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树枝状纤维形二氧化硅纳米粒子的研究进展

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摘 要: 与传统二氧化硅介孔材料相比, 树枝状纤维形二氧化硅纳米粒子(Dendritic Fibrous Nano-silica, DFNS), 特别是具备三维中心辐射状孔道和多级孔结构的球形 DFNS 拥有较高的比表面积、较大的孔体积、较高的孔渗透性和粒子内表面更易接触性等优点。客体物质(如极小的纳米粒子)能够沿着中心辐射状孔道进行负载和/或输送, 甚至与化学改性所得内部活性位点发生反应。因此, DFNS 是一种富有前景的载体平台, 可以用来构筑新型纳米催化剂、吸附剂、基因/蛋白质/药物的递送系统等。大量研究表明: 球形 DFNS 与生俱来的结构优势使其能够作为 MCM-41 和 SBA-15 的理想替代材料。但是, DFNS 领域依旧存在很多需要探讨的问题。因此, 本文主要归纳分析 DFNS 的结构特征、常用结构模型、新型结构和实时应用。希望能够给予材料和化学科学家一些参考, 促进 DFNS 的蓬勃发展。

关 键 词: 树枝状纤维形; 二氧化硅; 结构模型; 新颖结构; 实时应用

中图分类号: O611; TB383　　**文献标识码:** A

Research Progress of Dendritic Fibrous Nano-silica (DFNS)

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Abstract: Dendritic fibrous nano-silica (DFNS), especially the sphere-shaped with three-dimensional (3D) center-radial channels and hierarchical pores, possess higher specific surface areas, larger pore volumes, higher pore permeability, more accessible internal spaces, *etc*. Guest substances (*e.g.*, ultrasmall nanoparticles) can be loaded onto and transported in the radial nanochannels, or can even react with the chemically active sites in these nanochannels. As a result, DFNS can serve as promising platforms to construct novel nanocatalysts, adsorbent materials, and delivery systems for genes, proteins or drugs. A majority of investigations about DFNS have demonstrated that silica nanospheres with this special topography have inherent superiorities over traditional mesoporous MCM-41 or SBA-15, and can be perfect alternatives. Nevertheless, reviews on DFNS are limited, and there still exist plenty of issues that need to be probed into. Therefore, this comprehensive review provides a critical survey on DFNS’ structural characteristics, commonly used structural models, novel structures, real-time applications, *etc*. We sincerely expect that this paper

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could give material scientists and chemists certain inspiration to accelerate DFNS family's booming evolution.

Key words: dendritic fibrous; silica; structural models; novel structures; real-time applications

介孔材料一直以来受到广泛关注, 归因于其特殊的物理化学性能, 如比表面积大、介孔性高、机械性能优异等[1]。与同等尺寸的无孔实心结构材料相比, 多级孔结构或复杂多层级结构使得介孔材料性能提升, 作为载体有广阔的前景, 适用于催化、选择性吸附和二氧化碳捕捉等科学领域[2]。自 Mobil 公司于 1992 年开创性地制备 MCM-41 之后[3], 大量工作专注于介孔材料的理论研究、制备策略、表征方法和新兴应用领域。由赵东元等[4]于 1998 年合成的 SBA-15 将二氧化硅介孔材料发展推进到新的高潮。此后, 尽管众多课题组开展大量工作以制备新型二氧化硅介孔材料, 但研发过程困难重重、成果不多。

直到 2010 年, Polshettiwar 等[5]使用微波反应器, 通过简单的乳液法里程碑式地制备了树枝状纤维形二氧化硅纳米球, 命名为 KCC-1(类似于 MCM-41 命名规则)。KCC-1 为 KAUST Catalysis Center 的首字母缩写, 而 KAUST 代表 King Abdullah University of Science and Technology。不同反应条件可以调控 DFNS 内部介孔尺寸(2~30 nm)和纳米球直径尺寸(170~1120 nm)[6]。因此, KCC-1 这一称谓及树枝状纤维形纳米球被大多数研究人员认识、接受和使用[7-14]。同年, 杜鑫课题组[15]采用乙醚乳液体系制备了树枝状纤维形二氧化硅纳米球, 产物被命名为 Hierarchical Mesoporous Silica Nanoparticles (HMSNs), 对该类结构纳米粒子的发展做出了巨大贡献[16-21]。此后, 具有"树枝状纤维形"结构特征的纳米粒子开始蓬勃发展, 从单一简单结构进化为多级复杂结构, 应用范围也日益增大。2014 年, 赵东元院士课题组[22]采用油水双相分层法制备了层级结构可控的多代 DFNS, 命名为 Three dimensional dendritic mesoporous silica nanospheres (3D dendritic MSNSs)。所谓的多代层级结构可控是指每个壳层都具有相同的孔径尺寸, 而壳层与壳层之间具有不同的孔径尺寸。

图 1 为本课题组通过水热反应釜制备所得具有树枝状纤维形结构二氧化硅纳米球的透射电子显微镜(TEM, (a)~(c))和扫描电子显微镜(SEM, (d)~(f))照片[23]。照片显示单分散树枝状纤维形二氧化硅纳米球由沿着粒子中心到表面辐射方向排列的纳米褶皱组成。中心辐射状孔道相应地在纳米褶皱之间形成, 其孔径尺寸从粒子内部到外部逐渐增大。由褶皱挤压形成的多级孔不均匀散布于二氧化硅球表面, 随机测量的褶皱片厚度分布在 8.3~14.2 nm 之间(图 1(e)), 不规则多级孔的孔径在 10.9~35.2 nm 范围之间(图 1(f))。杜鑫和 Polshettiwar 课题组分别于 2015 年[16]、2016 年[24]和 2017 年[25]对 DFNS 学科做了综述, 介绍了 DFNS 的合成策略及应用进展。基于本文作者课题组和其他课题组的研究成果, 本综述则对上述文章未涉及部分进行补充(如结构模型分析), 对存在的一些要点进行尝试性探讨(如称谓统一), 也对近期发表的 DFNS 内容进行更新(新兴结构及实时应用)。

