

用于喷墨打印的 Cu_2Se 墨水的制备及表征陈小雨¹, 张骥昊², 叶佳意³, 王连军¹, 江 莞^{1,3}

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摘 要: 相较于传统块体热电器件, 柔性热电薄膜器件展现出更高的集成密度、更快的响应时间和更小的体积, 这使得它们在现代电子器件中具有更灵活的应用场景, 充分契合当前科技发展的趋势。然而, 传统的 Cu_2Se 薄膜制备方法在图案精确化和微型化设计方面存在一定的局限性, 限制了其在高性能微型器件中的应用。喷墨打印技术则能够有效弥补这些不足, 提供更为灵活的制备方案。通过探索不同的合成方法制备 Cu_2Se 纳米粉体, 并研究其在不同溶液中的分散效果, 成功开发出适用于喷墨打印的 Cu_2Se 墨水。这一工作为后续制备 Cu_2Se 热电薄膜及其温差电转换器件奠定了基础, 推动了柔性热电材料在实际应用中的发展。

关键词: 硒化亚铜; 喷墨打印; 热电; 墨水

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最近, 便携式和可穿戴微电子产品的快速发展推动了柔性热电材料的研究, 这些材料有望用于可穿戴设备, 例如通过皮肤与环境之间的温差实现自供电的发电机^[1]。在柔性基底上沉积高性能的无机热电材料已有相当广泛的研究^[2-4]。到目前为止, 大多数柔性薄膜和器件主要采用碲基材料制造, 因其具备优异的热电性能^[5-8]。然而, 碲的自然丰度相对较低, 约为 0.001×10^{-6} , 比常见的过渡金属如铜、镍低得多。而且碲及其部分化合物具有一定毒性, 长期暴露可能会对健康造成危害, 尤其是通过吸入碲蒸气或碲化物粉尘。这使得碲基材料在大规模商业化方面面临巨大挑战。因此, 研发高性能、低成本且无毒的热电薄膜替代碲基热电材料成为了一个迫切的需求。

硒化亚铜(Cu_2Se)作为一种典型的类液态热电材料, 近年来引起了人们的广泛关注和深入研究。 Cu_2Se 是一种本征 p 型半导体, 由丰富、低成本且无毒的元素组成, 使其在可持续能源领域展现出独

特的优势。在 400 K 左右, 它经历了一个从离子绝缘体到离子导体的结构相变^[9-10]。低于 400 K 时, Cu_2Se 的稳定相为单斜 Cu_2Se ($\alpha\text{-Cu}_2\text{Se}$)^[11], 当温度接近相变点时, Cu 原子发生重新排序使得单斜 Cu_2Se 转变为高温超离子反萤石 Cu_2Se ($\beta\text{-Cu}_2\text{Se}$), 在高温相中, Cu 离子具有高度的移动性, 展现出类似超离子液体的行为^[9]。这种特性使得 Cu_2Se 能够有效散射声子, 显著降低了热导率, 从而提高了其热电优值(zT), 使其在热电发电中展现出极大的潜力^[12-15]。

近年来已经报道了许多致力于获得高性能 Cu_2Se 薄膜的工作。例如, Lin 等^[16]使用旋涂工艺在刚性 Al_2O_3 衬底和柔性聚酰亚胺衬底上制备出 Cu_2Se 薄膜; Zhou 等^[17]采用脉冲激光沉积法在单晶 Si 衬底上制备了一系列取向的 $\alpha\text{-Cu}_2\text{Se}$ 薄膜; Zheng 等^[18]通过简便的共溅射方法制备了具有高热电性能的柔性 Cu_2Se 基薄膜; Li 等^[19]采用脉冲激光沉积技术制备了柔性 b 轴取向的 α 相 Cu_2Se 薄膜。然而, 这些

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传统制备工艺在图案精细化及微型化方面存在一定的局限性,限制了其在微型热电器件制备中的应用。

