d-orbital electrons in transition metal atoms also favor the formation of metal-H bond and therefore boost the undesired HER side reaction. Carbon-based materials featuring the tunable electronic structure, controllable electronegativity of carbon frameworks, and easy-making defects have significant potentials in catalyzing NRR. In fact, the strategies including doping with heteroatoms, creating defects, and surface functionalization have been widely used to improve the electrocatalytic NRR activity of carbon-based electrocatalysts in the past few years. However, the development in this topic is limited to the following issues: (1) The current research on carbon-based NRR electrocatalysts is case-by-case and lacks comprehensive and systematical talking; (2) the structure/composition-performance relationships are yet well understood and regularities in catalyst design are still not established. Therefore, a review on state-of-the-art carbon-based materials for NRR is urgently needed to provide coverage of recent advances in both theoretical and experimental aspects. Here, we review the state-of-the-art research advancements in carbon-based materials for electrochemical NRR under ambient, in the perspective of different strategies for efficient catalyst design, including heteroatom doping, edge site and topological defects, metal single atoms coordinated with nitrogen or other heteroatoms in carbon matrix. More importantly, the intrinsic relationships between the structures/configurations of the defective carbons and the NRR performance are discussed in detail, both theoretically and experimentally. After that, a summary is finally provided together with personal perspectives on critical challenges and future possible trends in the field. This review will provide an overall and prompt understanding on the recent development of carbon-based materials for NRR, which will shed new light on the advancement of this prosperous field.

electrocatalysis, nitrogen reduction, ammonia synthesis, carbon-based nanomaterials, defect engineering

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