凝胶法制备凝胶网络-单晶复合物

金心仪, 刘育京, 任劼, 李寒莹*

浙江大学高分子科学与工程学系, 高分子合成与功能构造教育部重点实验室, 杭州 310027

* 联系人, E-mail: hanying_li@zju.edu.cn

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摘要 一个多世纪以来, 凝胶作为介质被用于晶体生长, 成功制备出了大量单晶. 其中, 越来越多的单晶被证明能在晶体生长过程中将凝胶网络嵌入其中, 从而形成两相三维互穿的凝胶网络-单晶复合物, 这与自然界生物体中大分子嵌入单晶内部以增强晶体力学性能的现象如出一辙. 兼具单晶的长程有序特征和复合材料的综合特性使得这种单晶复合物受到研究者的广泛关注. 本文综述了凝胶法制备凝胶网络-单晶复合物的研究进展, 对具体技术手段、单晶中凝胶嵌入的表征、影响凝胶在单晶中内嵌的因素以及单晶复合物的功能化4个方面进行了介绍和讨论, 并对今后的研究方向与前景进行了展望.

关键词 凝胶, 单晶, 复合物

晶体通常具有均匀的组成成分和三维周期性的原子排列, 但近年来的研究发现, 自然界中的一些生物体能利用蛋白质、多糖等生物大分子“杂质”的嵌入来构建具有复杂结构层次的高分子-单晶复合物^[1~7]. 这些生物矿化形成的硬组织生物材料, 如软体动物的外壳等, 拥有和我们通常所认知的单晶不同的结构: 有机组分的掺入不仅没有改变其单晶的长程有序特性(衍射X射线或电子束时仍呈现为单晶特征的图案), 同时还克服了单晶的脆性, 赋予这种复合物优异的力学性能. 这一有意思的现象激起了研究者浓厚的兴趣, 大自然给予的灵感启发人们制备兼具单晶有序结构和复合结构的新型材料以拓宽晶体在各个领域的应用^[8~11]. 通过不断对单晶复合物结构和形成机理的研究, 越来越多的“杂质”, 如聚合物胶束、粒子、凝胶等均被成功嵌入单晶.

在合成的单晶复合物中, “杂质”可以是离散的聚集体(如胶束和粒子), 也可以是相互连接的网络(如

多孔凝胶). 在晶体生长的过程中, 晶体外表面碰到的“杂质”被不断嵌入到晶体中. 一方面, 对于离散的聚集体, 它们的嵌入主要是由于晶体和聚集体之间的相互吸引作用. 比如, 采用和生物矿化类似的方法, 利用表面特殊基团与晶体间的相互作用, 使胶束和粒子甚至二维材料嵌入不同单晶内部^[12~22]. 另一方面, 当生长的晶体接触到相互连接的网络, 在合适的条件下(如足够高的生长速度^[23]), 网络会限制晶体生长的空间, 成为其生长的“模板”, 从而发生两者的复合(图1). 这些网络包括有序的三维结构, 比如光子晶体^[24]等, 也包括更加无序、制备更为容易的凝胶网络. 有趣的是, 虽然凝胶法作为一种常用的晶体生长手段, 其悠久的历史可追溯到18世纪末^[25], 但直到1969年, 凝胶法生长晶体过程中凝胶网络能嵌入单晶内部的现象才被发现并报道^[26]. 然而该现象仅在一种晶体-凝胶体系中发现, 被认为可能是特例^[25], 而不具有普遍意义, 因此在发表后较长的时间里并

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图1 (网络版彩色)晶体与凝胶复合的示意图

Figure 1 (Color online) A schematic representation of the growth process of the gel-incorporated single-crystals

没有引起较大关注. 直到近年来, 越来越多的晶体才被证实能用凝胶法将凝胶网络嵌入内部形成两相三维互穿的复合物. 因为简单高效、且嵌入的凝胶网络均匀分布等特点, 凝胶法不仅大大丰富了单晶复合物的制备方法, 同时除了晶体-凝胶网络的二元复合, 凝胶法也被证明可以用来制备更加复杂的多元结构, 如晶体-凝胶网络-粒子的复合体系, 为功能性第三组分(如纳米粒子)的引入创造了便利^[27], 从而为实现单晶功能化提供了切实可行的途径和思路. 本文简要评述了凝胶法制备凝胶网络-单晶复合物的研究进展.