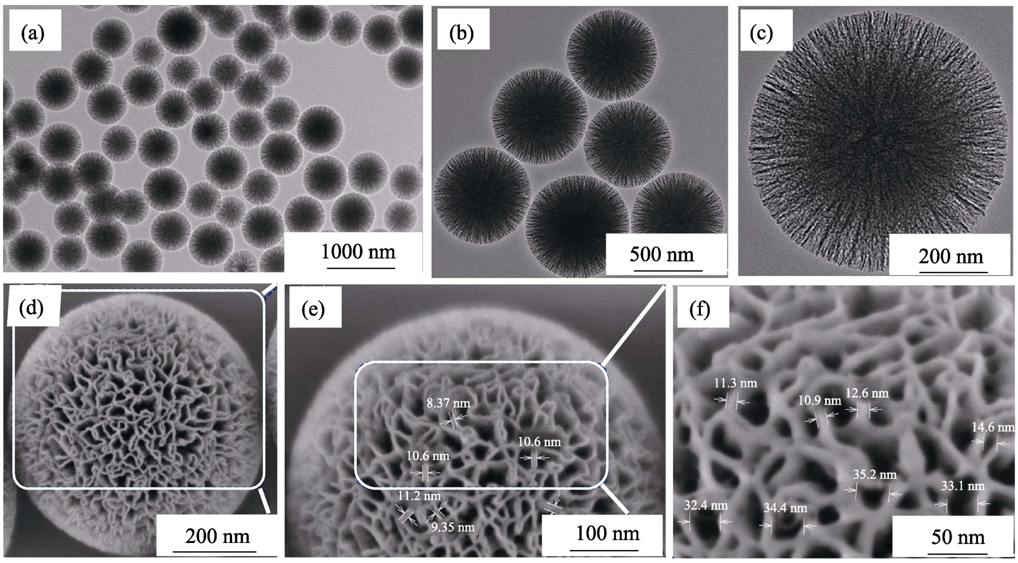

图 1　树枝状纤维形二氧化硅纳米球的透射电镜(a)~(c)和扫描电镜(d)~(f)照片[23]

Fig. 1　TEM (a-c) and SEM (d-f) images of silica-based nanospheres with dendritic fibrous morphologies[23]

1 称谓概述

1.1 各类称谓总结

随着学者们对树枝状纤维形二氧化硅纳米球的深入研究，众多称谓依次出现，导致了名称不统一现象。但是，这些称谓基本都在描述具有中心辐射状孔道和多级孔结构的 DFNS。表 1 归纳了常见的英文称谓、英文称谓缩写及中文名。由表可知: (1) “树枝状”和“纤维形”这两类修饰词使用较多，“褶皱状”修饰词偶尔出现；(2)部分称谓不能明确描述对象的具体结构。例如，当英文称谓缩写为 DMSNs、WMS 和 FSNs 时，不易看出所指对象为二氧化硅纳米球还是非球形纳米粒子；(3)部分称谓不能明确界定 DFNS 为纳米粒子还是微米粒子。笔者根据以上现象推断，正是鉴于这些原因，Polshettiwar 课题组[25-29]于 2017 年重新命名具有该类结构的纳米粒子为 DFNS。考虑到 Polshettiwar 课题组对 DFNS 纳米粒子的巨大贡献和影响力，本综述也遵循此命名称谓规范。需要对 DFNS 称谓作出如下说明: (1)笔者表述具有中心辐射状孔道和多级孔结构的 DFNS 为纳米粒子而不是纳米球。因为随着对具有该类结构纳米粒子的深入研究，非球形结构如羽毛球形[48]和椭球形[80]被相继开发出来。此外，英文称谓 “Dendritic fibrous nano-silica (树枝状纤维形二氧化硅纳米粒子)”和“Dendritic fibrous nano-spheres (树枝状纤维形二氧化硅纳米球)”的首字母缩写均为 DFNS，这会引起描述对象的不确定性。(2)“介孔”一词(Mesoporous)也没有出现在 DFNS 中，因为绝大多数 DFNS 的孔径或 DFNS 多级孔中的绝大部分均处在 2~50 nm 之间[6,35-36,65,81-87]，而这一范围正是 IUPAC 定义的介孔尺寸范围[88]。(3)由图 1 可知, TEM 能够展示纳米粒子总体形貌和结构特征(中心辐射状)，而 SEM 重在揭示细节结构特征(纳米褶皱)。DFNS 称谓中的“树枝状(Dendritic)”和“纤维形(Fibrous)”很大程度衍生自 TEM 照片。

1.2 对“树枝状”与“纤维形”的理解

首先，修饰词“树枝状(dendritic)”最先被杜鑫课题组[89]所采用，用来描述 DFNS 的结构特征(图 2(a))，继而才被 Polshettiwar 课题组(图 2(b))[11]，赵东元课题组[22,31-32]，及其他课题组采用[34-35,90]。需要特别强调的是，杜鑫课题组使用“树枝状(dendritic)”这一词语，则是受到树枝状有机聚合物大分子的启发。该类大分子通常呈球形，并具有三维分支构造(图 2(d))[16-17]，每一次分支代表一次迭代，而每一次迭代步骤被称为一代(Generation, G)[16,91]。图 2(d)代表了树枝状大分子结构代数 G 由 0 到 4 的逐步增迭过程。当第 4 代重叠在一起，其形成的二维结构则相似于 TEM 所显示出的结构形貌。其次，大多数树枝状纤维形二氧化硅纳米球遵循图 2(b)的形貌，兼备树枝状和纤维形特征。可以推测，当中心辐射状孔道开口极大的时候，球形 DFNS 呈“树枝状态”(图 2(a))；当中心辐射状孔道开口极其微小的时候，

表 1 树枝状纤维形二氧化硅纳米粒子称谓概括

Table 1 English and Chinese appellations, and their abbreviations for silica nanoparticles with dendritic fibrous structures

No.	English appellation	Appellation abbreviation	Chinese appellation	Ref.
1	Dendritic fibrous nanosilica	DFNS or (KCC-1)	树枝状纤维形二氧化硅纳米粒子	[25-28, 30]
2	Three dimensional dendritic mesoporous silica nanospheres	3D dendritic MSNSs	三维树枝状介孔二氧化硅纳米球	[22, 31-32]
3	Dendrimer-like silica nanoparticles with hierarchical pores	HPSNs	树枝状多级孔二氧化硅纳米粒子	[17,21,33-34]
4	Dendritic mesoporous silica nanoparticles	DMSNs	树枝状介孔二氧化硅纳米粒子	[35-42]
5	Dendritic mesoporous silica nanospheres	DMSNs	树枝状介孔二氧化硅纳米球	[43-45]
6	Fibrous mesoporous silica microspheres	FMSMs	纤维形介孔二氧化硅微球	[46-47]
7	Wrinkled silica nanoparticles	WSNs	褶皱状二氧化硅纳米粒子	[48-52]
8	Wrinkled mesoporous silica	WMS	褶皱状介孔二氧化硅	[53-56]
9	Wrinkled mesoporous silica nanoparticles	WMSNs	褶皱状介孔二氧化硅纳米粒子	[57-58]
10	Radial-like mesoporous silica	RMS	中心辐射状介孔二氧化硅	[59-60]
11	Fibrous silicon dioxides spheres	FSS	纤维形二氧化硅球	[61]
12	Fibrous silica nanoparticles or nanospheres	FSNs	纤维形二氧化硅纳米粒子或纳米球	[62]
13	Hierarchically and radially mesoporous silica	HRM	分层次和辐射状介孔二氧化硅	[63]
14	Hierarchically structured spherical mesoporous nanoflowers	HSMNF	分层次结构球形介孔纳米花”和	[64]
15	Mesostructured silica nanoparticles	MSNs	介孔结构二氧化硅纳米粒子	[33, 65-67]
16	“Dendritic”	–		[13, 68-70]
17	“Fibrous”	–		[71-79]