喷墨打印技术作为一种低成本、高效且高精度的数字化印刷工艺,提供了新的解决方案。该技术无需使用掩模或模板,通过编辑位元图形即可将墨水喷印为复杂图案,并且能够适用于各种基底材料,因此在柔性电子器件和可穿戴设备的制造中得到了广泛应用^[20-22]。然而,至今尚未有关于喷墨打印技术制备 Cu_2Se 薄膜的相关报道,这主要与适合喷墨打印的墨水配制问题尚未解决有关。

因此,本工作旨在探讨 Cu_2Se 纳米粉体的制备及其在不同溶液中的分散效果,以期制备出适合喷墨打印技术的 Cu_2Se 墨水。不仅为后续 Cu_2Se 热薄膜的制备奠定了基础,也为探索其在柔性电子器件中的应用提供了新的思路。通过优化墨水的配方和分散性,未来有望实现高性能 Cu_2Se 薄膜的喷墨打印,为其在新一代可穿戴设备中的应用开辟新的可能性。

1 实验

1.1 试剂

氯化铜(98.5%,质量分数,下同)、醋酸铜(98.0%)、五水硫酸铜(CP)、二氧化硒(99.0%)、抗坏血酸(AR)、聚乙烯吡咯烷酮(PVP, K30)、水合肼(85.0%)、氢氧化钠(AR)和无水乙醇(CP)购于国药集团化学试剂有限公司。硒粉(RG)购于上海泰坦科技股份有限公司,去离子水为自制(18.3 M Ω)。

1.2 仪器

采用 X 射线衍射仪(XRD, DX-2700B, 浩元仪器, 辽宁)确定物相;采用场发射扫描电子显微镜(SEM, TESCAN MAIA 3, 捷克)表征样品的微观形貌;采用高分辨透射电子显微镜(HRTEM, JEOL JEM-F200, 日本)来进一步表征粉体的微观结构。

1.3 Cu_2Se 纳米颗粒的制备与墨水的配置

1) 方法一(水热法):首先,将 5 mmol 氯化铜、2.5 mmol 硒粉、0.05 mol 氢氧化钠加入到 50 mL 去离子水中,并在室温连续搅拌 20 min,然后加入一定量(1/5/10 mL)水合肼溶液,并将混合物转移到 100 mL 对位聚苯酚(PPL)-不锈钢高压釜中。随后,将密封的高压釜反应器在 180 °C 加热 20 h,然后自然冷却至室温。将反应器底部的沉淀物离心(10 000 r/min),并用乙醇和蒸馏水洗涤数次后得到 Cu_2Se 粉体。

2) 方法二(水热法):首先将 1 mmol 二氧化硒、

2 mmol 醋酸铜加入到 65 mL 去离子水中,然后室温搅拌直至无沉淀物,缓慢加入水合肼搅拌 10 min,将混合物转移到 100 mL PPL-不锈钢高压釜中,随后将密封的高压釜反应器在 180 °C 加热 24 h,然后等待冷却至室温,将反应所得的沉淀物收集后进行离心清洗。在合成过程中采用控制变量法改变水合肼含量以探讨其对形貌的影响。

3) 方法三(湿法合成法):首先将 1.54 g PVP 分散在 77 mL 去离子水中,依次加入 1.92 mmol 二氧化硒(9.6 mL)和 11.52 mmol L-抗坏血酸(28.8 mL)溶液并搅拌 15 min,然后依次加入 3.84 mmol 五水硫酸铜(9.6 mL)和 15.36 mmol L-抗坏血酸(38.4 mL)溶液。在室温溶液经过磁力搅拌连续反应 16 h。接着用去离子水洗涤数次之后,通过在 11 000 r/min 离心收集得到 Cu_2Se 核壳纳米颗粒。

