



·前沿技术与交叉科学·综述·

液相等离子体及其在纳米材料制备中的应用*

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摘 要: 液相等离子体是冷等离子体的一个新分支, 具有温度低、传质传热快、常压操作、反应活性高等特点。基于液相等离子体的过程强化技术在纳米材料制备、挥发性有机物降解、杀菌消毒、化学合成等领域有广泛的应用前景。以液相等离子体中纳米材料的制备为研究对象, 介绍了反应体系可能存在的活性粒子、检测方法和反应机理; 对常见的反应器结构进行归纳整理, 按照放电是否在电解液内部进行将其分为非浸没式和浸没式液相等离子体两大类, 并列举了几种典型的反应器结构; 介绍了几类利用液相等离子体技术制备纳米材料的典例, 并对该领域的研究现状做了总结; 对该领域亟需解决的问题与发展方向进行讨论与展望。

关键词: 液相等离子体; 等离子体设备; 纳米技术; 等离子体-液相作用; 纳米材料

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Liquid plasmas and their applications in nanomaterial synthesis

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Abstract: As a new branch in non-thermal plasmas, plasma-liquid technology is characterized by low temperature, mass and heat transfer effectiveness, atmospheric-pressure operation and high reactivity. Process intensification techniques based on liquid plasmas have wide applications in nanofabrication, volatile organic compounds decomposition, sterilization and disinfection, chemical synthesis, etc. Taking the synthesis of nanomaterials by the liquid plasma as the research object, firstly, the reactive radicals that may exist in the system are introduced, together with the relevant characterization methods and possible reaction mechanisms; afterwards, the most widely adopted plasma-liquid systems are illustrated, which can be divided into non-immersed systems and immersed systems according to whether plasma is formed within the bulk of electrolytes; furthermore, several typical examples of nanomaterials synthesized by the plasma-liquid method are presented, with a summary of the state-of-art research in this field, finally, the challenges and development trends are discussed.

Key words: liquid plasmas, plasma equipment, nanotechnology, plasma-liquid interaction, nanomaterials

纳米科技的发展不断促进纳米材料在各个领域的应用, 其中在生物医学领域具有广阔的应用前景^[1], 如体内成像、靶向药物、生物传感器、病毒检测等。尽管近年在纳米材料的可控制备、反应机理、构效关系和应用等方面都取得了很大进展, 但制备过程仍存在一些不足。比如, 化学法^[2]普遍耗时长、工艺繁琐、条件苛刻, 且在制备过程中通常需要使用大量的化学还原剂和稳定剂, 其毒性和不易清洗等问题给纳米材料的应用带来潜在风险, 尤其在生命科学领域。物理法^[3]相对简单, 但通常能耗大, 对设备要求高, 所得到的产物粒径分布宽, 可控性差且易团聚, 很难用于临床试验研究。因此, 就现有技术而言, 简单高效、环境友好地制备粒径小、均一性好、性能可控的纳米材料仍非常具有挑战性。

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等离子体称为物质的“第四态”^[4],由大量离子、电子、中性分子、亚稳态基团、自由基、光子等组成。这些活性粒子之间的协同作用不仅能加快反应速率,而且能引发一些传统化学中难以发生的反应。因而等离子体可作为一种高效的过程强化介质。此外,等离子体本身不消耗额外的化学物质,也不产生化学残留物,为各类反应提供一个绿色高效的媒介。鉴于上述优点,等离子体已应用于臭氧制备、材料表面处理、挥发性有机物(VOCs)降解、冶金、煤化工等领域^[5]。

作为等离子体技术的一个新分支,液相等离子体近年备受关注。它指在液体或液体表面产生,作用于液相上的等离子体技术,有着比气相等离子体更多种类的活性物质^[6],如 OH^\cdot , OH^- , H_2O_2 , NO_2^- , NO_3^- , O_3 等。这些液相活性粒子能进一步拓展等离子体的应用范围,如杀菌、废水处理^[7]、固氮、水活化等。邓康等人^[8]利用脉冲电弧液相放电技术对污水进行灭菌处理,发现灭菌强度不仅与脉冲放电次数有关,而且与放电间距、等离子体功率等因素也密不可分。Sankaran 等人^[9]对等离子体辅助固氮进行总结,并讨论了以水和 N_2 为氮源,连续化生产氨、硝酸盐、亚硝酸盐。在纳米材料制备中,液相等离子体也呈现出很多显著优点,如液相温度低,散热快,能有效抑制纳米粒子间的团聚,得到粒径更小、均一性更好的产品,前驱体的选择范围更广;如可通过高能电子还原贵金属离子得到贵金属及其合金纳米颗粒,避免使用传统的化学还原剂以及后续繁琐的提纯工序。

鉴于液相等离子体的特性及其在纳米材料合成中的优势,整理归纳了近年国内外有关液相等离子体制备纳米材料的报道。首先介绍液相等离子体的特点和优势,并对可能存在的活性粒子种类、相关检测方法和反应机理进行总结。其次,根据是否在液相内部放电将等离子体分为非浸没式和浸没式两大类,并介绍一些典型的反应器结构。接着,列举了几个液相等离子体制备纳米材料的典例,探讨制备过程中的一些共性方法。最后,对该技术存在的挑战及发展前景做出展望。

1 液相等离子体的特点

液相等离子体放电涉及一系列传质、传热、流动及复杂的物理、化学过程,且存在大量活性粒子。要灵活运用该技术,必须对液相放电的特点、活性物种和检测方法、反应机理等有较好地了解。图 1 显示非接触式液相等离子体中有可能进行的传递、反应和存在的活性物组分^[10]。其中,高能电子 e^- 是等离子体最重要的活性物,在强电场的作用下,它会与空气和溶液中的水分子和氧气、氮气发生作用并引发一系列解离和电离反应,生成 H^\cdot , OH^\cdot , OH^- , H_3O^+ , O^\cdot , O_2^- 等自由基以及 H_2O_2 , NO , NO_2 , O_3 等强反应活性物,同时自身也会与液相主体形成水合电子 $e^-_{(\text{aq})}$ 。此外, NO , NO_2 等物质也会与溶液反应生成 NO_2^- , NO_3^- 等,起到固氮作用。

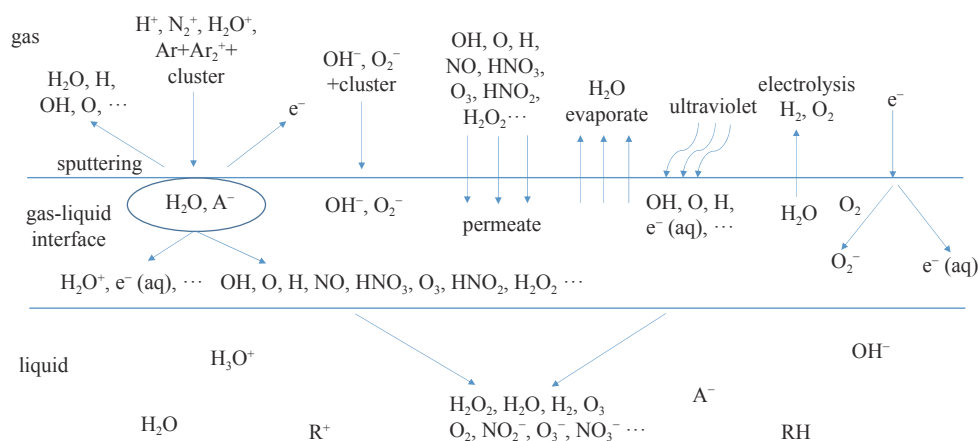


Fig. 1 Schematic diagram of mass transfer, reaction and active components that may exist in non-contact liquid plasma^[10]