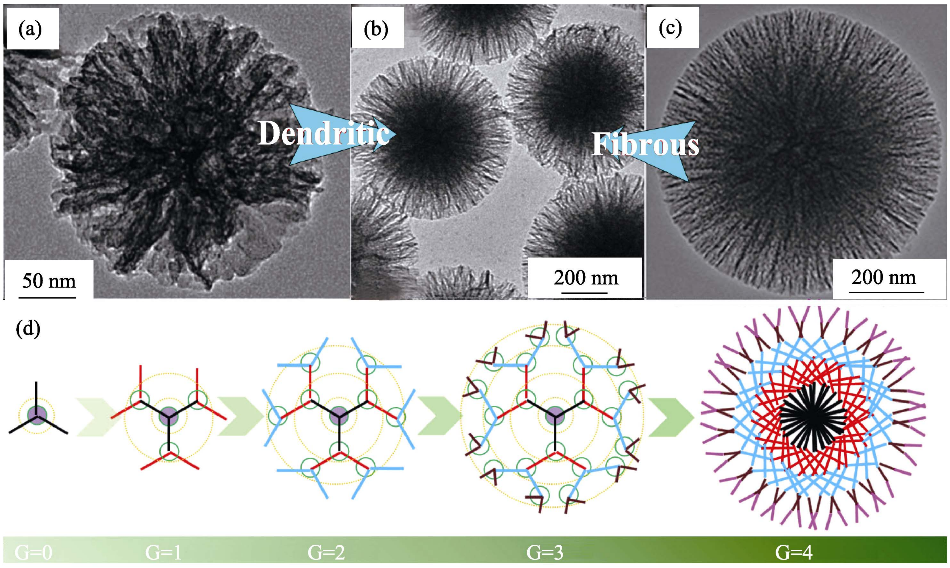

图 2　树枝状纤维形二氧化硅纳米球的结构态转变[89]

Fig. 2　The structural transformation of a DFNS from a quasi dendritic state[89] (a) to a quasi radially fibrous state[23] (c) through an intermediate state of "dendritic fibrous"[11] (b). The forming process of a dendrimer by iterative grafting steps (d)

DFNS 呈"纤维形态"(图 2(c))。因此, 没有强制要求同时使用树枝状纤维形去描述具有此类结构的纳米粒子, 描述性称谓需要根据实际形貌特征决定。但是, 最基本的命名原则为尽量使用"树枝状"或者"纤维形", 这样才能使具有三维中心辐射状和多级孔结构的纳米粒子称谓更加规范化。随着 DFNS 复杂结构的出现(如空心和多壳结构), 必须对该类结构纳米粒子的称谓提前作出统一, 否则其他结构修饰词会让复杂结构的名称更加混乱。

2　研究进展

过去五年, DFNS 越来越受到科研工作者关注(图 3(a))。依据 ACS、Wiley、RSC、Elsevier、Springer 以及 CNKI 数据库收录文献统计, 以 DFNS 为主题的文献总数达到约 200 篇, 包括期刊论文、会议论文、硕士博士论文、专利等。

DFNS 文献数量逐年增加, 且在 2014 年开始爆发式发展。截止 2018 年 4 月, 该主题发表论文总量已将近2017年全年发表文献总数量的一半, 依旧呈上升趋势。DFNS 应用领域极其广泛(图 3(b)), 包括催化[7,9-10,14,30,38,44,49,50,54-55,63,82,86,89-90,92-116], 癌症和肿瘤治疗[34,40,47,56-58,84,117-118], 药物递送[39,46,117-121], 基因和蛋白质递送[11,17,39,122-124], 水处理[125-129], 超湿润界面[20,76,130-132], 色谱分离[68-69,133-134], 荧光探针[135-137], 二氧化碳捕捉[100,138-139], 电池[61], 生物成像[31,34], 储热[59], 光子晶体[140], 复合材料[87]等。催化应用领域吸引了最多关注(约占 38%), 生物应用领域达到约 32%(包括癌症和肿瘤治疗、药物递送、基因和蛋白质递送等), 上述两个应用领域也是其他介孔材料应用研究热点。

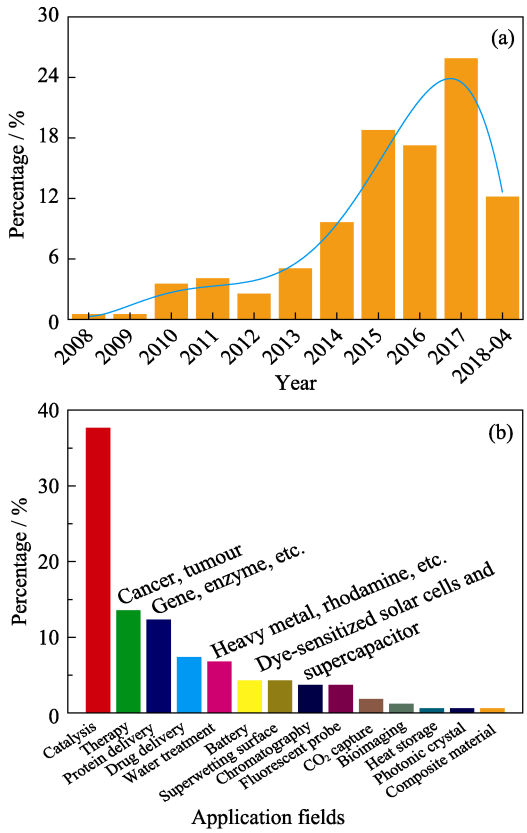

图 3　DFNS 相关文献逐年发表情况(a)及应用领域范围(b)

Fig. 3　The percentages of published literatures about DFNS from 2008 to 2018 (a), and the percentages of various applications for DFNS (b)

3 结构特征

3.1 大孔或/和微孔的存在性

依据 IUPAC 定义，介孔材料分为 3 类[88]：孔径小于 2 nm 的微孔材料、孔径分布于 2~50 nm 的介孔材料、以及孔径大于 50 nm 的大孔材料。DFNS 孔径大都位于 2~50 nm 之间[6,35,65,81-82,85]，但也有一些球形 DFNS 中心辐射孔道尺寸超出 50 nm。例如，杜鑫课题组[21]成功制备了平均孔径高达 148±45 nm，纳米球基体直径尺寸可控于 300~700 nm 的氨基官能团修饰的球形 DFNS。Seo 等[82]通过引入乙酸苄酯(BENA)来扩孔，随着 BENA 由 5 g 增加到 7 g 甚至9 g，平均孔径被扩张为40 nm至50 nm，甚至65 nm。由图 1 可知，沿中心辐射方向排列的纳米褶皱是构造 DFNS 骨架的基本结构单元，纳米褶皱的空间拓扑排列构成了中心辐射状孔道。孔径从粒子内部到表面逐渐增大，可以将这些不规则孔道形容成形状规则的圆锥形。因此微孔尺寸在纳米球中心(球核)出现的几率最大，而介孔尺寸大多集中在外表面附近。需指明一点，微孔可能不仅存在于圆锥形顶端处(纳米球中心)，也可能镶嵌于纳米褶皱内部。即 DFNS 多级孔结构由中心辐射状多级孔道和存在于纳米褶皱中的小尺寸介孔协同构成。