1 凝胶法制备单晶复合物

凝胶法生长晶体相比于溶液法而言, 能抑制液体对流和晶体的过度成核, 因而常被用来在室温下生长高质量的单晶. 它具有生长环境友好、过程可观、操作简单等特点. 迄今为止, 多种单晶已成功通过这种方法制备. 凝胶法通常是利用溶质或溶剂的扩散在凝胶体系中发生化学反应或物理过饱和, 析出目标产物从而长出晶体的过程, 可分为以下4类^[28].

1.1 化学反应法

化学反应法(reaction method)在生长水中难溶或微溶的晶体时具有特殊优势, 其装置主要有2种. 第1种方法的设计思想较为简单, 即将一种反应物加入已配制好的溶胶中, 待溶胶在试管中成胶后, 在凝胶上层加入第2种反应物溶液. 溶液缓慢扩散进入凝胶中与第1种反应物相遇并反应, 析出晶体. 若反应速率太快, 可在凝胶-溶液界面处加1层不含反应物的

空白胶作为缓冲, 从而降低反应物的扩散速度和凝胶中反应物浓度. 另一种方法需要采用U形管来生长晶体: U形管两端分别加入两种反应物溶液, 逐渐扩散进入U形管中间部分的空白胶中, 两者相遇反应, 当反应产物聚集到一定程度后产生过饱和, 成核结晶. 化学反应法常用来制备无机盐类晶体, 如方解石^[26]、草酸钡^[29]等.

1.2 化学还原法

化学还原法(chemical reaction method)是化学反应法的一种特殊情况, 即利用还原反应来生长晶体. 而这种方法又可细分为两种: 一种与前述反应法类似, 通常将金属盐加入凝胶中, 而后将含有还原剂的溶液加于其上, 随着还原剂逐渐扩散进入凝胶中发生还原反应, 在凝胶中生长出金属单质晶体^[30,31]; 另一种还可采用电解还原法, 即将含有反应物的凝胶通电电解来生长单质晶体, 如Au, Ag^[32,33]等.

1.3 降低溶解度法

降低溶解度法(solubility reduction method)常用来生长一些在水中溶解度较大的物质, 如 $\text{NH}_4\text{H}_2\text{PO}_4$, KH_2PO_4 (KDP), NaCl ^[34~39]等. 实验时可将水溶性物质配制在溶胶中, 待成胶后, 将非溶剂加至凝胶上层. 非溶剂的扩散会导致目标物质溶解度逐渐降低, 达到一定的过饱和度从而成核析晶. 有时为了减缓非溶剂的扩散过程以得到更高质量的单晶, 可以让非溶剂与凝胶不直接接触而是靠挥发扩散进入胶中, 或在含有目标物质的凝胶上做一层空白胶之后再加

入非溶剂. 当然, 对于一些不溶于水却易溶于其他溶剂的物质, 也可以用类似方法生长.

1.4 解复合法

解复合法(decomplexing method)是溶解度降低法的一种特殊情况. 对于在水中微溶的晶体, 如AgCl, AgI, CuCl^[40~43]等, 直接通过降低溶解度的方法显然不可行. 但这些物质能与某些易溶络合物从而显著增加其溶解度, 之后再缓慢稀释络合物溶液生长晶体就能很好地解决低溶解度的问题. 实验时可将络合物溶液加至凝胶上层, 目标晶体会随着络合物溶液逐渐扩散稀释至凝胶中析出. 或将络合物溶液加入溶胶中, 待冷却成胶后, 将水或低浓度配体溶液加至凝胶上层, 此时凝胶中的配体易溶物会扩散进入上层清液中, 难溶盐则会随着凝胶中配体浓度的降低解复合并析出结晶.

2 单晶中凝胶网络的嵌入

1969年, Nickl和Henisch^[26]首次报道了在硅胶中生长的方解石单晶能将硅胶的网络嵌入晶体中形成复合物. 他们将所得晶体用盐酸溶解一部分后发现, 晶体并不纯净, 剩余未溶解晶体的外部由一圈溶解后剩余的胶状物质围绕, 且胶状物质轮廓和原晶体相近. 将胶状物质和正常制备的硅胶冻干后用扫描电子显微镜(SEM)观察, 发现两者形貌结构一致, 说明这种胶状物质正是硅胶, 初步证实了方解石单晶中确实存在硅胶网络嵌入的现象. 同样, 1998年, Garcia-Ruiz等人^[44]采用硅胶作为介质制备了溶菌酶蛋白质单晶, 发现得到的其实是硅胶网络-单晶的复合物, 亲水性硅胶网络的嵌入使得溶菌酶晶体的力学性能得到了显著提高. 除了无机凝胶网络, 他们发现有机聚合物网络——琼脂糖凝胶同样能嵌入溶菌酶和铁蛋白等蛋白质晶体中^[45]. 除此之外, 明胶^[46]、聚丙烯酰胺水凝胶^[47]等各种聚合物网络均被证实既能作为晶体生长介质, 又能嵌入单晶内部形成复合物.

