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评　述

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热注射法制备金属硒化物纳米晶

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摘要　金属硒化物纳米晶由于其独特的物理、化学性质，在光伏、光电探测、热电和生物医疗探针等领域表现出了巨大的应用潜力，引起人们的广泛关注．热注射法是液相合成金属硒化物纳米晶最有效、最重要的方法之一．本文介绍了热注射法制备纳米晶的基本原理、实施过程和特点，并概述了国内外利用该方法制备金属硒化物纳米晶的研究进展．

关键词　金属硒化物，纳米晶，热注射法，绿色制备

纳米材料广义上是三维空间中至少有一维处于纳米尺度范围或者由该尺度范围的物质为基本结构单元所构成的材料的总称[1]．在众多的纳米材料中，金属硒化物纳米晶是近年来发展速度最快、研究最为深入的纳米材料之一[2~6]．1993年，Murray等人[7]采用高温金属有机法液相成功合成出高质量CdSe纳米晶之后，研究者已经制备出多种金属硒化物纳米晶．由于该类纳米晶具有量子尺度效应、多激子效应等独特的物化性质，它们在太阳能光伏、发光二极管、光电探测器、热电和锂电等新能源领域表现出广泛的应用前景．特别是在太阳能光伏应用方面，随着纳米晶墨水涂覆技术的日益成熟，使得制备高电池效率、低成本的金属硒化物纳米晶薄膜太阳能电池成为可能，为该类薄膜电池新工艺制备提供了新的研究思路．

目前，金属硒化物纳米晶的液相合成方法主要有热注射法、水/溶剂热法、单源前驱体法等．与其他方法相比，热注射法因实施过程巧妙，往往能得到形貌均一、粒径分布范围小、单分散性好的高质量纳米晶，广泛用于金属硒化物纳米晶合成．

简单地说，液相法合成纳米晶的基本原理是：合适的反应条件下，前驱体在合适的溶剂和表面活性剂体系中形核生长[8]．热注射法是一种典型的金属硒化物纳米晶液相制备方法，在其反应过程中，将冷的前驱体溶液迅速注射到高温溶剂中，瞬间引发爆炸形核，导致反应体系中前驱体浓度降低至临界形核浓度以下，伴随反应溶液的温度降低，晶核在较低的温度下生长，确保纳米晶的形核和生长在不同的温度下进行，避免了二次形核，这样就保证了最终生长所得到纳米晶具有均匀的粒径分布，其主要实施过程如图1所示．

Murray和Bawendi是热注射法制备金属硫属化合物纳米晶的先驱．1993年，Murray等人[7]提出了高温有机金属法，后被称为热注射法，并采用该方法制备了粒度分布范围小、接近于单分散的CdX(X=S, Se, Te)

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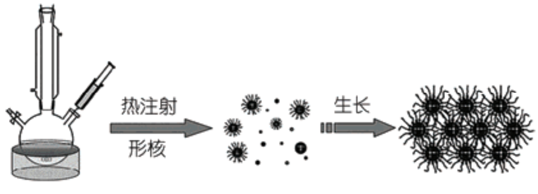

图 1 热注射法制备纳米晶示意图[9]

Figure 1 A schematic illustration of the preperation of nanocrystals by hot-injection method[9]

半导体纳米晶. 自此, 该方法被广泛使用, 许多高质量、单分散纳米晶采用该方法成功合成, 主要包括II-VI, III-V和IV-VI纳米晶[8], 如SnSe, CuSe, $Cu_{2-x}Se$, Ag_2Se, InSe, In_2Se_3, Bi_2Se_3, GaSe等一大批新型二元金属硒化物纳米晶[10~20].

热注射法较易实现对所制备金属硒化物纳米晶形貌的控制, 通过调整合适的实验参数, 如反应溶剂种类、表面活性剂种类及加入量、反应配方、温度、时间等, 实现特定形态、尺寸的金属硒化物纳米晶制备. 除了上述二元金属硒化物纳米晶的热注射合成以外, 多种I-III-VI_2和I_2-II-IV-VI_4纳米晶相继通过热注射法制备出来, 如$CuInSe_2$, $Cu_2(In_xGa_{1-x})Se_4$, $Cu_2ZnSnSe_4$和$Cu_2GeSnSe_4$等. 本文将阐述和总结近年来金属硒化物纳米晶在热注射合成方面取得的研究进展.

