低共熔溶剂用于功能碳材料制备的研究进展*

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摘 要： 作为一种类离子液体溶剂，低共熔溶剂（Deep Eutectic Solvent, DES）具有组分多样、成本低廉、制备简单、稳定性好等特点，近年来引起了研究者的广泛关注. 介绍了DES的定义、特点及种类，综述了DES在制备功能碳材料方面的研究进展，论述了DES作为溶剂、碳质前驱体和功能化剂的突出优势，旨在为基于DES的功能碳材料的设计制备提供参考.

关键词： 低共熔溶剂；碳材料；功能化剂

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Research Progress of Deep Eutectic Solvent on the Application of Functional Carbon Material

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Abstract： Recently, as a kind of green solvents and the analogues of ionic liquids, deep eutectic solvent(DES) have intensively attracted considerable attention from researchers due to their characteristics of various components, low costs, simple synthetic and well stability. This work introduces the definition, characteristics and types of DES, reviews the research evolution of DES in the preparation of carbon-functioned materials. Additionally, it also summarizes the preferable superiorities of DES severing as solvents, carbon precursors and functionalizing agents. The aim is to provide some references in the field of design and preparation of functional carbon materials based on DES.

Key words： deep eutectic solvent; carbon materials; functionalizing agent

0 引 言

作为一种新型绿色溶剂，相比传统溶剂，低共熔溶剂具有高热稳定性、难挥发性、绿色、低蒸气压和可回收性等特征，加之其制备过程简单、组分种类多样，被认为是非水溶剂和离子液体（ILs）的一种有效替代品[1−2]. 不同于由阳离子和阴离子缔合而成的ILs，DES是氢键供体（HBD）和氢键受体（HBA）组分在适当的温度下通过强氢键、弱静电以及范德瓦耳斯力相互作用形成的一类特殊液体.

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DES的发现源于2001年Abbott[3]等对ILs的研究. 该研究通过将不同化学计量比的MCl_2（M=Zn/Sn）与季铵盐[$Me_3NC_2H_4Y$]Cl（Y=OH、Cl、OC(O)Me、OC(O)Ph）混合，制得一系列新颖、稳定的Lewis酸性离子液体，其最低凝固点为23~25 ℃. Abbott等后续研究[4−5]发现，将氯化胆碱（ChCl）和尿素以化学计量比为1：2混合可得到低凝固点（12 ℃）的液态混合物，并基于此提出了DES的概念. 一般来说，HBA和HBD的种类较多，可通过改变其组合种类与配比，形成具有多样性的DES. 随着DES受到越来越广泛的关注，近几年出现了新的DES类型，如天然低共熔溶剂（NADES）[6]. 总之，DES具有制备方法简单、成本低、绿色、良好的可降解性、高的导电性、高热稳定性等优点，被广泛应用于生物转化[7−8]、分离提纯[9−10]、有机合成[11−13]、电化学[14−15]、催化[16]和纳米材料制备[17−19]等诸多领域. 近年来，DES作为反应溶剂和反应前体被广泛用于制备功能材料. 其中，利用DES制备功能碳材料成为当前的研究热点，目前已有较多的研究报道. 然而，目前关于DES应用于功能碳材料制备方面的综述性论文较少[20−21]. 因此，有必要对DES应用于功能碳材料制备的研究工作进行一次全面系统的总结.

本文简述了DES的特点及分类，重点综述了DES在制备功能碳材料方面的研究进展，阐述了DES作为溶剂、碳质前驱体和功能化剂的突出优势，为基于DES的功能碳材料领域的深入研究提供参考.

1 结果与讨论

1.1 DES的结构特点

由于组成DES的各组分之间形成了氢键，其凝固点显著低于单个组分的凝固点. 凝固点是DES的一个重要物理参数，DES的凝固点大多在-38~150 ℃之间，最近许多关于DES的报道指出，氢键作用力被认为是在DES形成过程中发生凝固点降低的关键，通常氢键作用越强，DES凝固点越低[22]. 研究表明，氢键本质上是静电相互作用，这意味着HBD和HBA物质之间存在电荷转移导致形成了部分共价键[23]. 在DES研究中，常通过傅里叶红外光谱、核磁共振光谱以及拉曼光谱来验证所研究DES体系中氢键的形成[24−27].

为进一步阐明DES的形成机制，研究者在传统实验基础上进行了大量的理论计算研究工作. 基于DES中性物种充当较小阴离子物种的络合剂，使负电荷从阴离子离域这一基础，将关于DES的理论假设为电荷离域是通过氢键作用发生的. 实验研究中最常使用的HBD和ChCl也是理论研究的主要对象. 如Wagle等[28]研究了3种不同类型的HBD（尿素、乙二醇、丙二酸）与ChCl的分子间相互作用，通过对体系的分子构型、电荷离域效应和热化学的研究表明DES的形成是由于氢键作用，同时发现DES的物理性质与ChCl和不同HBD的相互作用的键能大小直接相关. Wang等[29]研究了ChCl与多元醇之间的相互作用，结果表明ChCl中的Cl原子与多元醇中-OH基团的H原子之间形成了氢键相互作用，其强度随着多元醇中羟基数的减少而降低，这是DES形成的主要原因，该结果有利于进一步了解ChCl/多元醇型DES的微观结构和理化性质.