图 1 非接触式液相等离子体中可能存在的传质、反应和活性物组分示意图^[10]

液相等离子体中的活性物是引发化学反应的主要物质,但由于其活性强、浓度低、寿命短等特点,常规方法难以进行鉴定,定量测量则更为困难。随着检测技术的不断完善,越来越多的检测方法运用到液相活性粒子的检测中,如电子自旋共振(EPR)技术、高效液相色谱(HPLC)、荧光光度法、荧光探针法、化学显色法、同位素标记法^[11]等。几十年前 Rabani 等人^[12]便通过脉冲辐射实验和含有亚硝酸根阴离子的 $\text{C}(\text{NO}_2)_3$ 特定吸收峰来验证水合电子的存在和含量, Patrick 等人^[13]又对此测量方法进行优化,使得对水合电子含量的检测更为准确,并发现水合电子具有高斯红边和洛仑兹蓝边的特征,且在 720 nm 左右的强吸收光谱具有特殊的形状。

此外与液体中活性物相关的反应也逐渐剖析, Hart^[14]发现水合电子是高能电子轰击液体表面所产生的二次电

子与水结合形成,并具有很强的还原性,高能电子还会造成液体中分子裂解;在此基础上Chen等人^[15]通过光发射光谱探测到水分子在液面附近分解为H原子和OH自由基。Locke等人^[16]对H₂O₂的形成进行了系统的总结,除OH·之间相互结合外,还能通过如OH与H₂O·相互结合、H₂O·之间相互结合等许多不同的途径诞生;并详细阐述了影响H₂O₂存在的主要因素,如不同激发气体、放电方式和气液传质特性等。表1总结了国内外报道的关于液相等离子体中的活性粒子的检测方法、各自的优缺点以及相关反应^[17-49]。这些检测技术的发展和成熟以及对活性物反应的明晰能加强人们对液相等离子体的认识,为相关的理论和应用研究打下基础。

表1 液相等离子体中常见自由基的检测方法及相关反应

Table 1 Detection methods and related reactions of common free radicals in liquid plasma

species	detection method	advantages and disadvantages	correlation reaction	references
hydrogen peroxide (H ₂ O ₂)	(1) titanium sulfate reagent colorimetry (2) colorimetric or fluorometric analysis	(1) less interference, good stability, but limited sensitivity	OH + H ₂ O· → H ₂ O ₂ + H ₂	[17]
		(2) many interference factors (such as air, pH, solvent, etc.), but high sensitivity, lower detection limit ~ 10 × 10 ⁻⁶	O ₂ + 2H ⁺ + 2e ⁻ → H ₂ O ₂	[18]
			H ₂ O ₂ + H ⁺ + e ⁻ → H ₂ O + OH	[19]
hydrogen atom (H)	(1) EPR technology (2) isotope labeling	(1) high sensitivity, low detection limit, easy decomposition of the product, requiring excess capture agent		[20]
		(2) the source, distribution and chemical reaction of H atoms can be explored, but it is usually used in conjunction with the EPR method	H ⁺ + e ⁻ → H	[21]
				[22]
hydroxyl radicals (OH·)	(1) EPR technology (2) HPLC method (3) spectrophotometry	(1) high sensitivity and low detection limit, the most ideal method for the determination of hydroxyl radicals, the instrument is expensive, the choice of capture agent is critical		[23]
		(2) easy to implement, but its sensitivity and accuracy are still insufficient	H ₂ O → H + OH·	[24]
		(3) easy to operate, has high selectivity, and is not easily affected by other ions at specific wavelengths; insufficient accuracy and sensitivity, requires the capture agent or the adduct product with the hydroxyl to have characteristic fluorescence	OH· + H ⁺ + e ⁻ → H ₂ O	[25]
				[26]
superoxide anion (O ₂ ⁻)	(1) EPR technology (2) fluorescent probe method	(1) high sensitivity, low detection limit, expensive instrument		[27]
		(2) easy to operate, lower instrument price, but the sensitivity is low, and it is interfered by particles like H ₂ O ₂ , OH·	2O + H ₂ O + e ⁻ → H ₂ O + O ₂ ⁻	[28]
				[29]
ozone (O ₃)	(1) spectrophotometry (2) fluorescent probe method	(1) the operation is simple and fast, but the sensitivity is low, and it will be interfered by other oxidants		[30]
		(2) good selectivity, but it needs to be in a specific pH range; when pH ≥ 10, the probe will be destroyed in H ₂ O ₂	O ₃ + 2H ⁺ + 2e ⁻ → O ₂ + H ₂ O	[31]
				[32]
nitric oxide (NO)	(1) EPR technology (2) spectrophotometry (3) fluorescent probe method	(1) high sensitivity, low detection limit, wide application, but need to avoid oxidation of Fe ²⁺ particles in the reagent		[33]
		(2) easy to operate, instrument is relatively cheap, and the aqueous solution to be tested needs to be acidified in advance before the test	4NO + 2O ₂ + 2H ₂ O →	[34]
		(3) has good selectivity, but the pH of the aqueous solution to be tested needs to be higher than 5.5	4NO ₂ + 4H ⁺	[35]
				[36]
nitrite (NO ₂ ⁻)	(1) spectrophotometry (2) HPLC method	(1) the operation is simple and fast, but the sensitivity is low, and it will be interfered by other oxidants	2HNO ₂ → NO + NO ₂ + H ₂ O	[37]
		(2) easy to implement, but its sensitivity and accuracy are still insufficient	NO ₂ ⁻ + H ⁺ → HNO ₂	[38]
nitrate (NO ₃ ⁻)	(1) spectrophotometry (2) HPLC method	(1) the operation is simple and fast, but the sensitivity is low, and it will be interfered by other oxidants		[39]
		(2) easy to implement, but its sensitivity and accuracy are still insufficient	NO ₂ ⁻ + OH· → NO ₃ ⁻	[40]
				[41]
peroxynitrite (ONOO ⁻)	(1) colorimetric or fluorometric analysis (2) chemical reaction (3) fluorescent probe method	(1) multiple interference factors, extremely sensitive to light-induced oxidation, and specificity problems		[42]
		(2) the existence of ONOO ⁻ can only be indirectly proved by the concentration decay of NO ₂ ⁻ and H ₂ O ₂ , and the accuracy is insufficient	NO ₂ ⁻ + H ₂ O ₂ →	[43]
		(3) low selectivity, interfered by particles like H ₂ O ₂ and HClO, in the absence of HClO, the selectivity is enhanced	ONOO ⁻ → NO ₃ ⁻	[44]