1 二元金属硒化物纳米晶的热注射制备

1993年, Murray等人[7]最先采用热注射法制备出单分散、粒度均一的CdSe纳米晶. 在此实验方案基础上, Talapin等人[21]添加十六胺(HAD)作为表面活性剂, 在4,4′-(六氟异丙烯)二酞酸酐(HAD)/三辛基氧化膦(TOPO)/三辛基膦(TOP)混合溶液体系中, 制备出了粒径分布偏差仅5%的CdSe纳米晶, 提高了产品质量. 从2000年开始, 彭笑刚课题组[22~24]对CdSe纳米晶的绿色合成开展了深入研究, 并做出许多开创性工作. 首先, 以镉的氧化物、镉盐(包括醋酸镉、硝酸镉)为反应金属源, 在保证CdSe纳米晶质量的前提下, 成功替代了剧毒性镉源二甲胺镉. 然后, 采用非配位溶剂十八烯(ODE)替换掉反应溶剂TOPO, 与TOPO相比, ODE能够更好地控制Cd前驱体的反应活性, 提高了热注射实验过程的可操作性和安全性; 通过添加脂肪酸等表面活性剂, 成功地实现了对CdSe纳米晶形貌、尺寸的控制. 后来, 他们又发现使用脂肪胺作为反应溶剂, 能起到反应溶液介质和表面活性剂的双重作用, 与ODE反应体系相比, 能在反应温度降低100~200 ℃的情况下得到高质量CdSe纳米晶[25,26]. Alivisatos课题组[27]则致力于研究CdSe合成形貌控制, 通过控制单体浓度及表面活性剂比例等反应条件制备出点状、棒状、米粒状和四足状等形状的CdSe纳米晶(图2).

在这些开拓性工作之后, CdSe纳米晶的热注射制备研究主要集中在绿色低毒硒源的开发和通过掺杂、壳核结构设计、表面修饰等方法对CdSe纳米晶改性这两个方面. 在绿色硒源研发方面, 彭笑刚课题组[22~24]、邹炳锁课题组[28]和Mulvaney课题组[29]先后做了大量的研究工作, 并取得了一定的进展, 该内容将在第4节详细阐述.

由于CdSe量子点表现出优异的光致发光性能[30], 因此, CdSe的热注射合成过程往往与表面修饰、构建新型的纳米晶结构、掺杂改性等方式相结合, 以获得尽可能高的光致发光效率. Hines和Guyot-Sionnest[31]在CdSe粒子表面修饰一层ZnS, 该结构材料可以大幅度增加发光效率. Donega等人[32]通过调节实验条件, 控制CdSe纳米晶的尺寸及形貌, 以达到相对高的光致发光量子产率(PLQY). Knoll课题组[33]采用合金化方式热注射制备CdSe纳米晶, 然后掺杂Zn, 最终得到$Zn_xCd_{1-x}Se$合金化纳米晶(图3), PLQY提升至

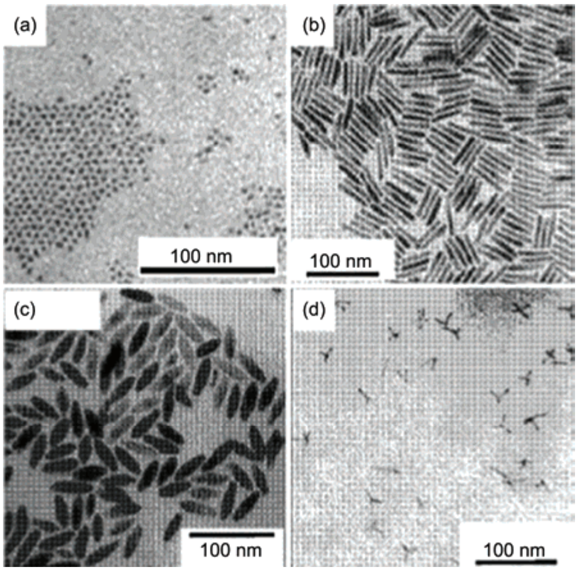

图 2 CdSe纳米晶透射电子显微镜(TEM)图片. (a) 点状, (b) 棒状, (c) 米粒状, (d) 四足状[27]

Figure 2 TEM images of different samples of CdSe nanocrystals. (a) Dots, (b) rods, (c) rice-shaped, (d) tetrapods-shaped[27]

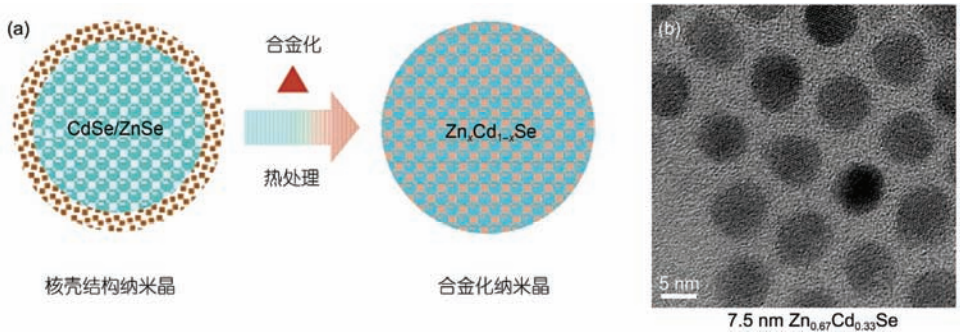

图 3 (网络版彩色)合金化制备成分可调的$Zn_xCd_{1-x}Se$纳米晶. (a) CdSe/ZnSe纳米晶转变成$Zn_xCd_{1-x}Se$合金化纳米晶过程示意图. (b) $Zn_xCd_{1-x}Se$合金化纳米晶高分辨TEM(HRTEM)图[33]

Figure 3 (Color online) Composition-tunable $Zn_xCd_{1-x}Se$ nanocrystals by rapid alloying process. (a) A schematic illustration of the kinetic alloying process from core-shell CdSe/ZnSe to alloyed $Zn_xCd_{1-x}Se$ nanocrystals; (b) HRTEM image of $Zn_xCd_{1-x}Se$ nanocrystals[33]

70%~85%.