采用超声分散法制备 Cu_2Se 墨水,将 Cu_2Se 纳米粉末分散在去离子水、乙醇 2 种分散剂中,在超声分散仪中超声 1 h,超声结束后静置待用。

2 结果与讨论

2.1 水热法合成 Cu_2Se 粉体物相与形貌表征

由于喷墨打印机的喷嘴直径较小,因此适于喷墨打印的 Cu_2Se 颗粒尺寸应为纳米级别且在溶液中分散均匀,才不会堵塞喷嘴。分别采用 3 种合成方法以及控制不同变量合成的 Cu_2Se 纳米颗粒进行物相表征及形貌分析。

水合肼在水热反应过程中充当还原剂,可以将金属离子还原为金属或低价态氧化物,而不同含量的水合肼会改变还原速度,从而影响晶体的成核和生长过程,从而影响形貌,因此,在方法一^[23]中通过调节水合肼的添加量来尝试控制 Cu_2Se 粉体的形貌。图 1 为所合成的 Cu_2Se 粉体 XRD 谱。由图 1 可见,衍射峰基本上与标准谱(JCPDS 27-1131)重合,且无杂质峰的存在,说明合成的 Cu_2Se 为 α 相纯相。XRD 谱主峰峰强随着水合肼含量的增加而逐渐减弱,说明所合成的 Cu_2Se 结晶性变差。图 2 为合成的 Cu_2Se 粉体的 SEM 照片。由图 2 可见,合成的粉体为片状,随着水合肼含量的增加,粉体的颗粒尺寸逐渐减小,因此在图 1 中能观察到峰宽增加,主峰峰强相对减弱。然而,即便在加入 10 mL 水合肼时,片状直径仍超过 10 μm 。可能是由于 NaOH 的浓度影响了反应溶液的 pH 值,从而改变晶体的成核和生长条件,导致 Cu_2Se 粉体形成片状结构^[24]。综上所述,尽管该方法能够合成纯相的 α - Cu_2Se ,

但其形貌特征并不适合喷墨打印的需求。这表明, 需要进一步优化反应条件以获得更适用于喷墨打印的粉体。

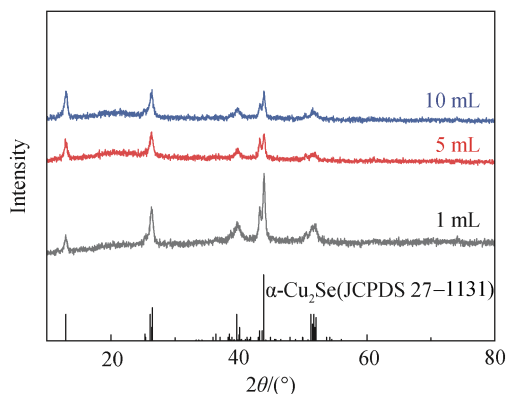


图1 方法一制备不同水合肼含量合成的 Cu_2Se 粉体的XRD谱
Fig. 1 XRD patterns of Cu_2Se powders synthesized with different amounts of hydrazine hydrate (method 1)

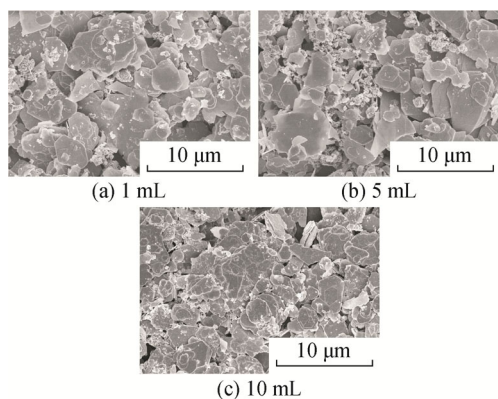


图2 方法一制备不同水合肼含量合成的 Cu_2Se 粉体的SEM照片
Fig. 2 SEM images of Cu_2Se powders synthesized with different amounts of hydrazine hydrate (method 1)