续表 1 Table 1 continued

species	detection method	advantages and disadvantages	correlation reaction	references
peroxynitric acid (O_2NOOH)	(1) HPLC method	(1) easy to detect, but the sensitivity is low, the detection environment requires low temperature and low pH value	$NO^3+H_2O_2 \rightarrow O_2NOO \rightarrow H_2O$	[45]
singlet oxygen (1O_2)	(1) EPR technology (2) fluorescent probe method	(1) good selectivity, high sensitivity, not affected by other free radicals, the detection reagent has a strong pungent odor and is easily oxidized in the air (2) the probe acts as a photosensitizer to generate singlet oxygen, and the probe is destroyed in hydrogen peroxide	$O_2+e^- \rightarrow ^1O_2+e^-$ $2^1O_2+2H^+ \rightarrow H_2O_2+O_2$ $^1O_2+H_2O_2 \rightarrow OH \cdot +OH \cdot +O_2$	[46] [47] [48] [49]

液相等离子体制备纳米材料最常见的反应体系是由贵金属离子溶液制备贵金属纳米颗粒,其反应机理如图 2 所示。等离子体中的自由电子在强电场力的驱使下进入溶液,根据 Mohan 等人^[50]的报告,其进入深度可达~10 nm。这些电子与水分子作用形成水合电子 $e^-_{(aq)}$,它们极不稳定且有很强的还原性,能将贵金属离子(M^+)快速还原成相应的金属原子(M^0)。由于金属原子具备很大的比表面积和能量,相互间非常容易团聚成原子簇团,同时为其他原子的团聚充当“核”的角色。在此基础上,原子簇团不断生长聚集,最终形成了贵金属纳米颗粒。在液相中形成的纳米粒子仍保留一定的电荷并相互排斥,使贵金属纳米粒子能均匀稳定地分布在溶液中,且抑制纳米颗粒的进一步生长。因此,该方法较传统的制备方法具有很高的效率,且获得产物纯度高、粒径小。

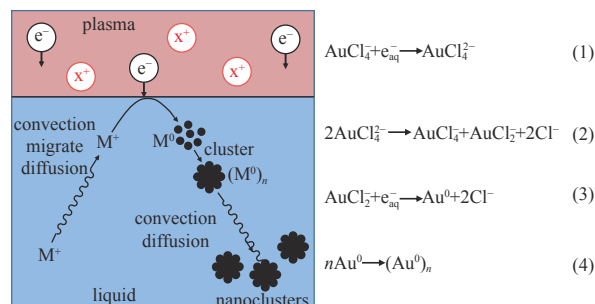


Fig. 2 Mechanism schematic diagram of liquid phase plasma system preparation of metal

图 2 液相等离子体制备贵金属机理示意图

2 典型液相等离子体反应器结构

目前,国内外已经研发了系列液相等离子体制备纳米材料的反应设备,它们有很多的分类方法,如按照电源种类可分为直流放电、交流放电、射频放电、脉冲放电等;按照等离子体工作气可分为空气、氩气、氧气、氮气、氦气等;按照放电方式可分为介质阻挡放电(DBD)、辉光放电、电晕放电、滑动电移弧放电、微波放电等类型。为简便形象地描述液相等离子体设备,在此按照放电是否在液相内部进行将其分为非浸没式和浸没式液相等离子体。

2.1 非浸没式液相等离子体

此类液相等离子体设备通常是将含有反应物的盐溶液作为电解液,并将一个电极浸于溶液内部,另一个电极在液体上方,2个电极分别与地线和高压电源相连接。通电后在电解液表面和高压电极之间形成等离子体。与此同时,工作气体不断输入等离子体区域,经电离产生高能电子,并进入电解液与金属离子反应生成相应产物。图 3 列举了该系列常用的液相等离子体结构,包括 DBD 等离子体^[51]、滑移弧等离子体^[52]、微等离子体^[53]、双电极等离子体^[54]等设备。目前运用此类液相等离子体已成功合成一系列纳米材料,如 Ag^[55]、Au^[56]、Ni^[57]、Fe^[58]等金属纳米单质和铁镍合金^[59]、金银合金^[60]等相应的金属合金纳米材料。

辉光放电等离子体作为制备纳米材料领域的新方法,可大规模应用于胶体纳米材料的工业生产。此类设备可在低压、高温条件下进行冷等离子体电化学反应。由于优异的导电性使得电子传递过程增强,导致活性物种可以快速地与选定的目标分子反应。介质阻挡放电因其较大的接触面积,一般用于表面改性、气体裂解、材料清洁以及纳米合成,其优势在于操作简单、常压运行、设备成本低,无需加入额外试剂控制纳米材料形成,产品纯度高。气液界面等离子体可在溶液上方产生空间和时间稳定的直流放电,与传统的放电系统相比,该方法可以有效合成尺寸和产量可控的金属纳米粒子。微等离子体可将放电限制在一个亚毫米尺度内,由于极小的电极间距和极大的比表面积,微等离子体不仅兼具常规等离子体的准电中性、复杂的集体效应等特征,同时还具有体积小、活性粒子密度高、易集成等优势,在纳米制备及其他领域都表现巨大的应用前景。

在非浸没式液相等离子体结构中,滑移弧等离子体和双电极等离子体具有独特的电极结构。Acayanka 等人^[52]运用滑移弧等离子体结构在常压下以 $TiCl_3$ 溶液作为前驱体,利用 $OH \cdot$ 和 NO 自由基从水性介质中氧化合成直径为 5~15 nm 的 TiO_2 纳米晶体。双电极等离子体与传统液相等离子体在结构上有很大不同,该反应器具有 2 个辉光放电电极,阳极将正离子辐射到溶液表面,阴极将电子辐射到溶液表面,合理利用阴阳电极活性物质的差异,对于复合材料的合成有着十分重要的作用。如 Shirai 等人^[54]利用双电极等离子体装置,从 $AgNO_3-HAuCl_4$ 和十二烷基