为了降低纳米晶热注射制备对于苛刻实验条件的要求，如无水无氧制备环境和相对昂贵的有机溶剂，近年来有人开始尝试在大气环境中制备CdSe纳米晶[34]，还有研究人员直接在水相体系中热注射合成CdSe和ZnSe纳米晶[35~38]，并取得了一定进展. 这些处理方法和优化方案都将为CdSe和其他纳米晶的改性及应用提供借鉴.

ZnSe是另外一种重要的金属硒化物，与CdSe一样，它在近紫外和蓝光范围内有非常优异的光致发光性能. Hines和Guyot-Sionnest[39]借鉴Murray制备CdSe纳米晶的方法，以二乙基锌为锌源，与硒粉共同溶解在TOP中进行反应，首次获得了高质量单分散的ZnSe纳米晶，该产物的PLQY达到20%~50%. Reiss等人[40]用性质稳定、更加环保的硬脂酸锌为锌源，在ODE溶剂体系中，制备了尺度可控(3~7 nm)的ZnSe纳米晶，同样表现出优良的光致发光性能. Li等人[41]在二十四烷和十八烯的混合溶剂体系中，加入少量的硬脂酸胺(ODA)为表面活性剂，采用锌羟酸盐为锌前驱体，同样制备出尺度形貌均一的ZnSe纳米晶，并证明ODA在合成过程中起关键性作用. Chen等人[42]在HDA反应溶剂中，以ZnO和十二烷酸为Zn源，获得粒径分布范围为2.5~6 nm的ZnSe纳米晶. 此外, Cozzoli等人[43]通过调整反应前驱体配方，在十八烯溶剂中合成了闪锌和铅锌矿两种结构的ZnSe纳米晶，产物包括球状、棒状和枝状等多种形态.

除以上两种II-VI族金属硒化物外，IV-VI族的PbSe纳米晶，由于具有窄禁宽、波尔半径大、载流子迁移率高、多激子生成效应、近红外光致发光效率效应强等独特的物理性质，其纳米材料的制备及在光伏、光电探测器、光催化领域的应用基础研究，是材料科学领域的一大热点. 从Murray首次报道制备出PbSe纳米晶以来，热注射法一直是制备高质量PbSe纳米晶的首选方法，只是随着热注射方法的不断成熟，变得更加简便且绿色，最初制备PbSe纳米晶过程中的有毒金属源及溶剂逐渐被低毒环保的试剂取代.

Sb_2Se_3是近几年逐渐受到关注和重视的一种二元金属硒化物，由于其物相单一、组成简单，具有优良的光、电及光电转换特性，被认为是最具商业化应用前景的薄膜太阳能电池材料之一[44~46]. 在Sb_2Se_3纳米晶热注射制备的工作进展如下：2009年，Deng等人[47]采用热注射法制备$Sb_2(Se_{3-x}S_x)_3$纳米管，并通过改变Se/S前驱体比例成功实现对纳米晶禁带宽度的调控(E_g=1.18~1.63 eV)；韩国三星电子Choi课题组[48]以油酸和硬脂酸为表面稳定剂，将$SbCl_3$前驱体溶液注射到硒粉溶液中，在十八烯溶剂体系中成功合成出长径比可调的Sb_2Se_3纳米线. 为使合成过程更加可控、环保、易操作，研究人员倾向选用硒粉作为前驱体硒源，并尝试在多醇溶剂中实施热注射法，并成功合成出形貌尺度均一的Sb_2Se_3纳米棒[49]. 本课题组[50]选用二甲基胺硼烷(DMAB)/Se/OLA可溶硒源，在油胺溶剂中热注射合成出形貌均一的高质量Sb_2Se_3纳米线，如图4所示，为该类纳米材料的热注射制备提供了新方法和新思路.