1.2 DES的类型

通过HBA和HBD的不同组合，可以形成多种多样的DES. 目前，常用的HBA有季铵盐、季膦盐、咪唑基盐、分子咪唑及其类似物等. HBD则包括酰胺类、硫脲类、尿素类、胺类、咪唑类、唑类、醇类、羧酸类、水和苯酚类等[30].

根据HBA/HBD的性质，早期Smith等[31]将DES定义为4种类型，如表1所示，包括季铵盐与金属卤化物组合的I型、季铵盐和水合金属卤化物组合的II型、季铵盐和氢键供体组合的III型以及金属卤化物和氢键供体组合的IV型.

表 1 DES的分类及组分简式[31]

类型	组分简式	项
Ⅰ	$Cat^+X^-zMCl_x$	M=Zn, Sn, Fe, Al, Ga, In
Ⅱ	$Cat^+X^-zMCl_x \cdot yH_2O$	M=Cr, Co, Cu, Ni, Fe
Ⅲ	Cat^+X^-zRZ	Z=$CONH_2$,COOH, OH
Ⅳ	$MCL_x+RZ=MCl_{x-1}^+ \cdot RZ+MCl_{x+1}^-$	M=Al, Zn; Z=$CONH_2$,OH

近年来，DES的研究热度不减，出现了新的DES类型，如非离子DES[32−33]和目前研究广泛的NADES[34−35]. Abranches等[32]研究发现在百里香酚-薄荷醇体系中，由于酚和脂肪族羟基的酸度差异，形成了基于强氢键相

互作用的DES．研究者认为这类强氢键相互作用是制备非离子DES的关键，也有相关文献将非离子DES归属为DES分类中的Ⅴ型[34]．NADES是近年来受研究者特别关注的一类，此类型是2011年由Choi等[35]提出的，他们认为NADES中HBA一般是自然界天然存在的糖、醇类、有机酸及胆碱衍生物等，HBD一般是尿素、酰胺、醇、羧酸和氨基酸等．因NADES的组分为天然产物，其毒性明显低于常规DES，且具有好的生物相容性、可持续性以及制备成本低等优点，在生物转化、生物质加工以及药物研究领域表现出巨大的应用潜力[36−37]．

1.3　基于DES的功能碳材料

1.3.1　文献检索结果分析

自第一篇介绍由ChCl/尿素形成DES的论文发表以来，DES受到持续关注，近十年来DES相关研究取得了巨大进展，被应用于多个领域，但大部分仍来自化学领域．如图1（a）所示，截至2023年3月16日，以DES作为关键词在Web of Science数据库中进行检索，共有9 713篇已发表文献，可以明显看出近几年对DES的研究居高不下．图1（b）是根据研究方向检索DES后的结果，可知DES在检索的25个领域中，于化学领域的应用占比可达28%．此外，约8%的文献来自材料科学领域，其中关于功能碳材料领域的文献约有288篇，占材料科学领域已发表DES文献总数的13.9%．本文试图以功能碳材料领域视角综述其研究进展，以期为DES在此领域的发展提供参考．

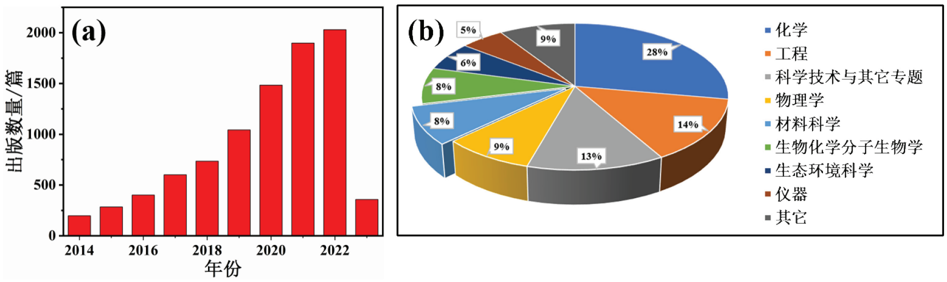

图 1　与DES相关的研究课题的出版分析

注：(a) 为每年的出版数量；(b) 为研究领域的百分比．

1.3.2　DES的功能性作用

近年来，DES因具有制备过程简单、成本低、组分多样、热稳定性好以及环境友好等优点，被广泛应用于功能纳米材料制备领域[38−42]．其中，DES用于碳材料制备成为近些年的研究热点．DES在碳材料制备中能够起到多重作用，不仅可以作为确保试剂均匀化的介质，而且因DES多样性的组分，常用作功能碳材料制备的一体化平台，在制备功能碳材料过程中起到碳质前驱体、掺杂、催化、模板等作用．