于是在第1种水热合成法的基础上改变条件, 去除碱性环境(NaOH), 具体步骤如方法二所示。同样采用控制变量法, 改变加入水合肼的含量, 以期控制合成粉体的尺寸, 图3为合成的 Cu_2Se 粉体的XRD谱。由图3可见, 合成粉体为立方相(β 相), 衍射峰基本上与标准谱(JCPDS 06-0680)一致。根据 Cu-Se 二元相图, 室温冶金法制备的块体 Cu_2Se 稳定相为 $\alpha\text{-Cu}_2\text{Se}$, 并在约400 K时发生 α 到 β 相的固态转变。然而, $\beta\text{-Cu}_2\text{Se}$ 也可以在400 K以下作为结晶稳定的产物出现, 例如通过溶剂热^[25-27]法和还原法^[27]制备的纳米粉末。与块体 Cu_2Se 不同, 低维 $\beta\text{-Cu}_2\text{Se}$ 在冷却过程中不会转变为 $\alpha\text{-Cu}_2\text{Se}$ 。这可能是由于纳米 Cu_2Se 具有较高的表面能和较高的无序度, 其动力学取向的 β 相更稳定^[27]。图4为4种不同水合肼含量下合成的SEM照片。合成的粉体形貌

均呈现出较大的不规则片状结构($\sim 500\text{ nm}$)和较小的颗粒状结构, 颗粒尺寸并没有明显的减小, 可能是由于水合肼含量变化并不大。但是, 颗粒之间存在非常明显的团聚现象, 这种团聚会导致颗粒因重力作用而沉降, 进而影响墨水的适用性, 尤其是在打印过程中。因此, 考虑在合成过程中引入聚乙烯吡咯烷酮(PVP)。一方面希望PVP可以作为有机配体包覆在 Cu_2Se 纳米颗粒的表面, 利用其空间位阻效应有效避免纳米颗粒的团聚, 从而提高体系的稳定性; 另一方面PVP在乙醇中的溶解度较大, 这有助于纳米颗粒在分散剂中保持良好的分散性。

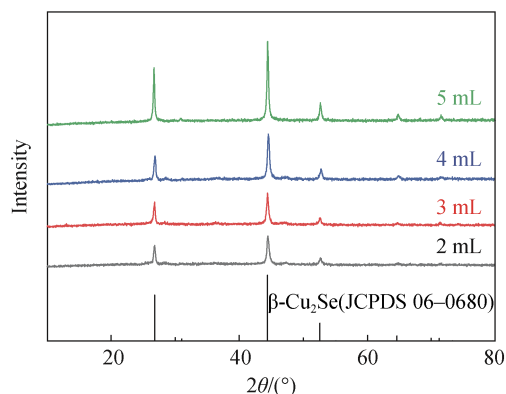


图3 方法二制备不同水合肼含量合成的 Cu_2Se 粉体的XRD谱
Fig. 3 XRD patterns of Cu_2Se powders synthesized with different amounts of hydrazine hydrate (method 2)

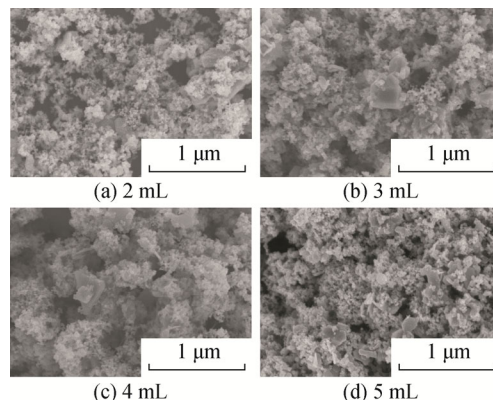


图4 方法二制备不同水合肼含量合成的 Cu_2Se 粉体的SEM照片
Fig. 4 SEM images of Cu_2Se powders synthesized with different amounts of hydrazine hydrate (method 2)

图5为控制反应过程中未加PVP与添加1 g PVP合成粉体的XRD谱。由图5可见, 合成物相与未加PVP时合成产物一致, 均为 $\beta\text{-Cu}_2\text{Se}$, 在加入PVP后的粉体XRD衍射峰的强度明显降低, 可能是由于合成过程中PVP包裹在 Cu_2Se 纳米颗粒表面。图6为所对应的样品的SEM照片。由图6可见, 在加入PVP后合成的粉体粒径有减小, 且未出现图