Seo 等[82]指出微孔和介孔共存于球形 DFNS，是多级孔的一种不规则和分层次组合。Zhang 等[83]通过 Barrett Joyner Halenda(BJH)方法计算出微孔和介孔所占比例，前者约占 1/7，而后者约为 1/3。其他研究小组先后也确定球形 DFNS 氮气吸脱附曲线为 IV 型，并伴有 H_3 型滞后环[141-142]。依据 IUPAC 规定，H_3 型滞后环的出现起源于片状结构堆积而成的微孔结构[88]。Suendo 等[12]通过 Scherrer 方程求得镶嵌于纳米褶皱内部的微孔孔径约为 1.2 nm。

3.2 结构和形貌模型

需要强调一点，本章节所指的结构模型均归属于树枝状纤维形二氧化硅纳米球，因为到目前为止，球形 DFNS 占该学科研究的绝大部分。树枝状纤维形二氧化硅纳米球的模型也包括三维(3D)示意结构和二维(2D)示意结构[16,40,50,53,84]。对于 3D 模型来说，Lee 等[143]给出的模型最大程度地保留了 DFNS 的结构特点(类似于图 1(d))。本课题组给出如图 4(a)所示的 3D 模型，从图 4(a_1)到(a_3)，多级孔道的孔径随纳米褶皱间距增大而变大。另外一个常用来描绘球形 DFNS 的结构模型如图 4(b)所示[17,22,44,53,144-145]，可称为理想模型。从图 4(b_1)到(b_3)，圆锥形孔径逐渐增大。赵东元等[22,146]利用图 4(b)模型描绘其课题组制备的多层级结构可控 DFNS，模型与实际产物形

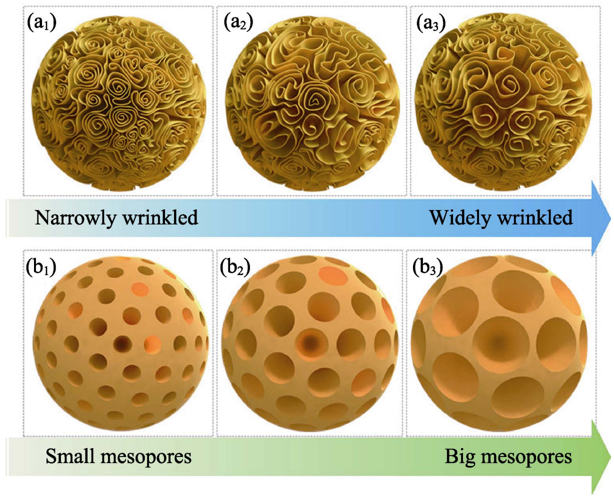

图 4 球形 DFNS 常用结构模型

Fig. 4 The commonly used morphological models for DFNS spheres.

(a) The practical and the most appropriate models, as well as (b) the ideal ones

貌贴切。但是，图 4(b)模型也被用来示意一些核–壳状介孔硅球[147]，模型与实际所得产物形貌相差较大，实际产物的 TEM 照片观察不到树枝状结构纹理。与真正核-壳树枝状复合纳米粒子对比，图 4(b)模型不适用于这些研究的反应产物示意。反面理解，通过 KCC-1 方式制备的以沸石 TS-1[80]、ZSM-5[107,148]和 Fe_3O_4[8] 为核的 DFNS，其壳均呈现树枝状纤维形，与图 1 中的 SEM 和 TEM 结果相近。因此，笔者推荐读者使用图 4(a)模型来描述球形 DFNS，图 4(b)模型需斟酌慎用，易引起混淆。

对于 DFNS 的 2D 模型来说，可以想象 DFNS 纳米球沿球心被切开。因此，相应的 TEM 照片能够反映该结构，如图 1(c)所示。Wang 等[114]使用球形 DFNS 的 TEM 照片来示意其结构，贴切实际形貌且简单易懂。也有课题组[127]采用不同长度的实线取向排列，绘制类似树枝状纤维形的 2D 图像来表示球形 DFNS 的结构特征(图 5(a))。早在 2011 年，杜鑫等[149]将具有多级孔结构的二氧化硅微米球或纳米球分为 4 类，其中包括放射状分层次结构的介孔球(图 5(b))和具有不同孔径分布的介孔球(图 5(c))。Lin 等[150]使用图 5(d)示意复合纳米粒子 $Fe_3O_4@nSiO_2@mSiO_2$ 的结构，$nSiO_2$ 和 $mSiO_2$ 分别代表均匀的二氧化硅层和介孔二氧化硅壳。笔者认为更应该用图 5(c)和磁性核的复合结构来描述 $Fe_3O_4@nSiO_2@mSiO_2$(图 5(e))，其与该研究中实际产物的 TEM 照片完美契合。最近，Dong 等[97,110]采用图 5(f)所示的太阳花状示意图描述核–壳结构的 γ-$Fe_2O_3@SiO_2@$KCC-1，本论文作者认为 γ-Fe_2O_3 和图 5(a)的组合结构更加贴切，才能显示树枝状纤维形纹理。

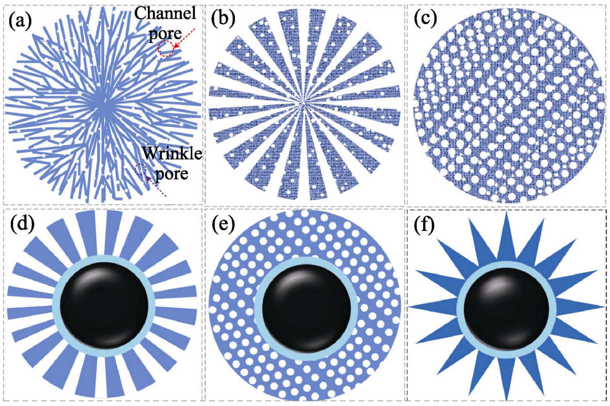

图 5　不同结构二氧化硅纳米粒子的二维示意图[110,127,149-150]

Fig. 5　Schematic diagrams of 2D planar structures from various silica nanospheres[110,127,149-150]

(a) DFNS; (b) Hierarchical radial porous sphere; (c) Hierarchical porous sphere; (d) Radial porous sphere with a magnetic core; (e) Porous sphere with a magnetic core; (f) Sunflower-like magnetic porous sphere