琼脂糖凝胶在晶体中的纳米纤维网络结构又进一步被Estroff课题组^[23,48,49]的实验所证实. 他们利用琼脂糖凝胶作为介质生长方解石晶体, 得到的晶体用去离子水刻蚀之后用SEM观察, 发现刻蚀坑洞中存在凝胶纤维(图2(a)). 进一步采用聚焦离子束技术将晶体超薄切片后进行环形暗场扫描透射电子显微镜(LAADF-STEM)分析, 明显观察到嵌入晶体中琼

脂糖凝胶的纳米纤维网络(图2(c)). 同时, 层析显像术得到的晶体结构图显示凝胶以三维网络的形态连续分布在晶体内部(图2(b)). 有趣的是, 选区电子衍射(SAED)却表明, 即使有琼脂糖纳米纤维的嵌入, 方解石晶体仍呈现单晶的长程有序特性(图2(d)). 之后, 他们还在琼脂糖凝胶中生长了酒石酸钙和甘氨酸的单晶^[50], 同样发现凝胶网络嵌入单晶之中.

随后, 具有同样凝胶网络-单晶复合结构的多种晶体-凝胶组合被相继报道, 如无机半导体晶体PbI₂/PbS和硅胶的组合^[51]、有机半导体蒽晶体/二苯基蒽晶体和苯基硅胶的组合等^[52], 对于这些复合体系, 嵌入到晶体当中的凝胶物质虽然隐藏在晶体当中, 但它们可以通过溶解晶体而暴露出来. 因此, 可以在光学显微镜下连续观察晶体的溶解过程, 晶体溶解后剩余的不溶解物质(即凝胶物质)通常具有与原晶体相近的形状. 当晶体的尺寸较小、难以用光学显微镜观察时, 电子显微镜便成为主要的表征手段. 对无机晶体而言, 常采用刻蚀晶体的方法来暴露部分的凝胶网络, 然后采用SEM观察残留晶体表面的凝胶结构; 对于有机晶体, 可采用将晶体升华的方法来暴露凝胶结构. 除了定性的表征以外, 嵌入晶体中的凝胶含量可以采用热失重分析法以及电感耦合等离子体原子发射光谱法来定量分析. 另一方面, 复合物中晶体的长程有序性可以通过偏光显微镜、单晶衍射、电子衍射等一系列方法表征.

3 影响凝胶在单晶中内嵌的因素

作为晶体生长介质的凝胶, 一般是由三维多孔的纤维网络加上溶剂组成, 是一种半固状物质, 它的化学组成、结构、与晶体的作用力等共同影响着晶体的成核与生长. 通过改变凝胶的强度、晶体生长速率以及凝胶网络和晶体之间的相互作用, 可以有效调控凝胶在晶体中的内嵌含量.

3.1 凝胶网络的强度

Khaimov-Mal'kov^[53]曾提出, 在凝胶中生长的晶体, 生长过程中会向周围的凝胶网络施加一定的结晶压力. 若凝胶网络强度较低, 不足以抵抗该压力, 凝胶网络会在其作用下断裂, 从而被晶体推开. 反之, 若凝胶的强度足以抗衡结晶压力, 凝胶就会在结晶过程中嵌入晶体. Li和Estroff^[23]用两种强度不同的琼脂糖凝胶培养方解石单晶, 并采用热失重分析出

图2 (网络版彩色)琼脂糖凝胶网络-方解石单晶复合物。(a) 方解石单晶在去离子水中刻蚀后的SEM图, 白色箭头指明了刻蚀坑洞中凝胶纳米纤维的存在, 插图为放大倍数较小的照片。Reprinted with permission from Ref. [23], Copyright © 2009 Wiley; (b) 层析成像法所得晶体内部凝胶网络图; (c) LAADF-STEM下, 方解石晶体切片中的琼脂糖纤维网络; (d) LAADF-STEM下方解石晶体的晶格照片, 插图为SAED图, 所选区域同时包含晶体和琼脂糖纤维。Reprinted with permission from Ref. [48], Copyright © 2009 AAAS