以上CdSe, ZnSe, PbSe, Sb_2Se_3四种主流金属硒化物纳米晶的热注射制备对自身材料的发展和应用起到了推动作用，填补了纳米晶形成机理的理论空白，并且这些成功的制备经验和方法往往可以运用到其

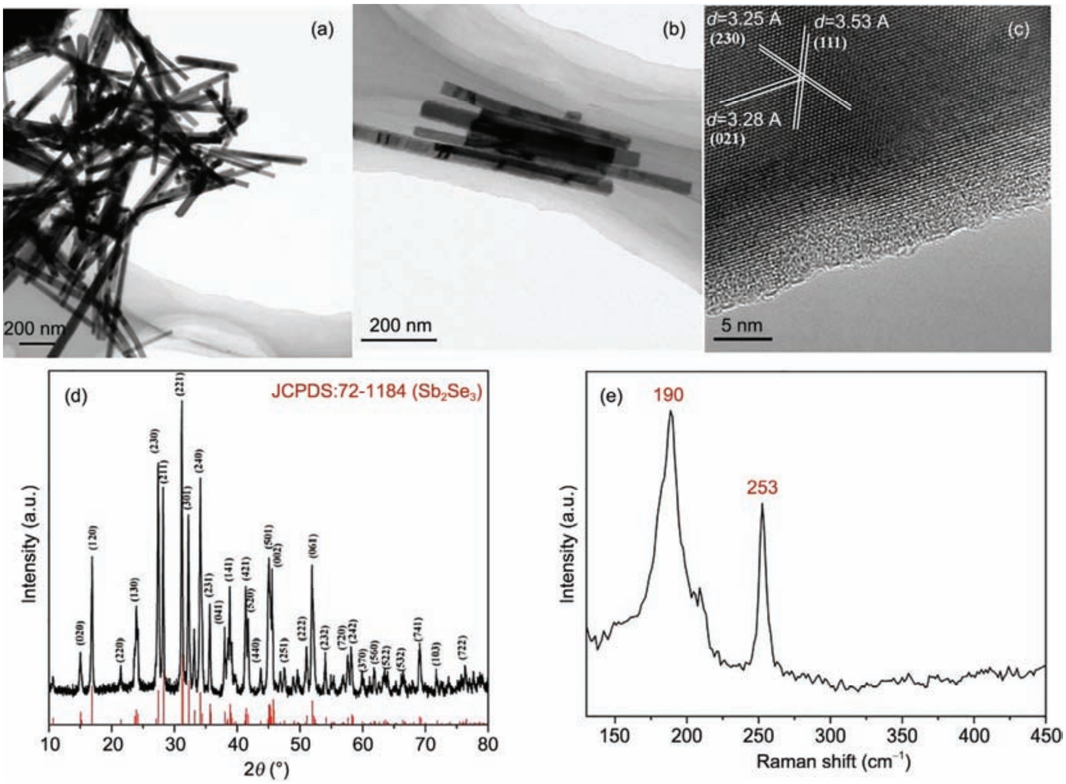

图 4 (网络版彩色)典型Sb_2Se_3纳米线测试结果. (a)~(c) TEM图片, (d) XRD谱图, (e) Raman谱图[50]

Figure 4 (Color online) Test results of the as-synthesized Sb_2Se_3 nanowires. (a)–(c) TEM images, (d) XRD spattern, (e) Raman spectrum of the Sb_2Se_3 nanowires[50]

他二元、三元、四元乃至多元金属硒化物纳米晶材料的制备. 采用热注射法, SnSe, CuSe, $Cu_{2-x}Se$, Ag_2Se, In_2Se_3, WSe, Bi_2Se_3和GaSe等一大批新型二元金属硒化物相继被合成出来[14~20,51]. 值得一提的是, 过渡金属硒化物纳米晶, 特别是片层状结构的纳米材料, 如SnSe, WSe_2和$MoSe_2$等, 由于具有类石墨烯的结构, 为锂离子、钠离子提供了脱嵌位, 加之材料具有较好的光催化活性, 在锂离子电池、超级电容器和光催化领域表现出了良好的应用前景.

2 三元金属硒化物纳米晶的热注射制备

二元金属硒化物纳米晶的制备及应用在过去20年内取得了巨大的成功, 但是其中最为重要的CdSe和PbSe纳米晶含有有毒元素重金属Cd和Pb, 在制备过程及使用中不可避免地会对环境造成一定污染, 限制了其使用和发展. 此时, 更加绿色、环保的三元金属硒化物纳米晶成为最有可能的替代者. 同时, 以$CuInSe_2$, $CuGaSe_2$和$AgInSe_2$为代表的I-III-VI_2族三元金属硒化物作为重要的太阳能电池材料受到广泛关注. 基于二元化合物纳米晶的制备方法, 人们开始尝试合成三元硒化物纳米晶, 并取得了一定的成功. 与二元相比, 三元金属硒化物纳米晶制备的关键是在合成过程中避免分相的形成, 得到纯相的目标产物. 目前, 通过选择合适的表面活性剂和反应条件, 三元金属硒化物纳米晶的制备可以在TOPO, 脂肪胺等配位溶剂或十八烯等非配位溶剂中制备, 这些溶剂或表面活性剂与前驱体之间具有强烈的络合作用, 抑制了杂相的形成.