4　合成方法

4.1　经典合成方法的适用性

DFNS 的合成策略及应用领域在前述的三篇综述已有详尽报道[16,24-25]，读者可自行查阅，本文主要侧重分析合成方法的优越性和实时进展。表 2 对比分析了由 Polshettiwar、杜鑫和赵东元等开发的 KCC-1 环己烷乳液法、乙醚乳液法和油水双相分层法的优越性。经本课题组重复试验，上述 3 种方法均能成功制备球形 DFNS。然而油水双相分层法需要更加细致的操作，这使得该方法操作过程更具规范性(与其合成机理有关，参见文献[22])。尽管 KCC-1 环己烷乳液法和乙醚乳液法制备的球形 DFNS 粒径范围均可控于 100~1300 nm 范围，但是一锅制备出的终产物粒径分布不均匀[5,10,17,21,109]，而油水双相分层法制备的纳米粒子粒径十分均匀[22]。从 KCC-1 环己烷乳液法到乙醚乳液法，存在于 DFNS 表面的孔逐渐变得不规则，这是因为不同体积的乙醚冲破乳液滴，形成极其不均匀的孔道[15,17,21]。只在乙醚乳液法产物中观察到了副产物[21]，包括 1~10 μm 的空心介孔球、1~2 μm 空心介孔球和具有多级孔的空心介孔球(这些副产物可以通过逐级离心分离法去除)。

综上所述，每一种方法具有自身优势，如乙醚乳液法能够制备孔径尺寸极大的介孔，有利于大分子和大尺寸纳米粒子负载于 DFNS 孔道内。KCC-1 环己烷乳液法和乙醚乳液法均能得到生长不成熟的中间产物，油水双相分层法没有中间产物的形成。为了制备球形 DFNS，KCC-1 衍生的乳液制备方法被广泛采用(~70%)，接着是乙醚微乳液法(~17%)，最后是油水双相分层法(~3%)。大量研究亟需投入到乙醚乳液法反应体系和油水双相分层法中去。

4.2　其他合成方法概述

基于强抗衡离子机理，Zhang 等[81]在温和反应条件下使用溶胶–凝胶技术通过软模板法成功制备了公斤级的单分散球状 DFNS，粒子尺寸集中在 100~150 nm，纳米褶皱的厚度偏大，约为 10~20 nm。该课题组利用嵌段共聚物(聚环氧乙烷$_{106}$-聚环氧丙烷$_{70}$-聚环氧乙烷$_{106}$, Pluronic F127)作为粒子增长抑制剂，不同烷基链长度的咪唑鎓盐离子液体作为助表面活性剂，制备了金原子掺杂的复合纳米粒子 Au&DFNS，粒子尺寸在 50~300 nm 范围可控[35]。

最近，该课题组采用十二烷基苯磺酸钠(SDS)和溴代十六烷基三甲基铵(CTAB)为双模板，制备了公斤级的球形 DFNS，粒径约为 100 nm[151]。Guo 等[152]用醛类化合物代替乙醚，制备了介孔结构可调和

表 2　KCC-1 环己烷乳液法、乙醚乳液法和油水双相分层法适用性对比

Table 2　Comparison of the approaches applied to synthesize DFNS spheres, including: cyclohexane emulsions for KCC-1, ethyl ether emulsion for HSMNs, and biphase stratification technique for 3D dendritic MSNSs

Synthetic approach	Cyclohexane emulsions for DFNS or KCC-1	Ethyl ether emulsion for HSMNs	Biphase stratification for 3D dendritic MSNSs
Pore size range	*ca.* 2–30 nm	*ca.* 8–200 nm	*ca.* 2.8–10 nm
Particle size range	*ca.* 170–1120 nm	*ca.* 100–1100 nm	*ca.* 180–280 nm
Repeatability	Excellent	Excellent	Excellent
Maneuverability	Easy	Easy	Normal
Particles' uniformity	Poor	Poor	Excellent
Pores' uniformity	Good	Average	Excellent
By-product	None	Some	None
Intermediate products	Some	Some	None
Universality	~70%	~17%	~3%
Significance	Facility and universality	Macropores for diverse guests	Uniformity for fine control

尺寸可控的球形 DFNS。当短链的乙醛被用作共溶剂, DFNS 粒子尺寸能够通过改变反应液 pH 和乙醛用量来控制在 40~850 nm 范围内。当长链的丙醛或丁醛被使用时, DFNS 形貌尺寸小于 130 nm, 但辐射状介孔开口变大且大量小孔嵌在其中, 形成多级孔结构。

5 新兴结构

5.1 核–壳结构

5.1.1 磁性核–壳结构

Liu 等[8]成功制备了单分散磁性核–壳状 Fe_3O_4@SiO_2@KCC-1。首先, 170 nm 的 Fe_3O_4 磁性核通过溶胶–凝胶法包覆一层非介孔二氧化硅层。然后, 通过静电作用将溴化十六烷基吡啶(CPB)自组装在 Fe_3O_4@SiO_2 表面, 形成表面活性剂模板胶体。最后, 通过 TEOS 的水解缩合以及模板剂的去除, 形成了如图 6(a)所示的复合纳米球。直径约 320 nm 的 Fe_3O_4@SiO_2@KCC-1 被用来吸附亚甲基蓝, 饱和吸附量为 48.0 mg/g。动力学吸附实验表明: 在最初震荡处理 5 min 内, 吸附能力达到 78%, 且在 30 min 内达到吸附平衡, 中心辐射状孔道和多级孔结构加速了吸附速度。Sadeghzadeh 等[153]则首先用 3-氯丙基三乙氧基硅烷对 Fe_3O_4@SiO_2@KCC-1 进行化学改性, 然后将氯功能化的复合纳米粒子浸入苄基四氮唑、正丁基锂和氯金酸溶液。所得磁性 Fe_3O_4@SiO_2@KCC-1&Au 能够高选择性环化 CO_2 和炔丙基胺, 高产率生成恶唑烷酮。Piao 等[154]将 5~10 nm 的氧化铁纳米晶自组装为 280 ± 37 nm 树莓状磁性核(Superparamagnetic Iron Oxide Nanocluster, SION), 在其表面制备 DFNS 壳, 生成 317±56 nm 的复合纳米粒子 SION@DFNS。将 TiO_2 纳米颗粒载入树枝状纤维形孔道内, 形成 SION@DFNS/TiO_2 催化剂。相对于商业化的二氧化钛 P25 粒子, 该复合催化剂展现了更快的染料降解能力。Zhang 等[13]制备了磁性 Fe_3O_4@KCC-1, 将脂肪分解酵素(Candida Rugosa Lipase, CRL)负载于该多级结构。28 d 后, 所得 Fe_3O_4@(KCC-1)/CRL 结构中的脂肪分解酵素活性保持为 89%, 而没有负载于 Fe_3O_4@KCC-1 的 CRL 活性仅为 25%。赵东元等[144]开发了一种剪切力辅助的双液界面共自组装方法来合成磁性核–壳 DFNS 复合纳米粒子。首先, 在水溶性的 Fe_3O_4 纳米粒子表面覆盖一层由凝胶–溶胶聚合而得到的间苯二酚甲醛树脂保护壳(Fe_3O_4@RF)。然后, 通过己烷溶胀的CTAB和TEOS复合物共自组装在 Fe_3O_4@RF 表面, 形成 Fe_3O_4@RF@DFNS。用 3-缩水甘油醚氧基丙基三甲氧基硅烷(GLYMO)修饰后, 胰蛋白可以通过氨基酸和 GLYMO 中的环氧基反应, 从而固定在磁性复合纳米粒子的孔道中。所得复合纳米粒子催化剂对小分子蛋白质展现了出色的尺寸选择性和稳定性。