1.3.3　溶剂和碳质前驱体

DES一般在常温下是液态且具有较高的溶解性，可作为溶剂有效混合或均匀分散反应前驱体．2010年，Gutiérrez等[15]首次将多壁碳纳米管（MWCNTs）分散在间苯二酚、尿素和ChCl形成的DES中，先经间苯二酚和甲醛的缩聚反应制得酚醛树脂，最后经高温碳化制得了MWCNTs均匀分散的碳-碳纳米管复合材料；Li等[43]以1,3,5-三乙基苯和1,3,5-三溴苯为原料，以有机溶剂和3种DES（ChCl/乙二醇、ChCl/苯酚、ChCl/尿素）作为反应溶剂，通过交联聚合制备了氢取代石墨炔；Liu等[44]报道了一种以ChCl/尿素型DES作为反应溶剂制备纤维素纳米纤维/还原氧化石墨烯复合膜的方法；Zhang等[45]提出了一种ChCl/乙醇（化学计量比为1∶3）型DES为反应介质制备新型N掺杂碳量子点修饰球形多孔SiO_2的简易绿色合成策略，认为DES作为一种新型纳米材料改性SiO_2的溶剂，可以替代传统的挥发性有毒溶剂．

据调研，碳材料制备中将DES单纯作为溶剂的研究工作相较其作为碳质前驱体来说是比较少的，大多数工作将DES既作为溶剂又作为碳质前驱体，del Monte团队在这一领域作出了系列开创性工作，自2010年起，他们将DES引入到传统的酚醛缩聚反应体系，通过调节DES的组成、聚合反应条件以及碳化温度，无需添加嵌段共聚物等模板剂直接制得了结构可调的多孔碳．该课题组利用四乙基溴化铵/间苯二酚/4-己基间苯二酚型DES合成了具有微孔结构的碳材料[46]；利用3种不同DES（ChCl/间苯二酚、ChCl/4-己基间苯二酚、ChCl/对硝基酚）作为碳质前驱体，制备了具有分级多孔结构的N掺杂碳材料[47]．这些研究工作所涉及到的传统缩聚反应体系具有前驱体价格低廉、碳转化率高的特点，加之DES本身具有的诸多优势，为实现低成本制备功能碳材料带来了

希望[48]．近几年，也不断出现其他研究组将DES作为碳质前驱体制备碳基材料的研究报道[49−52]．

1.3.4 功能化助剂

DES在碳材料制备过程中不仅可以作为溶剂和碳质前驱体，而且因DES组分的多样性，在制备碳材料过程中同时能够起到催化、掺杂和模板/结构导向等功能性作用．这些研究工作为基于DES设计制备功能碳材料提供了新思路．

DES作为催化活化剂应用于碳材料制备研究已有相关报道．Chen等[53]报道了一种快速、可调的间苯二酚-甲醛碳气凝胶的合成策略以及其作为锂离子电池负极材料的潜在应用，该研究采用含铁DES（ChCl/乙二醇/$FeCl_3$）作为聚合和石墨化的反应介质和催化剂介导聚合和相分离过程，从而制得具有丰富多孔结构的碳材料．Xu等[54]将硼酸/尿素型DES作为催化剂、溶剂，同时作为杂原子源制备了一种具有优异电化学性能的新型多孔碳材料．本课题组[55]在含聚合反应单体和活化剂的DES（$ZnCl_2$/间苯三酚）中加入甲醛，并以磷酸为催化剂和杂原子源进行缩聚反应先制得有机聚合物凝胶前驱体，再经过高温碳化和活化制备出磷掺杂分级多孔碳材料，将其作为超级电容器电极材料表现出高比电容、优异的倍率性能和循环稳定性．

DES作为杂原子掺杂剂的研究也越来越深入．作为DES组分的尿素是制备碳材料的常用氮（N）掺杂剂，因此将尿素型DES作为氮源来制备N掺杂碳材料已有较多报道．Fechler[56]课题组报道了利用多酚/酮与尿素组成的一类DES作为碳质前驱体，制备出高吡啶氮含量的N掺杂碳材料；Luo等[57]以单宁酸/尿素型DES作为碳质前驱体，$ZnCl_2$作为造孔剂制备出N掺杂多孔碳，材料具有优异的电催化氧还原性能；Zhong等[58]以苯酚-甲醛树脂为碳源，$ZnCl_2$/尿素型DES中的尿素作为氮源，$ZnCl_2$作为活化剂及造孔剂，制备出N/O共掺杂分级多孔碳材料；Xiong等[59]基于葡萄糖/尿素型DES制备了N掺杂多孔碳材料（NCM），NCM具有高的比表面积、丰富的微孔结构，对4-硝基苯酚或亚甲基蓝表现出良好的吸附性能；本课题组[60]以设计制备的$ZnCl_2$/酪氨酸/尿素三元DES为前驱体，经一步高温碳化制备出N掺杂多孔碳材料，组装的固态电容器展现出较高的能量密度．