$CuInSe_2$具有合适的禁宽, 优良的光学和电学性能, 光电转换性能优异, 是重要的太阳能电池材料之一. 1999年, Malik和O'Brien[52]以TOPO为溶剂和表面活性剂, CuCl, $InCl_3$和TOPSe为反应前驱体, 首次热注射合成$CuInSe_2$纳米晶, 但是产物的质量较差, 分散性和光学性质都不好. 与二元金属硒化物纳米晶的发展类似, 考虑到TOPO溶剂的剧毒性, 研究人员随后尝试在脂肪胺或者添加表面活性剂的非配位溶剂中合成$CuInSe_2$纳米晶. 结果表明, 脂肪胺在热注射制备I-III-VI_2族纳米晶中具有一定的普适性, 通过

改变前驱体种类，可以控制纳米晶的形貌和物相. Korgel课题组[53]以CuCl, $InCl_3$和硒脲为前驱体，在油胺中制备出金字塔形的$CuInSe_2$纳米晶.

Norako等人[54]以CuCl, $In(acac)_3$和二苯基二硒醚为前驱体，在油胺溶剂中合成出亚稳态六方铅锌矿的$CuInSe_2$纳米晶. Guo等人[55]以CuCl, $InCl_3$和硒粉为前驱体，在油胺中合成出闪锌矿和黄铜矿两种结构的$CuInSe_2$纳米晶，研究表明，硒前驱物加入油胺反应溶剂体系的顺序对产物的物相起关键性作用；同时，采用刮涂的方式将纳米晶涂覆成膜，加工成电池，获得了2.82%的电池效率(图S1). Tang等人[11]以$Cu(acac)_2$，$Ga(acac)_3$，$InCl_3$和硒粉为前驱体，将金属源注射到硒油胺溶液中，合成了$CuInSe_2$，$CuGaSe_2$和$Cu(InGa)Se_2$纳米晶，表现出良好的光电转换性能.

另外，在二元硒化物纳米晶的制备中获得成功的非配溶剂，如十八烯，也被成功运用于制备$CuInSe_2$纳米晶. 钟海政课题组[56,57]以CuCl，$InCl_3$和TOPSe为前驱体，采用十八烯和正十二硫醇为溶剂和表面活性剂，热注射制备黄铜矿结构的$CuInSe_2$纳米晶，延长反应时间至3 h以上，纳米晶变成三角片状. 正十二硫醇表面活性剂在纳米晶合成中的作用很大，可以有效抑制I族离子(如Ag^+，Cu^+)的反应活性，使I族离子和III族离子同时与VI族离子反应，避免形成分相，有利于$CuInSe_2$纯相纳米晶的形成.

在$CuInSe_2$纳米晶的引领下，多种三元硒化物纳米晶相继制备出来，主要包括$CuGaSe_2$，$CuAlSe_2$，Cu_3SbSe_3，Cu_2SnSe_3和$AgInSe_2$等[10~12,58]. 其中包含Sn，Sb和Bi元素的三元铜基硫属化合物Cu-A-X(A=Sn, Sb, Bi; X=Se, Te, S)半导体材料，具有较好的光电转换特性，其纳米晶也先后被合成，并制备成薄膜太阳能电池器件. Cu_2SnSe_3, Cu_3SbA_3和Cu_3SbA_4(A=S, Se)是优良的热电材料[59]，通过掺杂、结构形貌控制大大提升了其热电性能，近年来该类材料纳米功能化研究也一直备受关注.

3 四元及多元金属硒化物纳米晶的热注射制备

热注射法制备二元和三元硒化物纳米晶取得较大成功后，人们又将目标瞄准到四元或多元金属硒化物纳米晶的合成. 相对于三元硒化物，四元及多元硒化物由于多了一种或几种组元，其合成体系变得更加复杂、难控制，特别是如何调节溶液中各种金属前驱体的反应活性，往往对最终产物质量起到重要影响. Tang等人[11]在热注射合成$CuInSe_2$和$CuGaSe_2$纳米晶的基础上，进而合成了$CuInGaSe_2$纳米晶，其成功的关键在于采用将金属源注射到Se/OLA溶液的方式，实验过程对金属前驱体盐的选择和Se/OLA硒源溶液都做了精细处理. Hsiang课题组[60]在反应前对金属盐前驱体进行预处理，促使其完全溶解、络合，同样采用将金属源注射到Se/OLA溶液的方式制备$Cu(In_{0.7}Ga_{0.3})Se_2$纳米晶，实现了对铟镓元素的精确控制. Zamani课题组[61]使用十八烯作为溶剂，添加十六烷基胺和十四基磷酸为表面活性剂，CuCl，ZnO，$GeCl_4$为金属源，将过量的硒粉在180℃下溶解于十八烯溶剂中形成饱和溶液作为反应硒源，利用热注射法制备$Cu_2ZnGeSe_4$纳米晶. 之后，他们采用同样的工艺合成了$Cu_2CdSnSe_4$纳米晶[62].