Yang 等[47]将 9 nm 的 Fe_3O_4 纳米晶体嵌入 KCC-1 纤维孔道中, 生成具有磁性的纳米复合结构。严格来说, 该 KCC-1/Fe_3O_4 结构不属于核–壳结构, 如图 6(b)所示。将阿霉素(DOX)负载于 KCC-1/Fe_3O_4 之上, 所得 KCC-1/Fe_3O_4-DOX 复合结构可用来治疗癌症。

5.1.2 非磁性核–壳结构

Wu 等[80]将沸石 TS-1 封入 KCC-1 内部, 形成 TS-1@KCC-1。不同于 KCC-1 的球形, TS-1@KCC-1 保留了 TS-1 的椭圆形貌(图 6(c))。TS-1@KCC-1 能够很好地分散和稳定 $Rh(OH)_3$, 形成的核–壳状 (TS-1)@KCC-1/$Rh(OH)_3$ 能够一锅串联催化过氧化氢氨和苯甲醛。当沸石 ZSM-5 作为中心核时, ZSM-5@KCC-1 为球状, 复合纳米粒子能够用一氧化碳甲烷化[107], 乙苯脱氢和异丙基苯加氢裂解[148]。Qu 等[134]成功制备了以实心二氧化硅球为核的 SiO_2@DFNS 核–壳结构(图 6(d))。亲水性 SiO_2@DFNS 通过十八烷基三氯硅烷改性至疏水, 然后填充于高效色谱分离柱, 用来分离多肽类和蛋白质混合物。树枝状纤维形结构使得分离效率高达 225000 plates/m。该课题组也使用核–壳状 SiO_2@DFNS 快速分离小体积蛋白质、小分子、多肽类化合物和大体积蛋白质[77]。此外, SiO_2@DFNS 对芴类化合物的分离效率高达 264531 plates/m[69]。最近, 该研究小组将金属有机骨架化合物(Metal-organic Frameworks, MOFs)ZIF-8 修饰于 SiO_2@DFNS 孔道表面。其对二甲苯同分异构体的分离效率达到 210000 plates/m, 复合结构 SiO_2@DFNS/ZIF-8 兼备 ZIF-8 的高选择性能和 DFNS 的高分离性能[68]。Yu 等[155]以富勒烯(C_{60})掺杂的二氧化硅为核, 树枝状纤维形二氧化硅层作为壳, 核–壳状 DFNS 纳米球(C_{60}&SiO_2@DFNS) 能够负载单克隆抗体。富勒烯掺杂的硅核在紫外激发下产生单分子氧气($^1O_2$), 能够作为光敏剂和生物成像荧光剂。将上述复合纳米粒子递送于细胞内, 不仅能够用于细胞检测, 还能释放单克隆抗体来阻止细胞凋亡。

5.2 空心结构

在油水乳液中引入封端剂聚乙烯吡咯烷酮(PVP), 于 200℃下可成功制备空心状 DFNS(图 6(e))[86]。

空心状 DFNS 负载 CRL 所形成的 DFNS&CRL 能够高效活化庚酸和乙醇的酯化反应。采用囊泡自组装方法, 通过一锅法技术, 可合成氨基均匀分布于骨架的、呈正电性的空心状 DFNS[156]。所得 DFNS-NH_2 因而能够担载负电性蛋白质, 展现了出色的细胞摄取能力, 更有效地将生物活性酶(*β*-半乳糖苷酶)传送至 CHO-K1 细胞[156]。

5.3　Janus 双面神结构(不对称结构)

Balkus 等[121]将镁纳米粒子嵌入 DFNS 的孔道中, 然后将金/钯涂覆在 DFNS/Mg 半球表面, 记为 DFNS/Mg@Au 或 DFNS/Mg@Pt(图 6(f))。当不对称结构浸入盐溶液, Mg 纳米粒子在 Au 或 Pt 的催化下和水反应, 产生的氢气(H_2)推动复合纳米粒子移动, 因而形成了能够应用在生物平台的运载纳米马达[121]。Lee 等[48]通过一锅法合成了羽毛球形不对称 DFNS, 中心放射褶皱形成于半球表面(图 6(g))。最近, Yu 等[157]制备了类似羽毛球形的 DFNS, 将它们称为“头–尾形貌(Head-tail morphology)”。与对称结构或球形结构相比较, 头–尾形 DFNS 作为强有力的辅佐剂能够摄取和活化小鼠体内的抗原递呈细胞。该课题组继进一步证明“头–尾形貌”DFNS 具有尾长度–依赖的溶血活性, 优异的血液相容性, 并且展示出对免疫细胞较高程度的摄取能力[158]。Zhang 等[41]也制备了伪–羽毛球形 DFNS, 只是树枝状纤维形二氧化硅包裹在 RF 核半球表面, 此制备法存在 TEOS 和 RF 的聚合竞争反应机制。

5.4　蛋黄–蛋壳结构(摇铃形)

赵东元等[144]制备了 Fe_3O_4@RF@DFNS 核–壳双层结构, 当 RF 通过高温煅烧去除后, 成功制备了蛋黄–蛋壳形貌的 Fe_3O_4@DFNS(图 6(h))。Zhang 等[78]制备了 Fe_3O_4@SiO_2@RF@DFNS 复合结构, 经过高温煅烧处理, RF 树脂和 DFNS 结构中的 CTAB 模板剂被去除, 形成了磁性蛋黄–蛋壳结构。氨基功能化后, 磁性蛋黄–蛋壳结构复合纳米粒子能够通过戊二醛将 CRL 固定在其分层结构。15 次磁分离实验后, CRL 活性依旧保持不变。