除尿素外，其它含氮DES组分作为N掺杂剂的研究工作也有报道．Sánchez-Leija等[61]在3种DES（氯化苯胺/乙二醇、氯化苯胺/甘油、氯化苯胺/乙醇酸）中加入苯二胺进行聚合反应，植酸为交联剂和磷源，制备了高导电自支撑的聚苯胺干凝胶，后经高温碳化后制得N/P共掺杂多孔碳材料，材料表现出优异的电催化性能．Tabaraki等[62]选取ChCl/硫脲型DES作为溶剂、掺杂剂，采用微波辅助策略制备出N、S、Cl掺杂的碳点．

DES作为其它杂原子掺杂剂甚至是金属源的研究工作也相继有报道．Lópezs等[63]报道了在ChCl/对甲苯磺酸型DES中加入六亚甲基四胺和糠醛，以对甲苯磺酸为聚合反应催化剂和硫源，经缩聚反应、再经高温碳化制备出S掺杂多孔碳材料，研究了材料的电催化氧还原性能；Zhou等[64]报告了一种基于葡萄糖/尿素型DES制备杂原子掺杂多孔碳纳米片的研究工作，通过改变5种葡萄糖基DES的组成，KOH活化后制备了N掺杂或N/S共掺杂的多孔碳纳米片，其电容性能得到了很大的改善．Thorat等[65]报道了以1：2化学计量比组成的ChCl/氯化锡型DES，并将其作为溶剂、碳质前驱体和锡源辅助合成Sn/SnO_2@C复合碳材料的工作．Bai等[66]通过由$ZnCl_2$/乳酸型DES作为木质素去除剂和ZnO前体，在木材上原位生长ZnO晶体制备具有卓越CO_2吸附能力和油水分离能力的ZnO涂层泡沫碳．Mondal等[67]利用ChCl/$FeCl_3$型DES，并将其作为Fe源、模板和催化剂，与海藻混合热解生成了Fe功能化的石墨烯纳米片．

DES在碳材料制备过程中作为模板/结构导向剂也是目前研究的热点．作为DES组分的尿素是制备碳材料的常用模板剂，因此，利用其组成的DES作为模板剂的研究工作近几年也陆续有报道．Xue等[68]根据一种新型DES（$ZnCl_2$/2,5-二羟基-1,4-苯醌/尿素）作为碳质前驱体、自模板和N掺杂剂，制备出具有微/介孔的N/O自掺杂空心碳纳米棒（HCNs），该碳材料应用于超级电容器领域具有高的能量密度和好的循环性能；Wei等[69]以ChCl/硼酸/尿素三元DES为前驱体和模板剂制备出多孔硼碳氮（BCN）材料；本课题组[70]以天冬氨酸/尿素型DES为聚合反应溶剂、反应单体、氮源和模板剂，硼酸为聚合反应催化剂和B源，外加甲醛后先制得聚合物凝聚，再经一步高温碳化制备出B/N掺杂多孔碳材料，该材料在碱性和天冬氨酸/尿素型DES电解液中均表现出优异的电容性能．除尿素外还有其它类型的DES也可作为模板制备碳材料[52,67,71−75]．Gutiérrez等[73]将ChCl/间苯二酚/3-羟基吡啶型DES作为反应介质、碳质前驱体、N掺杂剂和自模板，通过间苯二酚与3-羟基吡啶的缩聚反应，经高温碳化后制得碳球材料，材料对CO_2吸附性能优异．Kamath等[74]以有毒生物杂草为碳源，以ChCl/$FeCl_3$型DES为软模板和催化剂，采用更环保的溶剂热法合成了卷须状功能碳材料．

2　结 论

作为一种绿色的类离子液体溶剂，DES被广泛应用于生物转化、分离提纯、有机合成、电化学、催化和纳米材料制备等领域. 近年来利用DES设计制备功能碳材料也受到了研究者的青睐. 本文简要介绍了DES的定义、特点及种类，重点论述了DES用于功能碳材料设计制备的研究进展. 基于DES组分的多样性，在碳材料的制备过程中DES可展现多重作用：既可作为一类非水溶剂均相溶解或分散碳质前驱体，也可作为掺杂、催化、模板等功能性助剂制备新型功能碳材料，这为功能碳材料的构筑提供了新思路.

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