万立骏课题组[63]以油酸铜、油酸锌、二乙基已酸锡和二苯二甲基硒为前驱体，在油胺溶剂制备了铅锌矿结构的$Cu_2ZnSnSe_4$(CZTSe)纳米晶. 俞书宏课题组[64]选用SeO_2/ODE为硒源，油胺和十八烯混合溶剂，以CuCl，$Zn(CH_3COO)_2 \cdot 2H_2O$，$SnCl_2 \cdot 2H_2O$为前驱体，制备了非化学计量比的CZTSe纳米晶，该方法制备的纳米晶产率高，单次反应的纳米晶达到10 g左右，一定程度上实现了该类纳米晶的量产，如图5所示.

综上所述，四元硒化物纳米晶的热注射合成已经基本放弃剧毒的TOPO溶剂，通常使用油胺和十八烯作为反应溶剂，使合成过程更加环保且易操作. 金属硒化物纳米晶的绿色合成已经成为该研究领域的发展趋势.

4 金属硒化物纳米晶热注射绿色制备

过去20年，研究人员在金属硒化物纳米晶制备方面取得的种种成果，极大地推动了纳米晶液相制备的发展. 金属硒化物纳米晶的热注射法制备从Bawendi课题组最初的方案，逐渐简化实验步骤，提高实验的可操作性，降低原料的毒性，向简单化、易操作化、绿色化的方向发展. 彭笑刚课题组最早使用氧化镉和羟基镉替代剧毒性镉源二甲基镉，开启了金属硒化物纳米晶热注射绿色制备的先河. 目前，金属源基本都采用各种低毒或无毒可溶的金属盐或金属氧化物，同时，TOPO溶剂也被低毒的ODE, OLA等溶剂替换. 但是，硒源前驱体在2005年之前仍以含膦

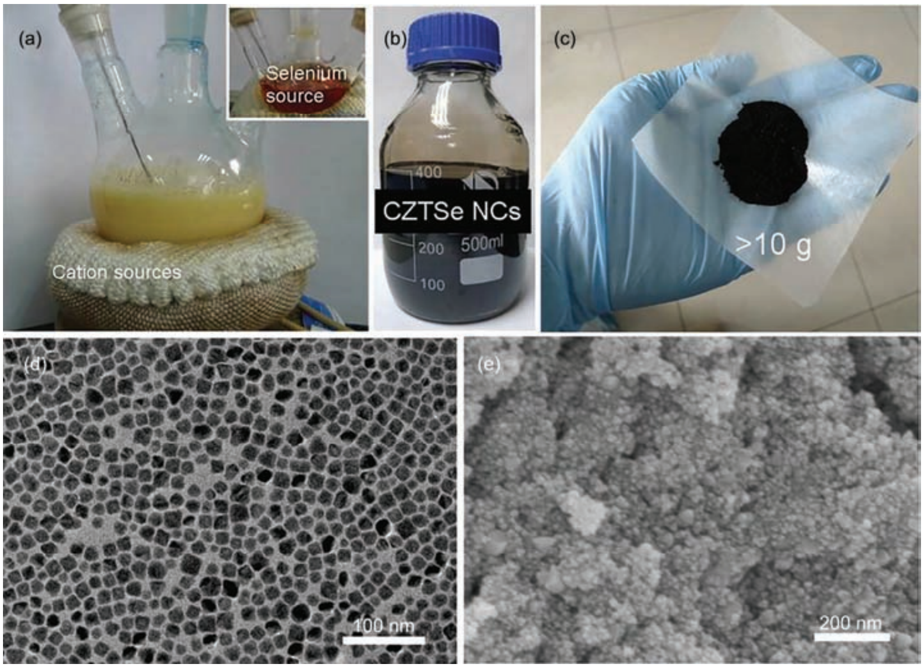

图 5 (网络版彩色)非化学计量比$Cu_2ZnSnSe_4$纳米晶实验过程及结果图片. (a) 硒源及阳离子前驱体照片; (b) $Cu_2ZnSnSe_4$纳米晶墨水; (c) 清洗干净的$Cu_2ZnSnSe_4$纳米晶颗粒; (d) $Cu_2ZnSnSe_4$纳米晶TEM图片; (e) $Cu_2ZnSnSe_4$纳米晶扫描电子显微镜(SEM)图片[64]

Figure 5 (Color online) Experiments and results for non-stoichiometric $Cu_2ZnSnSe_4$ nanocrystals. (a) Photographs of the reaction flasks. (b) The obtained non-stoichiometric $Cu_2ZnSnSe_4$ nanocrystals dispersed in hexane. (c) The surface-cleaned non-stoichiometric $Cu_2ZnSnSe_4$ nanocrystals. TEM (d) and SEM (e) images of the non-stoichiometric $Cu_2ZnSnSe_4$ nanocrystals[64]

有机硒源TOPSe, TBPSe和$(TMS)_2Se$为主.