Figure 2 (Color online) Agarose network-calcite single crystal composite. (a) A SEM image of a calcite crystal grown in agarose gel after etching. White arrows highlight the incorporated gel fibers. Inset: An image with a lower magnification. Reprinted with permission from Ref. [23], Copyright © 2009 Wiley. (b) Tomographic reconstruction of an agarose network inside of a section of as-prepared crystal. (c) A LAADF-STEM image of a thin section cut from a gel-grown calcite crystal. (d) A LAADF-STEM lattice image of the composite. Inset: A SAED pattern of the cut section. The examined area contains both crystal and fibers. Reprinted with permission from Ref. [48], Copyright © 2009 AAAS

晶体内嵌凝胶含量, 发现两种凝胶中获得的晶体内的凝胶含量不同, 高强度的凝胶更容易被嵌入晶体(图3(a)), 实验结果符合Khaimov-Mal'kov的猜想。有趣的是, Gavira和Garcia-Ruiz^[45]通过计算发现, 琼脂糖凝胶中生长溶菌酶晶体的结晶压力高于琼脂糖凝胶的断裂强度, 但实验证明溶菌酶晶体在生长过程中却没有将凝胶破坏, 反而将网络嵌入晶体内部, 这与Khaimov-Mal'kov的猜想是相反的。所以纯粹从凝胶强度来判断凝胶能否嵌入晶体不够合理, 还需考虑更多其他因素。

3.2 晶体生长速率

除了凝胶强度, Estroff研究组^[23,50]在2009年提出晶体生长速率也是影响凝胶嵌入晶体的一个关键因素。借鉴以往对于粒子杂质与生长的晶体之间的相互作用的研究^[54], 他们猜想, 如果晶体生长速率越快, 凝胶网络受到的黏滞阻力就越大, 促使其更加容易嵌入晶体。同时, 凝胶网络阻碍了分子向晶体生长前锋的扩散, 尤其是被凝胶纤维所覆盖的这部分生长前锋, 导致晶体更加容易在没有纤维覆盖的区域生长, 形成对纤维的包覆, 使其最终嵌入晶体。晶体

图3 影响凝胶在单晶中内嵌的因素。(a) 不同Ca²⁺浓度、不同凝胶强度条件下制备的方解石单晶的热失重(TGA)曲线。琼脂糖IB制备的凝胶较强,而琼脂糖IX制备的凝胶较弱;(b) 用不同Ca²⁺浓度在琼脂糖凝胶中生长的方解石晶体的热失重情况。随着Ca²⁺浓度的增加,热失重的量逐渐增加然后稳定在一个平台;(c) 琼脂糖凝胶网络嵌入生长中方解石单晶的机理示意图,较快的结晶速率和较高的凝胶强度有利于凝胶网络嵌入晶体形成复合物。Reprinted with permission from Ref. [23], Copyright © 2009 Wiley

Figure 3 Factors that influence the incorporation of gel-networks into single crystals. (a) TGA curves for calcite grown in agarose IX gel and agarose IB gel with different Ca²⁺ concentrations. (b) The relationship between Ca²⁺ concentration in growth media and weight loss from TGA. (c) A schematic representation of the proposed mechanisms by which the agarose network is incorporated during crystal growth. Stronger gel media and faster growth rate favor the gel incorporation. Reprinted with permission from Ref. [23], Copyright © 2009 Wiley

生长速度越快,这种传质作用的影响就更大,也更有利于凝胶网络的嵌入。为了验证生长速度的影响,他们通过提高反应物浓度来提高结晶速度,在溶解有不同浓度CaCl₂的琼脂糖凝胶中培养方解石晶体,并采用热重分析法定量分析晶体中内嵌的琼脂凝胶的质量分数。研究表明,随着凝胶中CaCl₂浓度的增加(即晶体生长速率的加快),琼脂糖的内嵌量显著增加并趋于一个饱和值(图3(a), (b))。对此,他们认为琼脂糖凝胶中有一些相对较强的网络结构,而在强的主网络结构上还有一些弱的悬挂链,当生长速度较低时,只有强的主网络结构被嵌入,随着生长速度提升,弱的悬挂链也会慢慢被嵌入(图3(c)),凝胶嵌入量逐渐上升至临界值,随后基本持平,说明凝胶内嵌量达到饱和。