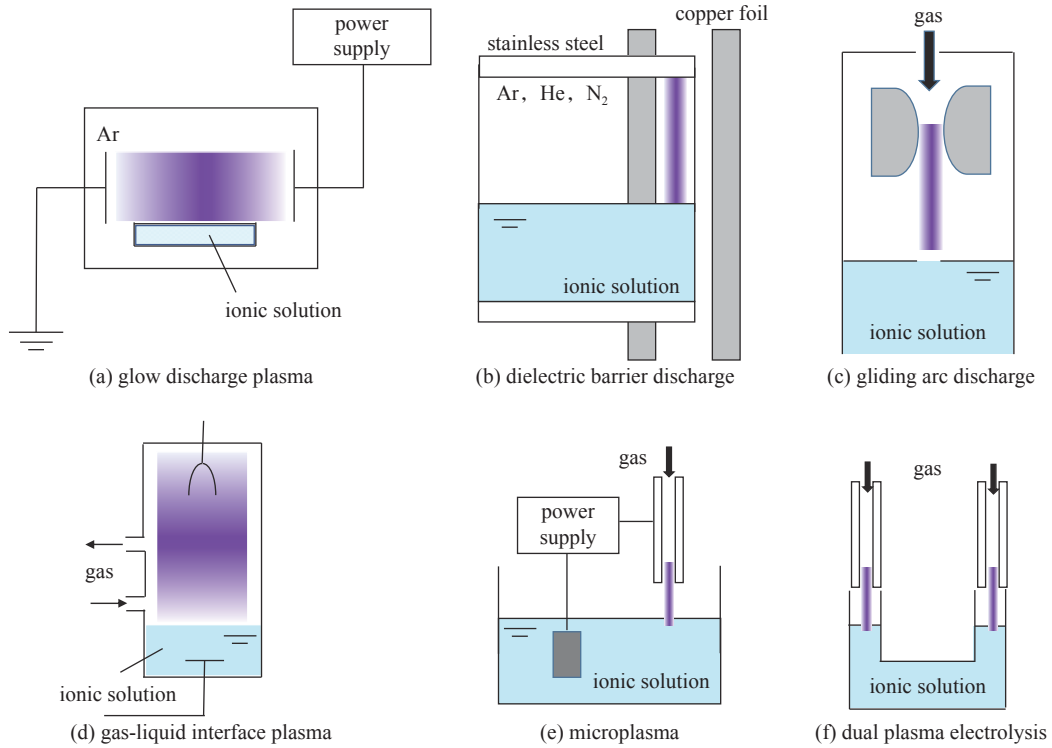


Fig. 3 Non-immersion liquid phase plasma^[61]

图 3 非浸没式液相等离子体设备^[61]

硫酸钠(SDS)的混合溶液中成功制备了金核-银壳结构的纳米颗粒,并指出 SDS 浓度和金银离子浓度比都是影响其核壳结构形成的重要因素。

常见的非接触式等离子体又因电极差异可细分为板式和针式电极,如图 4 所示。板式电极处理面广,纳米颗

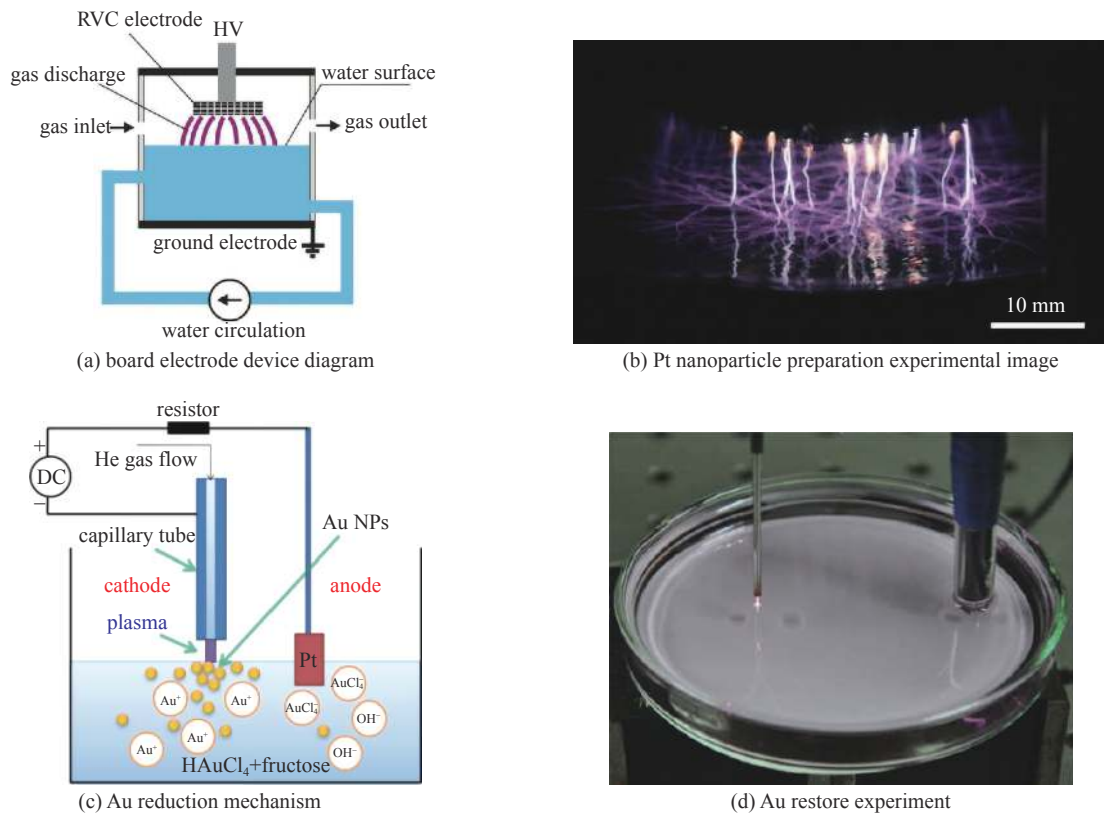


Fig. 4 Schematic of non-immersion electrode structure^[62-63]

图 4 非浸没式电极结构示意图^[62-63]