众所周知, 硒单质在常温或中低温下一般很难溶解到长碳链脂肪酸、脂肪胺等有机溶剂中形成均一溶液, 极大地限制了金属硒化物纳米晶的绿色合成. 从2005年开始, 一些研究组开始涉足环保、高活性热注射硒源的研发. 邹炳锁课题组[28]用硒粉作为硒源, 先在脂肪胺中将硒粉还原成H_2Se, 然后与CdO前驱体反应, 在石蜡溶剂中制备了CdSe纳米晶, 开启无膦制备硒化物纳米晶的先例. Mulvaney课题组[29]将硒粉长时间加热保温溶解到ODE中, 配成Se/ODE硒源溶液, 合成制备了闪锌矿结构的CdSe纳米晶. Sapra课题组[65]使用Se/橄榄油溶液为硒源, 以油胺为表面活性剂, 制备出高质量、单分散性好的CdSe纳米晶. 还有研究人员选用SeO_2/ODE为硒源, 制备了CdSe, ZnSe, $CuZnSnSe_2$纳米晶[64,66~68]. 彭笑刚课题组[69]直接将硒粉分散到ODE溶剂中, 形成硒的悬浊液(Se-SUS)作为反应硒源, 成功合成出CdSe, ZnSe, $CuInSe_2$纳米晶, 实现了纳米晶掺杂, 研究结果表明Se-SUS具有较高的反应活性. Se-SUS高活性硒源及其相关产物如图S2所示. 之后, Zeger课题组[70]同样将硒粉直接分散到ODE或OLA溶剂中, 分别形成Se-ODE和Se-OLA悬浊液, 以此合成CdSe, ZnSe, CuInSe等纳米晶, 值得一提的是, 他们采用Se-OLA悬浊液为硒源, 还制备出了黄铜矿结构的$Cu_2ZnSnSe_4$四元纳米晶. Raston课题组[71]对硒粉在ODE溶液中的溶解机理及Se-ODE前驱体反应活性的变化做了较为系统的研究. 结果表明, 在高温下将硒粉与ODE溶液保温一段时间, 硒粉由环硒或长链硒裂解成短链硒化物(如ODE-2Se, 2ODE-Se), 然后溶解到ODE中, 该类短链硒化物具有很高的反应活性, 对硒化物纳米晶的合成起到至关重要的作用. 合适的反应温度和溶解时间决定了最终Se-ODE硒源前驱体的反应活性.

与以上将硒粉或硒化物直接溶解、分散到有机溶剂的硒源制备思路不同, 有的研究人员则采用添加助溶剂的方式, 首先将硒粉还原成低价的Se^{2-}, 在有机溶剂中发生络合作用, 形成均一、稳定的硒源溶液, 用于热注射反应. Wei等人[15]用$NaBH_4$作为助溶剂, 在油胺OLA中首先将硒粉还原成Se^{2-}, 低价态的硒随后与OLA形成OLA-Se, 配制成可溶性的硒源, 成功

制备了Ag_2Se, CdSe, ZnSe, PbSe等多种硒化物纳米晶. 利用该硒源前驱体, 形态结构更加复杂的Mo掺杂ZnSeS纳米晶被合成出来, 并且表现出优异的光致发光性能[72]. 随后, Zimdars和Bredol[73]对比了使用Se-$NaBH_4$可溶硒源时, 油胺和十八烯两种溶剂对生成的金属硒化物纳米晶的影响. 结果表明, 油胺溶剂中生成的纳米晶结晶度更好, 具有更优的光学性能. 邹炳锁课题组[74]采用该硒源制备了核壳结构的ZnSe/ZnS纳米晶. 采用相同的思路, 张皓课题组[75]以正十二硫醇(DT)为助溶剂, 在室温下配制出了可溶性硒源Se/DT/OLA, 并制备了$Cu_2ZnSnSe_4$纳米晶. 采用该硒源, 最近还合成了成分可调的Ag-In-Se纳米晶, 并制成发光二极管(LED)器件, 表现出良好的发光性能, 主要实验结果如图S3所示[76]. 戴松元课题组[77]同样以DT为助溶剂, 在十八烯溶剂中配制可溶硒源Se/DT/OA, 并以此合成出高质量$CuInSe_2$量子点. 与前面阐述的硒粉在ODE溶剂中溶解机理类似, 通过添加还原助溶剂(如$NaBH_4$和DT), 与OLA交联的环硒或长链硒还原分解成低价硒, 低价硒再与OLA形成短链的OLA-Se复合物[15,75,78](如OLA_2Se, OLA_mSe_n), 实现其溶解. 最终形成的短链OLA-Se_x复合物与反应温度和试剂密切相关, 且x越小, 复合物硒源前驱体反应活性越高. 受此启发, 本课题组[50,79~81]采用二甲基胺硼烷(DMAB)为助溶剂, 开发了DMAB/Se/OLA高活性可溶硒源, 以此热注射合成了Bi_2Se_3, Sb_2Se_3, Cu_3SbSe_3, Cu_2SnSe_3和$Cu_2FeSnSe_4$等一系列金属硒化物纳米晶, 具有一定的普适性.

为实现金属硒化物纳米晶热注射的绿色合成, 人们做了大量的研究工作, 并取得了一定进展. 但是, 到目前为止, 各种无膦硒源各有利弊, 并没有哪一种方法已经达成共识, 发展成为普适的标准方法. 因此, 高活性可溶绿色硒源仍有待进一步研发.