3.3 凝胶网络与晶体之间的相互作用

Chen等人^[55]研究了NaF, NaCl, KBr, KDP 4种晶体在硅胶中的生长。研究发现,NaF与KDP晶体能很好地将硅胶网络嵌入其中,且硅胶的嵌入量与理论计算值(该计算假设晶体碰到的所有凝胶网络都被嵌入)几乎一致,而NaCl和KBr晶体则几乎无硅胶内嵌。

他们认为NaF与KDP晶体可以通过氢键与硅胶网络形成较强的相互作用,从而有利于凝胶嵌入;而NaCl和KBr晶体则因无法形成氢键,与硅胶的亲合力较弱,在晶体生长过程中凝胶易于被晶体推开。Ren等人^[52]的研究也进一步证实了该结论。他们发现,在未经修饰的硅胶中生长2种共轭分子(蒽和9,10-二苯基蒽)的晶体,得到的晶体均无法内嵌凝胶。而在硅胶网络上引入疏水的苯基之后,增强了凝胶网络与共轭分子之间的相互作用,从而成功将凝胶嵌入单晶内部;且随着苯基含量升高,晶体内嵌凝胶量也相应增加。上述研究均证明了凝胶-晶体之间的相互作用在凝胶嵌入过程中的重要性。

4 单晶复合物的功能化

通常认为,在生物矿化过程中,晶体将有机物质嵌入其中以获得优异的力学性能。这促使人们开始思考,是否能够通过合成晶体当中嵌入功能性的杂质,从而赋予单晶非本征性质,实现单晶复合物的功能化。一方面,凝胶网络本身可能作为功能性的杂质来改性单晶,比如增强单晶的力学性质^[44]、调控单晶的形貌^[56]等。另一方面,近年来的研究发现,在将

功能性杂质引入单晶的过程中,凝胶网络可以起到媒介的关键作用.

Liu 等人^[27]在2014年利用琼脂糖凝胶作为介质,首先在凝胶中均匀分散金纳米粒子,然后生长方解石单晶,使得原本无色的单晶获得光学吸收,实现了晶体的“染色”(图4). 同样地,在均匀分散有磁性纳米粒子 Fe_3O_4 的凝胶介质中生长方解石单晶,能赋予所得晶体本不具备的顺磁性(图4(d)). 对此类改性晶体的一系列表征结果证明,晶体确实在嵌入琼脂糖凝胶网络的过程中将其负载的功能性粒子一并吸收,同时仍保持长程有序的单晶特性. 研究进一步发现,若在均匀分散有功能性粒子的溶液中生长方解石单

晶,晶体会将粒子推开至表面而无法嵌入其中. 他们因此推测,凝胶网络减缓了功能性粒子的扩散速度,并将其限制在三维网络中,晶体在嵌入凝胶的同时也嵌入了凝胶内分散的粒子,从而实现单晶的功能化. 类似地, Kim 等人^[57]利用木葡聚糖凝胶作为载体,在方解石单晶中嵌入 ZnO 和 Fe_3O_4 纳米粒子,赋予单晶非本征的光学和磁学性能. 除了单晶的功能化,第三组分嵌入单晶还可能改变第三组分本身的性质. 例如, 2016年, Liu 等人^[58]用同样的方法将碲化镉量子点和聚合物发光纳米粒子 PF-10BT (poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-1-thiadiazole)]), PF-5DTBT (poly-(9,9-dioctylfluorene)-co-(4,7-

图4 (网络版彩色)单晶复合物的功能化. (a) 晶体在分散有功能性纳米粒子的凝胶中生长的示意图; (b)~(d) 在不同琼脂糖凝胶中生长的方解石晶体的光学显微镜(OM)图片. (b) 纯净的琼脂糖凝胶; (c) 分散有金纳米粒子的琼脂糖凝胶; (d) 同时分散有金纳米粒子和 Fe_3O_4 磁性纳米粒子的琼脂糖凝胶. Reprinted with permission from Ref. [27], Copyright © 2014 Wiley

Figure 4 (Color online) Functionalized single crystals. (a) Crystallization in gel media containing dispersed nanoparticles. (b)~(d) OM images of calcite crystals grown in agarose gel (b), agarose gel containing Au nanoparticles (c), and agarose gel containing both Au and Fe_3O_4 nanoparticles (d). Reprinted with permission from Ref. [27], Copyright © 2014 Wiley

di-2-thienyl-2,1,3-benzothiadiazole))嵌入方解石单晶中,发现嵌入晶体后的量子点和聚合物发光纳米粒子的光稳定性和荧光寿命都有所提高.他们认为可能是密集的单晶外壳有效阻止了氧分子扩散进入单晶内部,从而避免了氧组分参与的降解.