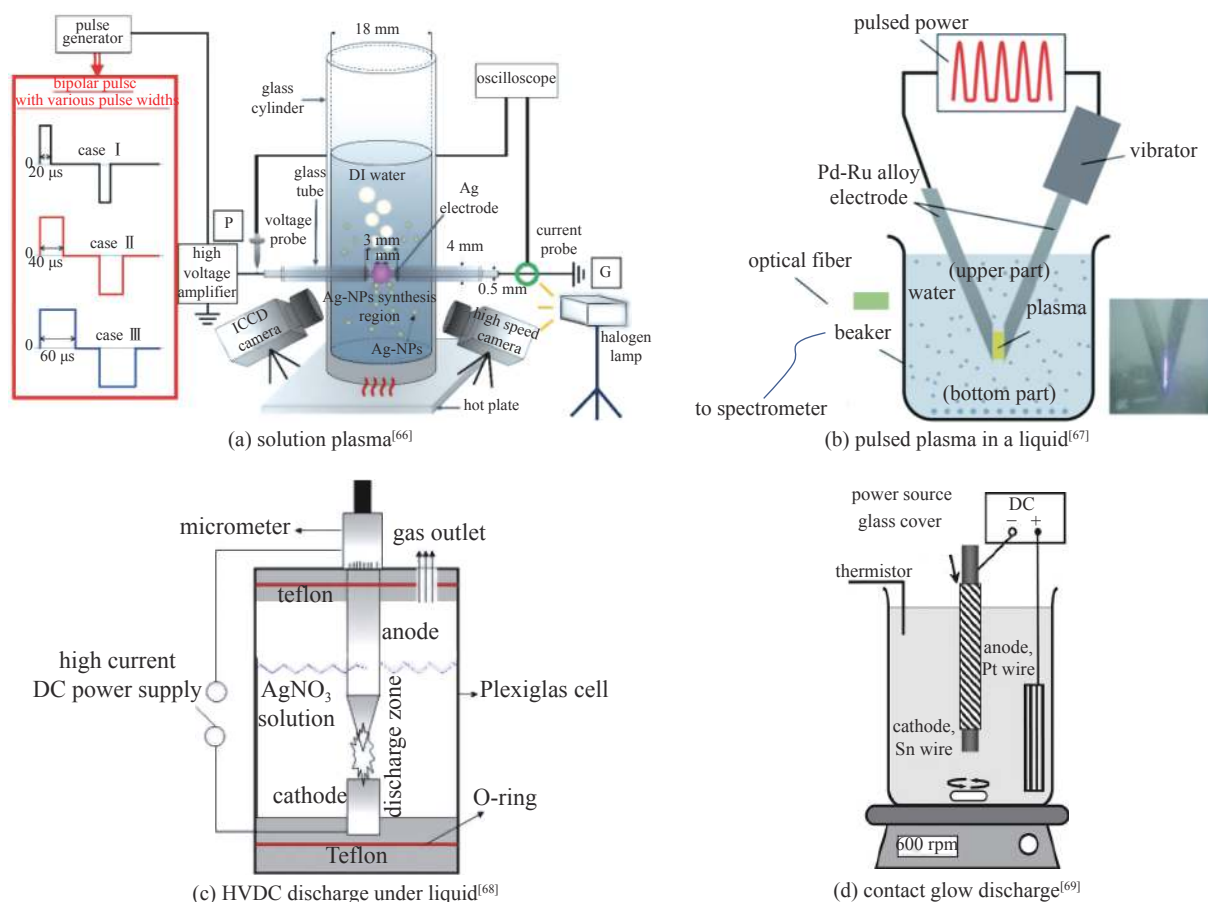
粒分散均匀不易聚集。Kaneko^[62]利用平板式等离子体的装置(图4(a)、图4(b))合成了分散均匀、直径为1~2 nm的铂纳米颗粒。在该研究中反应器的阴极为直径15 mm的圆形铂片,阳极为相同直径的不锈钢(SUS)板,电极间距70 mm,将阴极固定在直径为20 mm,深度为10 mm的玻璃池中。与此同时,在反应体系加入1-丁基-3-甲基咪唑四氟硼酸盐作为离子液体, PtCl_2 作为铂源。结果发现,放电电弧均匀分散在电解液和高压电极的任意位置,随输出功率增加,水合电子、氢自由基等活性物浓度增大, Pt 离子的还原速率加快。因此,运用该液相等离子体设备制备纳米颗粒可以有效控制其反应速率和尺寸。

针式电极是另一种常见的非浸没式等离子体电极结构,如图4(c)、图4(d)所示。与平板式放电相比,针式放电能量比较集中,可以在较低能耗下产生局部高浓度活性物质,缩短反应时间。Huang 等人^[63]运用非浸没式针状放电装置从氯金酸溶液中成功制备出金纳米颗粒。该装置分别采用不锈钢毛细管(内径180 μm ,长5 cm)和铂箔(1 cm \times 1 cm)作为阴阳电极,并将铂电极浸入溶液中。不锈钢毛细管置于电解液液面上方2 mm处,接通电源后,在不锈钢电极尖端和溶液界面之间形成等离子体区域,随反应进行,溶液颜色迅速变红。此外,经实验发现金纳米颗粒的尺寸受还原电流、温度、搅拌作用的影响。随电流增大,更多电子进入溶液附着在金纳米颗粒上,在静电斥力的作用下,金纳米颗粒的聚集和生长受到抑制,导致尺寸偏小;随温度升高,大尺寸金纳米颗粒增多;搅拌作用的存在使得金纳米在界面停留时间缩短,有利于制备尺寸细小、均一的纳米颗粒。

2.2 浸没式液相等离子体

浸没式液相等离子体是指在液体内部产生放电的一系列等离子体结构(见图5),包括液相脉冲等离子体、液下高压直流放电、接触辉光等离子体、空心阴极等离子体等设备。该类等离子体电极都浸没在电解液中且距离可变、形式多样。常见的液相放电发生在针对针或针对板电极之间,在这种结构中放电是高动态、瞬时的,往往需要一个快速的击穿过程。这个击穿过程可以由强电场来驱动,也可以通过气泡内爆^[64]或高压脉冲^[65]实现。一种常见的产生电流的方法是通过一个瞬时开关(如电火花空隙)给电容器放电,产生微秒脉冲放电。当电流在液相中形成,溶液由于电解和蒸发产生蒸汽层,等离子体在蒸汽层内形成。

溶液等离子体^[66]作为非平衡等离子体可以在溶液中快速产生活性物,促进纳米颗粒迅速合成。与大气等离子体相比,具有能量高,外界影响因素少等优势,可直接合成各种纳米材料,但纳米颗粒的形貌受气泡影响严重,需



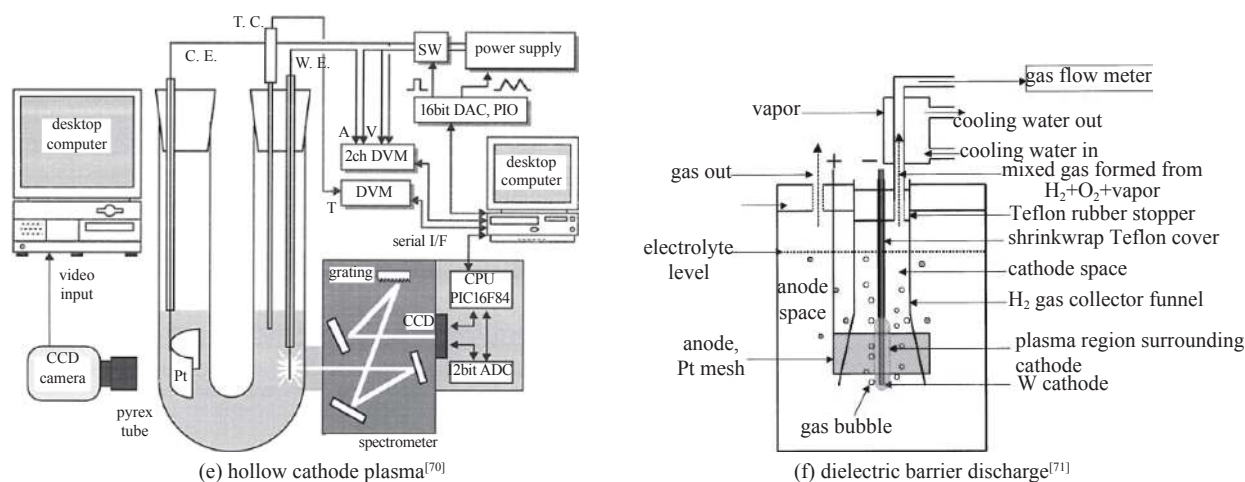

 Fig. 5 Diagram of submerged liquid plasma equipment^[66-71]