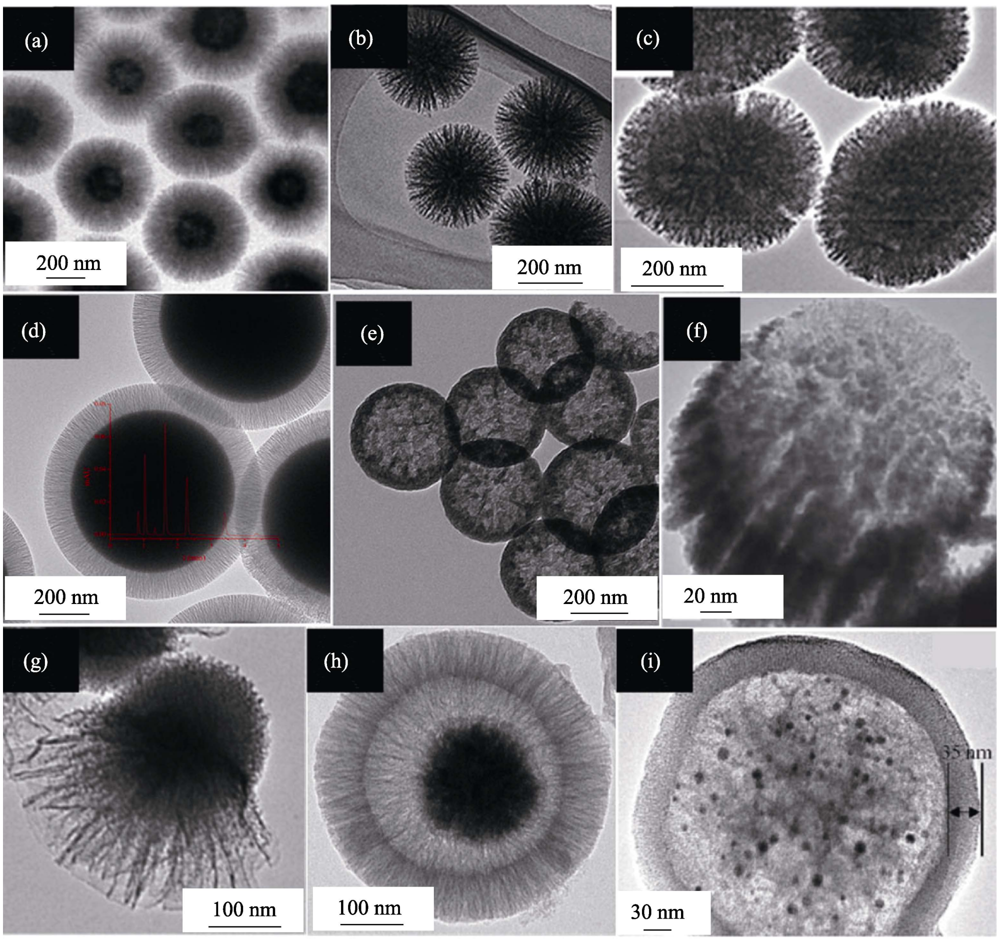

图 6　不同结构 DFNS 类复合纳米粒子的 TEM 照片

Fig. 6　TEM images of nanoparticles with diverse morphologies developed by means of DFNS reaction systems

(a) Core-shelled Fe_3O_4@SiO_2@KCC-1[8]; (b) Fe_3O_4/DFNS composites[47]; (c) Core-shelled TS-1@KCC-1[80]; (d) Core-shelled SiO_2@DFNS[134]; (e) Hollow DFNS [86]; (f) Janus DFNS/Mg@Au[121]; (g) Shuttlecock-shaped DFNS Au@Mg-DFNS[48]; (h) Yolk-shelled Fe_3O_4@DFNS[144]; (i) Yolk-shelled DFNS/Pt@MSS[159]

5.5 其他特殊结构

最近，杜鑫等[159]制备了一种极其稳定的蛋黄–蛋壳形异质催化剂，用来催化还原对硝基苯酚。不同于上述蛋黄–蛋壳结构的纳米粒子，树枝状纤维形壳结构在纳米粒子外部。此处，树枝状纤维形二氧化硅纳米球作为蛋黄结构，而介孔二氧化硅层作为保护壳(Mesoporous Silica Shell, MSS)。首先，将铂纳米颗粒载入 DFNS 核，形成异质结构的 DFNS/Pt 蛋黄。然后，在其表面分别覆盖 RF 树脂和介孔硅壳，形成 DFNS/Pt@RF@MSS。最后，通过高温煅烧去除 RF 有机树脂，形成蛋黄–蛋壳形 DFNS/Pt@MSS (图 6(i))。该复合催化剂能够出色地催化一氧化碳氧化和环化反应[159]。Li 等[31]以球形 DFNS 为核，在其中心辐射状孔道负载 CdTe 量子点后，于表面制备了一层介孔二氧化硅层。所得 DFNS/CdTe@MSS 具有出色的稳定性和 MSS 壳厚度相关的细胞毒性，能够用于荧光生物成像。Zhou 等[160]使用 PVP 作为封端剂，调节环己烷–乙醇–水反应体系中的 CTAB 浓度，成功制备了以 DFNS 为蛋黄的摇铃形复合纳米粒子。

6 实时应用概述

DFNS 具有独特的三维中心辐射树枝状纤维形超结构，粒子内表面具有高度可接触性(可进入性)。尤其是 DFNS 结构骨架存在硅羟基(–SiOH)，有机官能团能够通过化学嫁接法修饰于其表面。不同尺寸的分子(如药物和生物大分子)以及功能性纳米粒子(如贵金属和荧光量子点)等都能够通过共价键合、静电作用或疏水作用被原位负载或者共负载，所形成的特定功能化 DFNS 作为载体/支撑体/支架/平台富有应用前景(图 3(b))。

随着 DFNS 蓬勃式发展，实时更新其应用领域范围是必要的，尤其是前面所提三篇综述未涉及内容。本文在介绍非应用领域时(如第 5 节的新兴结构)，讲解了部分最新应用进展。现将 2017~2018 年 DFNS 出现的其他新颖应用实例介绍如下。

6.1 DFNS 相关的 Pickering 乳液

Qu 等[116]将表面活化的人造酶(Surface-active Artificial Enzymes, SAE)纳米粒子负载于 DFNS 孔道，所得 DFNS/SAE 加入水和十二烷的混合液，超声作用下形成 Pickering 乳液。其中，制备了三种类型的 SAE，包括多肽类、金属复合物类和脱氧核酶类，分别用于实现具有催化性能的仿生脂肪酶活性、磷酸二酯酶活性和过氧化氢酶活性。Wu 等[118]将尼罗红(Nile red)负载于聚异丙基丙烯酰胺(PNIPAM)功能化的球形 DFNS，其作为 Pickering 乳化剂。加入 5(6)-羧基荧光素(CFDA)并紫外照射，pH 响应的单体聚合形成杂化胶体状微反应器，其对 pH 和温度有双刺激响应，即在不同温度和 pH 条件下尼罗红和 CFDA 能被选择性活化释放。通过 Pickering 微乳液方法，Jiang 等[161]使用脂肪酶功能化的球形 DFNS(Lp-DFNS)构筑了具有磁性及较强酶催化作用的生物催化微胶囊(Colloidosome)。该生物催化微胶囊能够催化不同烷基链长度的脂肪酸和醇的酯化反应，比单纯脂肪酶催化的体系具有更高的产率。此外，此微胶囊能够催化丙三醇的酯基转移反应，从而获得丙三醇碳酸酯，转化率为 85.2%。Yang 等[45]结合二甲基十八烷基[3-(三甲氧基硅基)丙基]氯化铵修饰的球形 DFNS 和离子液体技术，通过 Pickering 乳液制备了用于十二烯烃多相加氢甲酰化的新型催化剂。