5 结语

热注射法在过去20多年极大地推进了金属硒化物纳米晶的发展, 从形成机理、材料制备、性能优化和应用基础研究等各方面都取得了长足的进步. 与此同时, 热注射法自身制备工艺、方法也在不断的改进和优化中, 向着简单化、易操作化、绿色无毒化、可控精准化的方向发展. 金属硒化物纳米晶热注射制备的发展趋势可概括为以下几个方面: (1) 金属硒化物纳米晶的制备从简单二元向多元、成分可调、结构可控方向发展. 随着热注射方法的日趋成熟, 研究者将不断尝试合成新型纳米晶, 并通过合金化、掺杂等手段, 实现纳米晶成分的精准可调, 最终实现该类材料性能的最优化, 拓展新用途. (2) 绿色、环保、无毒制备工艺的探究. 从热注射法最初被引入到金属硒化物纳米晶制备开始, 研究人员已经不断尝试改进工艺, 摒弃剧毒、昂贵的反应试剂, 降低反应温度, 简化制备过程. 在金属源和反应溶剂方面已经有了较好的选择, 目前的研究重点主要集中在低毒、可溶、高活性的硒源开发上. 在确保纳米晶质量的前提下, 绿色高活性的新型硒源对金属硒化物纳米晶的绿色制备和大规模推广应用将起到至关重要的作用. (3) 工业化量产和大规模应用. 金属硒化物纳米晶热注射合成能够轻易地同比例扩大规模、提高产能, 对稳定、单分散和形状可控纳米晶的实际应用来说至关重要. 但是, 目前实验室采用该方法制备的纳米晶往往产量太低, 一般仅有几克, 一次产出较大的也只有十几克, 离规模化量产还有较大的差距. 等比例大规模量产的反应动力学、工艺的改进和相应反应装置的设计等关键问题都有待进一步研究探讨. 以上这些问题和研究方向是目前限制金属硒化物纳米晶热注射制备和大规模应用发展的关键, 同时也为该类材料的控制合成提供了新的机遇和挑战.

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Summary for “热注射法制备金属硒化物纳米晶”

Preparation of metal selenide nanocrystals with hot-injection method

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Nanomaterials have received extensive and growing research interests due to their unique properties and potential applications in various fields. They have contributed immensely to modern materials science and technology during the last three decades. Among various types of functional nanomaterials, metal selenide nanocrystals have attracted considerable attention because of their special properties. These nanomaterials have been applied in a wide range, such as medicine, electronics, photonics, energy conversion and storage devices, etc. Interestingly, when metals are chemically combined with selenide in the form of nanocrystals, they exhibit semiconductor-like electronic properties. These metal selenide nanocrystals have attracted significant attention in recent years due to their potential applications in solar energy conversion and storage, which are the most important challenges to be addressed to meet the world’s rising demand for clean energy in the future. Hot-injection method is an effective method for the synthesis of metal selenide nanocrystals. The success of this approach lies in the use of non-ionic precursors in high-boiling organic solvents. This makes it possible to grow the nanocrystals relatively slowly at a high temperature, which yields defect-free, well-passivated nanocrystals. The anther important aspect of this method is the separation of the nucleation and growth stages. Due to this, a high degree of monodispersity can be achieved. The fundamental principle of hot-injection method with concrete steps has been introduced. This review surveys the recent progress of the preparation of metal selenide nanocrystals by hot-injection method in terms of binary metal selenide nanocrystals, ternary metal selenide nanocrystals, quaternary, and multinary metal selenide nanocrystals. For binary metal selenide nanocrystals, four important binary metal selenide nanocrystals including CdSe, ZnSe, PbSe, and Sb_2Se_3 nanocrystals are discussed. Then the achievement of synthesis for $CuInSe_2$ and $CuGaSe_2$ nanocrystals by hot-injection method and their application in photovoltaic field are systematically cataloged as well. And the progress in preparation for $CuInGaSe_2$ and $Cu_2ZnSnSe_4$ nanocrystals by hot-injection method has been clarified clearly. Organoselenide chemicals are generally toxic and unstable. The replacement of phosphine containing compounds in the synthesis process of metal selenide nanocrystals via hot-injection method has received considerable attention in recent years. Many attempts have been made to replace trioctylphosphine (TOP) as a medium for delivering selenium in these reactions, but each alternative possesses has significant limitations. This review mainly emphasizes on the recent advances toward the development of methods to achieve “green Se precursor” with high activity and “facile green synthesis” of metal selenide nanocrystals involved in various approaches. Two kinds of different schemes for synthesis and utilization “green Se precursor” are described. Finally, technical challenges and future trends are presented for synthesis of high quality metal selenide nanocrystals, in terms of composition-tunable and structure-controllable multinary metal selenide nanocrystals, green synthesis, industrial production and large-scale application.

metal selenide, nanocrystals, hot-injection method, green synthesis

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