 图 5 浸没式液相等离子体设备^[66-71]

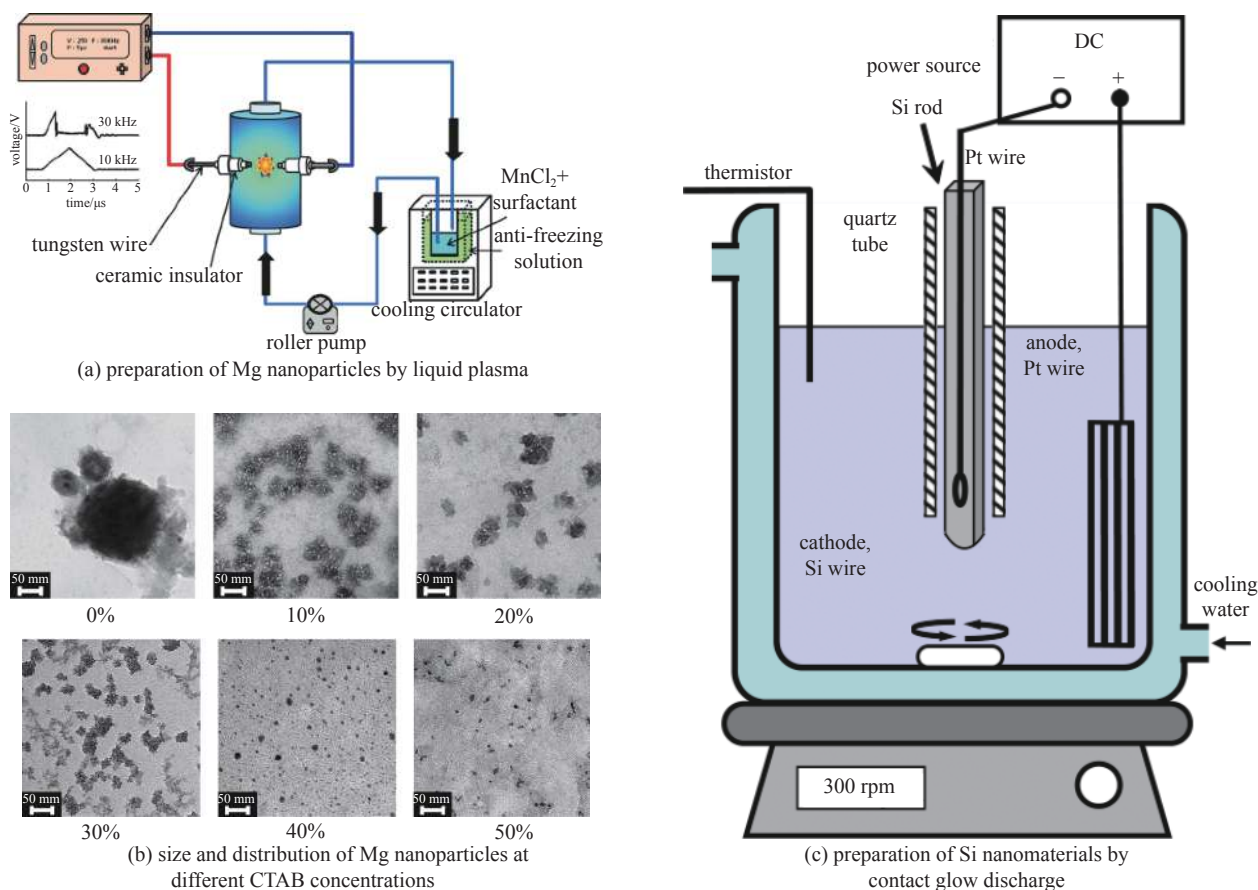
实时观测液体内部气泡形成的变化。液相脉冲等离子体^[67]所制备纳米材料具有高表面积、高分散性以及高表面能等特性，且纳米材料在单次脉冲中产生，由于极短的反应时间和周围冷液体的猝灭效应，使其能够获得非常小、晶型可控的亚稳态的粒子。液下高压直流放电^[68](HVDC)具有设备简单、杂质引入少、不需要真空设备、生产步骤少、高通量和低成本等优点，在大规模生产纳米材料领域具有一定的可行性。接触辉光放电设备^[69]在工作时电极表面形成了高温等离子体鞘层，鞘层中元素在高温下解离，导致非法拉第过程的反应产物形成，且溶液电导率对接触辉光等离子体有较大影响，高电导率溶液所制备纳米粒子尺寸较大，因此该方法常用于胶体溶液中制备纳米材料和污水净化。空心阴极等离子体^[70]与介质阻挡放电^[71]可在反应器中连续生产纳米材料，但由于产生的辉光等离子体不能有效还原溶液中的金属离子，因此通常采用固体电极作为合成纳米材料的原料，且在周围溶液的猝灭效应下很难制备复合材料。

液相等离子体是典型的针对针放电，该技术可以产生相互对称的等离子体，并能及时清除电极附近形成的产物，确保等离子体稳定运行，如图 6(a)所示。Kim^[72]运用外径 40 mm、高度 80 mm 的环形管式反应器从氯化锰溶液中成功制备锰纳米颗粒，液相脉冲等离子体在具有陶瓷绝缘体涂层的钨电极(直径 2 mm)之间产生，电极间距为 0.3 mm。研究发现，增加等离子体处理时间(30~60 min)，锰纳米颗粒的形貌从球形逐渐转变为四方晶体。此方法产生的电弧集中在电极区域，纳米颗粒团聚较严重。Saito 等人^[61]就此问题提出了两种解决方法：①将阳极尖端用玻璃管屏蔽，避免产生不均匀电场；②采用金属板电极替换针状电极，可有效分散电流强度。此外，加稳定剂也是常见的方法，如图 6(b)所示，加入十六烷基三甲基溴化铵(CTAB)稳定剂，所获得的纳米颗粒具有更好的分散性和更小的尺寸。

针对板电极可用于接触辉光放电结构中，如图 6(c)所示，Genki 等人^[73]运用接触辉光放电技术以硅棒电极为原料一步合成了硅纳米颗粒。他们针对不同电解液和外加电压对产物的影响做了研究。结果表明，在 0.1 mol HCl 或 HNO₃ 溶液中生成的硅纳米既有无定形颗粒，也有多晶颗粒，其中较小的纳米粒子倾向于无定形态，当使用 0.1 mol K₂CO₃ 溶液时，由于高温碱性气体对 Si 的刻蚀，会生成非晶态的 SiO₂ 颗粒。等离子体激发温度随外加电压的增加而升高，颗粒尺寸也会随之增大。他们也用类似的方法成功制备了 Ni-Cu^[74] 双金属纳米和 Sn^[75] 纳米。