5 展望

凝胶法作为一种简单的生长单晶的方法,由于凝胶网络在晶体生长过程中嵌入其中并提升其力学性能的这一现象,不仅为研究者研究生物矿化过程提供了新思路,也为制备拥有优异特性的新型单晶复合材料提供了可能性.一方面,对这一现象背后的

机理,目前尽管有了大致的理解,却仍需进一步深入挖掘,这需要系统地扩展一系列不同晶体与凝胶组合形成的单晶复合物.另一方面,这种存在内部两相(甚至多相)异质结构网络互穿的单晶复合物有望形成功能材料.这需要设计具有特定功能的凝胶体系^[59],也需要逐步研究功能性的单晶(如半导体晶体^[51,52])在凝胶中的生长和复合.这类兼具高界面面积和单晶的长程有序性的新材料具有光电材料所需要的结构特征,很可能在光电器件中得到应用.同时,以凝胶网络作为媒介向单晶中引入功能性纳米材料的策略为制备单晶复合功能材料提供了简便的途径,有望衍生出一系列功能化和多功能化的单晶复合材料.

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Summary for “凝胶法制备凝胶网络-单晶复合物”

Gel-network/single-crystal composites formed in gel media

JIN XinYi, LIU YuJing, REN Jie & LI HanYing*

Ministry of Education Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

* Corresponding author, E-mail: hanying_li@zju.edu.cn

Gel-grown method has been adopted to grow single crystals for over a century, and has triggered increasing interest with a large number of single crystals obtained. Some organisms construct their hard tissues where foreign macromolecules have been incorporated into the brittle crystals to enhance their mechanical properties. In 1969, the researchers found out that gel-network could be incorporated into the single-crystalline matrix in the similar way. The unique property of the gel-incorporated single-crystals is the combination of long-range order (single-crystallinity) and composite structures, which has enlightened the research on not only understanding biomineralization, but also exploring possible applications of these unique composites. This review will briefly introduce recent progress in gel-network/single-crystal composites formed in gel media in five aspects.

Firstly, we will discuss the growth process of the composites. The growth procedures fall into four categories: (1) The reaction method, (2) the chemical reduction method, (3) the solubility reduction method, (4) the decomplexing method, and various types of crystals have been testified the successful inclusion of gel media including soluble and insoluble compounds, metal, etc.

Secondly, we will briefly introduce several characterizations to demonstrate the distinctive structure of the composites. Incorporated gel fibers can be seen clearly inside the etched pits of the composite under scanning electron microscope. The fibrous structure can be further demonstrated using scanning transmission electron microscope and electron tomography by imaging a thin section cut from a gel-grown crystal. For example, tomographic reconstruction of an agarose network inside of a section of the crystal proves the three-dimensional random-interpenetrating structure between the gel guest and the crystal host while selected-area (area contains both crystal and fibers) electron diffraction pattern shows that the crystal remains its single-crystallinity.

Thirdly, we will discuss several factors, which influence the effective absorption of gel inside the crystals. By measuring the amount of incorporated gel-network using thermal gravimetric analyzer, researchers have concluded that gel-network with higher strength tend to be embedded inside the crystal while weaker gel is more likely to be pushed away. Besides, faster growth rate as well as stronger interaction between the crystal host and the gel guest favors the gel incorporation.

Fourthly, we will discuss a new approach to functionalize single crystals. The reinforced mechanical properties of gel-incorporated crystals inspire scientists to introduce other functional components inside the crystals to achieve multiple nonintrinsic properties. The gel-mediating strategy offers a facile way to realize this idea by trapping functional nanoparticles within gel media and inducing inclusion of nanomaterials into crystals along with gel-networks.

Finally, we will put forward some promising research directions in this area including intensive study of the mechanism involved, exploring more crystal-gel combinations, putting heroic efforts on the functionalization of the composites and most importantly, digging up potential application prospects.

gel, single crystal, composite

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