6.2 实时生物应用

Zhang 等[162]将球形 DFNS 用氨基硅烷、琥珀酰酐、阿仑膦酸钠(ALN)和铁络合剂二乙三胺戊乙酸改性，形成以 ALN 为骨靶向配体的复合平台担载 Gd^{3+}和地塞米松(DEX)。终产物能够提高碱性磷酸酶活性，从而提升间叶干细胞的结节形成能力。Hu 等[163]将疏水性的量子点(Quantum Dots, QDs)负载于巯基改性的 DFNS 纳米孔道，在 DFNS/QDs 表面涂覆烷基硅烷层，形成的 DFNS/QDs 胶体粒子能够灵敏且持久地免疫测定临床 C 反应蛋白样品(C-reaction protein)。Bein 等[164]用氮杂–二苯并环辛炔(DBCO)改性巯基化的大孔开口球形 DFNS，来引发无铜催化的叠氮化合物配合点击化学反应(如 5-羧基四甲基罗丹明叠氮化物，TAMRA)。终结构 DFNS-DBCO-TAMRA 能够将 TAMRA 受控释放于子宫颈癌传代细胞。Jonuleit 等[165]将肿瘤坏死因子 TNF-α 封装于聚乙烯亚胺和聚乙二醇(PEI-PEG)改性的球形 DFNS，然后将 DFNS-(PEI-PEG)/TNF-α 递送于不同癌细胞和树枝状细胞中，来诱导细胞凋亡。

6.3 球形 DFNS 作为硬模板

球形 DFNS 一个非常重要的应用是作为硬模板(牺牲模板)，通过纳米铸造的方法，来制备具有相似结构或相反结构的功能粒子，例如：树枝状纤维形硅钛杂化纳米球[30,38,52,54-55,102]、树枝状纤维形碳纳米球[61,129,142]和树枝状纤维形碳氮杂化纳米球[90,114]。由于这一部分涉及内容较多，将在后续的文章中详细介绍。

6.4 其他实时应用

Costantini 等[166]将 β-葡糖苷酶(Glucosidase, BG)

负载于 DFNS 的纳米褶皱孔道, 用来催化纤维二糖水解, 四次循环可使得纤维二糖完全水解。Polshettiwar 课题组[71]将超细 Au 纳米粒子负载于 NH_2-DFNS, 所得催化剂不仅能高效催化氧化有机硅烷生成硅醇, 还能实现硅烷醇解及醛类氯化。该课题组[29]最近将 DFNS&Au 作为过氧化物酶, 相对于天然的辣根过氧化物酶, 所得复合催化剂对四甲基联苯胺催化具有很高酶催化活性。Polshettiwar 等[27]在 DFNS 存在的螺吡喃溶液中观察到了对光反应变色现象。具体为, 包含 DFNS 和螺吡喃的无色悬浊液在紫外照射后变为蓝色。如果外加搅拌, 无色悬浊液变为红色。研究者进一步用 DFNS 吸附螺吡喃溶液中的部花青, 生成的红色杂化材料在可见光照射下显示出消极的对光反应变色现象[28]。

7 总结及展望

本综述主要归纳总结了树枝状纤维形二氧化硅纳米粒子的研究进展、结构特征、新兴结构及实时应用领域等。对比分析了已开发 DFNS 合成方法的优劣性, 众多称谓的适用性、常用结构模型等。大量研究成果表明: DFNS 独特的三维中心辐射状孔道和多级孔结构, 使之极有可能替代传统二氧化硅介孔材料(如 MCM-41 和 SBA-15)[75,102,138-139,167], 成为一种富有前景的平台/支撑体/载体。DFNS 已经推动了一些新合成策略和应用领域的发展, 随着研究的进一步深入, 今后的研究重点主要集中在以下三个方面(图 7)。

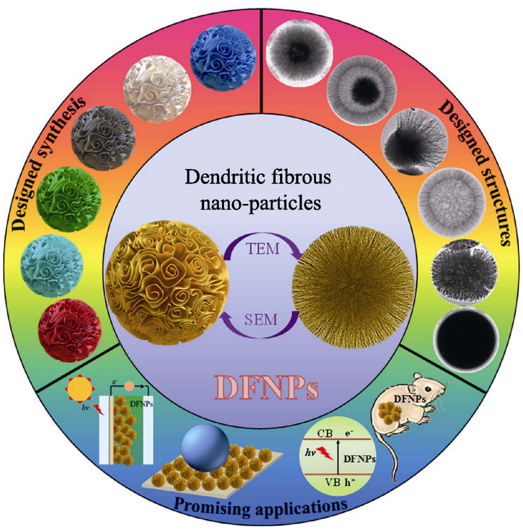

图 7　树枝状纤维形纳米粒子的设计合成、结构设计以及应用前景示意图

Fig. 7　Schematic illustration of designed synthesis, designed structures, and promising applications for dendritic fibrous nano-particles

7.1　设计合成

DFNS 的合成方法启发众多研究课题组直接合成其他本体元素基的树枝状纤维形纳米粒子(Dendritic Fibrous Nano-particles, DFNPs), 如树枝状纤维形活性生物玻璃纳米球[122]。或通过引入新元素对 DFNS 骨架掺杂改性, 如树枝状纤维形硅碳杂化纳米球[128]、树枝状纤维形硅铝杂化纳米球[168]、枝状纤维形硅铜铝杂化纳米球等[104]。以上两种策略是控制合成的重点, 也是合成新型 DFNPs 的手段。

7.2　结构设计

基于不同元素组成的树枝状纤维形纳米粒子, 设计合成新颖结构或复杂多级结构依旧是该方向的热点。例如, Yu 等[169]近期成功制备了空心状、双层壳结构的树枝状纤维形有机–无机硅杂化纳米球。

7.3　开拓新应用领域

元素组成和独特结构共同决定了 DFNPs 的应用前景。如上述空心双层壳结构的树枝状纤维形有机–无机硅杂化纳米球能够应用于生物体进行药物递送, 进而达到肿瘤治疗的目的[169]。一方面, 有机–无机硅杂化骨架较传统无机硅骨架更加稳定, 也更加容易被化学修饰进而负载治疗药物。另一方面, 空心状、双层壳、树枝状纤维形特殊结构可以控制释放载药的速度, 对细胞摄取也具有超强作用。

综上所述, 以应用为目的, 通过设计合成和结构设计, 树枝状纤维形纳米粒子这一学科展现出蓬勃的生命力, 大量工作亟需投入其中。

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