与非浸没式等离子体相比，浸没式等离子体具有两个突出特点：一是可以用固体电极作为纳米合成的原材料。Takai 等人^[76-77]尝试以金属丝电极为原料，采用液相脉冲等离子体装置在大气压下制备了球状(1.25, 0.5 nm)、晶型良好的纯金团簇。该方法可以在不加入添加剂的情况下成功制备纳米颗粒，具有高效、稳定的优势，且有固体电极的存在，使得高纯度的纳米材料可以在蒸馏水中形成。二是可以合成一些非浸没式结构无法合成的纳米材料，如碳纳米^[78]和石墨烯层^[79]。

除了高压电源外，微波和激光等也可以作为液相等离子体的能量源^[80]，且逐渐运用到纳米材料的合成中。由于制备过程中产物和电极可以完全不接触，因而这些方法得到的产物不含杂质，在制备极高纯度的纳米材料方面有很大的应用前景。需要注意的是，这些方法对设备和操作要求较高，还未广泛应用。

Fig. 6 Structure diagram of immersed plasma electrode^[72-73]图 6 浸没式等离子体电极结构图^[72-73]

3 液相等离子体制备纳米材料典例

纳米材料由于独特的性质成为了研究热点,而液相等离子体由于操作简单,产物纯度高,生产纳米材料尺寸、形貌可控等优点,近年来运用其合成纳米材料的研究热度越来越大,关于液相等离子体合成纳米材料的领域也不断拓宽。本节将根据纳米材料的种类,介绍几类基于液相等离子技术制备的纳米材料,如图 7 所示。

3.1 贵金属纳米材料

由于贵金属离子容易被电子还原,且能稳定地存于液相中,已出现不少有关液相等离子体制备贵金属纳米材料的报道,如金^[81]、钯^[82]、铂^[83]、银^[84]及其合金等贵金属纳米颗粒。常见液相等离子体技术制备贵金属纳米材料的方法有两种:一是以含有氯化物或硝酸盐离子的前体充当电解液,如 Yan 等人^[60]对金银合金纳米颗粒的制备,该方法以不锈钢管为阴极,铂片为阳极,金属盐/稳定剂混合物为反应液,在液相中成功合成了粒径为 10~12 nm 的金银合金颗粒。该方法能耗低,可制备均一性良好、金银配比可控的合金纳米材料,但是只能间歇性制备,需要对电解液频繁更换。二是以金属电极作为原料来源,以金铂合金的制备为例, Hu 等人^[85]运用液相脉冲等离子体技术,反应器阴阳两极分别使用不同类型的金属棒,在外加电压作用下,溶液中发生溅射放电,产生了大量高能离子和自由基粒子(如 H^+ , $OH\cdot$, O_2^- 等),随高能自由基粒子的轰击,金和铂原子从固体电极对的尖端喷入等离子体区域,在等离子体的持续作用下,金铂原子达到过饱和状态,从而在溶液中聚集团簇成纳米颗粒。该方法不用引入化学试剂(如表面活性剂、稳定剂、还原剂等),产品纯度高,但存在较大的温度梯度难以控制粒子粒径大小。因此如何连续可控制备出高性价比、高纯度的贵金属及其合金是目前研究的关键。

3.2 金属纳米材料

镍、铜、铁、锡等金属纳米材料不稳定,制备时易氧化。利用液相等离子体技术制备金属纳米材料,反应迅速高效,可避免氧化过程的发生,此外,溶液的散热作用使得这类纳米材料具有窄的粒径分布。为了合成这类金属纳米材料,试验条件也需经过精心优化。如 Xie 等人^[86]运用液相脉冲放电技术,使铜电极中的铜原子分散在 CTAB 和抗坏血酸溶液中,成功制备出粒径 10~15 nm 的铜纳米颗粒。Saito 等人^[75]也通过类似的方法,以锡棒作为电

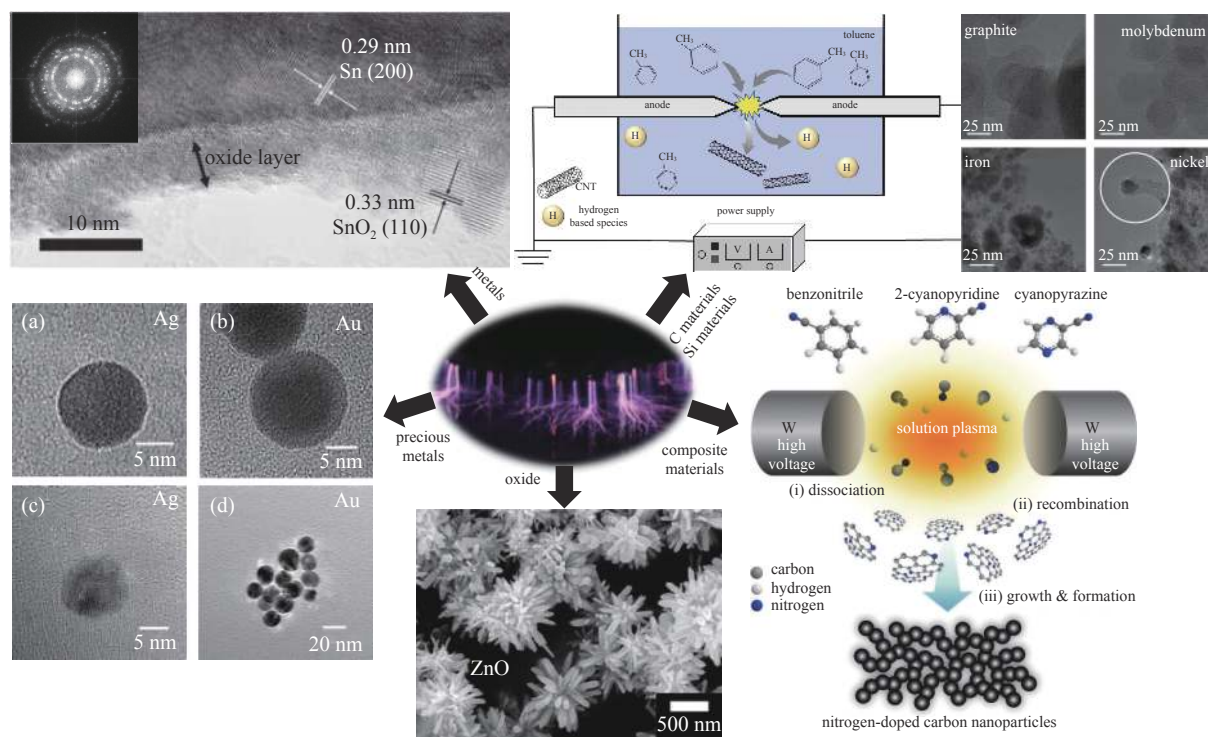


Fig. 7 Typical examples of preparation of nanomaterials by liquid plasma

图 7 液相等离子体制备纳米材料典例

极,从 CTAB 溶液中成功制备出锡纳米颗粒,并研究了不同 CTAB 浓度对制备锡纳米颗粒的影响,发现生成物中锡纳米颗粒所占比例随 CTAB 浓度增加而增加。金属合金纳米材料的制备与贵金属合金相似,但金属合金活泼性较高,在纳米颗粒生成的同时往往伴有相应的氧化物形成。

3.3 氧化物纳米材料

在合成金属氧化物纳米材料时,高温等离子体(如电弧放电)会消耗固体电极,随后产生的纳米颗粒或生成的金属蒸汽与周围电解液反应形成氧化物。胡秀兰等人^[87]采用等离子体诱导技术在 Cu 电极周围制备出生长方向为 [010] 的 CuO 纳米棒,还用此装置合成了生长方向为 [001] 的 ZnO 纳米棒和纳米花。Hosokai 等人^[88]以 Zn 棒为原料,探究了 $Zn(OH)_4^{2-}$ 沉积制备 ZnO 的合成路径,并通过调控反应功率与电解液浓度得到形貌不同的 ZnO 纳米花。在液相等离子体合成氧化物沉淀期间,化学试剂(如表面活性剂、分散剂)、液体温度和电解液浓度将会影响纳米产物的最终形态和组成。氧化物纳米材料在较低的溶液温度下会导致其晶体的结晶度降低,有时在合成后会观察到亚稳相或缺陷结构^[89]的纳米颗粒。

3.4 碳纳米材料、硅纳米材料

运用液相等离子体技术合成碳纳米材料时,石墨电极在电弧放电过程中消耗,随后碳原子聚集团簇形成碳纳米材料。碳材料的形成会受催化剂的影响,如 Ni, Fe 和 Co 等金属催化剂存在时,碳原子趋向形成碳纳米管结构^[90]。除石墨电极作为碳源之外,甲苯、乙醇和丁醇等有机溶剂也可用作碳源。尤其是甲苯,因为其结构对称,分解均匀发生^[91],形成的碳材料对称性较高。

硅纳米材料在锂负载电池、光感元件等领域有巨大的应用前景,等离子体制备硅纳米粒子基本符合“自下而上”的方法,以硅棒、硅片或二氧化硅为原料,在等离子体作用下裂解聚集而成,用硅棒作为电极在溶液中脉冲放电制备硅纳米粒子时,为防止电极过热,需要考虑硅电极的电阻和导电性能。

3.5 纳米复合材料

液相等离子体技术合成金属(非金属)/碳纳米复合材料具有高效、安全等优势。Hamdan^[92]通过此技术成功将铂、铁、铝、镍等金属分别负载在碳纳米管上形成金属/碳纳米复合材料,并对合成产物的精细形态进行研究,在去除外加电场的情况下,通过自身聚合也能产生非常稳定的复合纳米结构。此外, Panomsuwan 等人^[93]以含氰基的芳香族分子为前驱体,得到均匀分散的氮掺杂碳纳米复合材料,与传统 Pt/C 复合材料相比,此类材料在碱性和酸性溶液中具有更好的长期耐久性和对甲电氧化的不敏感性,使氧还原反应(ORR)活性损失最小。这些金属(非金属)/

碳纳米复合材料在催化、电分析、传感器、燃料电池和锂电池领域具有巨大的潜力。

综上所述,利用液相等离子体技术来驱动化学反应有很多优点。随液相等离子体技术持续开发,该技术在合成纳米材料的领域也不断拓宽。表2总结了部分基于液相等离子体合成纳米材料的典型例子。

表 2 基于液相等离子体技术合成纳米材料
Table 2 Synthesis of nanomaterials based on liquid phase plasma technology

nanomaterials	examples	liquid plasma type	references
precious metal element	Au	contact glow discharge	[56]
		microplasma discharge	[63, 94]
		two-electrode pulsed plasma	[76-81]
	Ag	arc discharge	[55, 84]
	Pd	gas-liquid interface plasma	[82]
	Pt	flat electrode plasma microplasma discharge	[62] [83]
precious metal alloy	Au - Ag alloy	two-electrode plasma	[54]
		microplasma discharge	[60]
	Au - Pt alloy	two-electrode pulsed plasma	[85]
metal element	Ni	solution glow discharge	[57]
	Cu	submerged arc discharge	[86]
	Fe	high voltage cathodic polarized discharge	[58]
	Mn	solution discharge	[72]
	Sn	dielectric barrier discharge	[75]
metal alloy	Fe - Ni alloy	solution discharge	[59]
	Ni - Cu alloy	dielectric barrier discharge	[74]
oxide	CuO/ZnO	two-electrode pulsed plasma	[87]
	ZnO	contact glow discharge	[88]
	Cu ₂ O	microplasma discharge	[95]
	TiO ₂	gliding arc discharge	[52]
	defective TiO ₂	submerged pulse discharge	[89]
carbon material	carbon nanotubes	alternating current arc discharge	[78]
	graphene	submerged arc discharge	[90-91]
		submerged arc discharge	[79]
silicon material	Si	dielectric barrier discharge	[73]
composite material	carbon - metal nano	contact glow discharge	[92]
	carbon - non-metal nano	solution discharge	[93]
		plasma induced cathode discharge	[96]

4 结 论

液相等离子体含大量高能电子、离子、自由基等活性物质,不仅能加速化学反应速率和效率,而且能引发一些传统化学中难以发生的反应。因此,它逐渐成为一种高效的过程强化手段,在应用于纳米材料的制备中具有操作简便、环境友好、产物纯度高、尺寸可控等优点。虽然该技术发展潜力巨大,但仍有许多挑战亟需解决,主要包括3个方面:①反应机理尚未明晰。由于等离子体活性粒子寿命短,浓度低,现有的检测技术难以检测反应过程中的瞬态中间体。因此需开发高灵敏的检测技术,并通过试验结合计算机仿真对等离子体制备纳米材料的过程进行模拟,从分子层次解析反应机理,为纳米材料的可控制备提供指导。②该技术产量低,能耗大,目前仍处于基础研究阶段。阵列式微等离子体有望成为一种有效的放大途径并减少能耗,但该类反应器在大规模生产中的结构、稳定性和可控性还有待检验和完善。此外,液下高压直流放电由于设备成本低、通量大等优势,也有望提高产量,应用于工业化批量生产,但该反应器需对电解液、放电功率和液体流速速率等条件加以调整与完善,以便降低能耗,得

到晶型可控、尺寸均一的纳米材料。③等离子体制备纳米材料仍属于新型的反应方式，且属于多学科交叉，现有生产设备以自主开发构建为主，相关商业化设备还不成熟，如针对纳米材料制备的标准化电源、反应器、电极结构、电极材质等，需要来自不同领域的科学工作者联手合作。上述问题的解决能促进液相等离子体技术由基础研究往工业应用的转变，或许会引发新一轮的技术革新和产业升级，并将产物运用到能源、环境、生物医学等领域。综上所述，液相等离子体制备纳米材料是一个充满机遇和挑战的研究领域。

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