6a 中的大颗粒,说明合成过程中由于 PVP 的包覆性使得颗粒并没有继续长大成片状,而是保持小尺寸的不规则纳米颗粒状,但是能明显看出颗粒依然紧紧团聚在一起,这会使后续打印过程出现明显的喷嘴堵塞的现象。综上所述,改变水热合成的环境可以控制合成 Cu_2Se 粉体的形貌,但无法解决产物易团聚的问题,因此后续改变合成方式去制备 Cu_2Se 粉体。

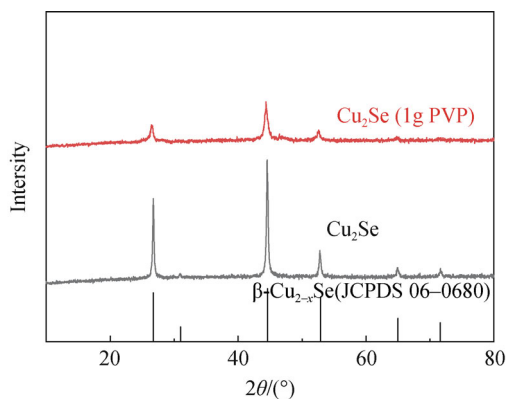


图 5 未加 PVP 与有加 PVP 合成的 Cu_2Se 粉体的 XRD 谱
Fig. 5 XRD patterns of Cu_2Se powders synthesized with and without PVP

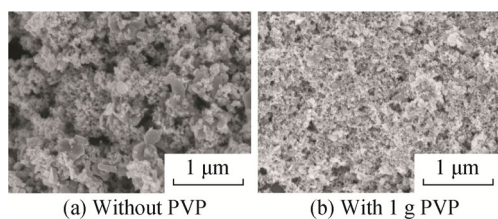


图 6 不加 PVP 与有加 PVP 合成的 Cu_2Se 粉体的 SEM 照片
Fig. 6 SEM images of Cu_2Se powders synthesized with and without PVP

2.2 湿法合成 Cu_2Se 物相分析与形貌表征

文献[28–29]报道采用模板辅助方案合成 $\text{Au-Cu}_2\text{Se}$ 化合物混合纳米结构,通过用抗坏血酸(Vc)还原 SeO_2 ,在水中将无定形 Se 沉积到预制的柠檬酸盐稳定的 Au 核上。随后,加入通过用抗坏

血酸还原 Cu^{2+} 制备的 Cu^+ 。然后 Cu^+ 催化元素 Se 的歧化反应生成 Se^{2-} 和 Se^{4+} ,并进一步与 Se^{2-} 反应生成 Cu_2Se [30]。由于抗坏血酸的存在,反应副产物 Se^{4+} 再次还原为 Se^0 。因此,当使用过量的 Cu^+ 时,Se 可以完全转化为 Cu_2Se 。最后, Cu_2Se 组分在空气中自然硒化,成为自掺杂的等离子体 $\text{Au-Cu}_2\text{Se}$ [31]。反应过程中添加适当的稳定剂(水溶性聚合物或表面活性剂)以提高整个反应过程中的胶体稳定性。否则,在第 1 步沉积 Se 壳层的过程中,纳米晶会迅速聚集。非离子型 PVP 是一种常见的表面活性剂,它被在此被用作模型稳定剂来合成 $\text{Au-Cu}_2\text{Se}$ 杂化纳米粒子。

基于该方法合成 Cu_2Se 粉体,但不预先制备 Au 核,仅合成纯 Cu_2Se 单相化合物,基本原理相似。图 7 为湿法合成 Cu_2Se 粉体的 XRD 谱,其同样具有立方结构($\beta\text{-Cu}_2\text{Se}$),且无杂相存在。由图 8 可见,所合成的纳米颗粒形貌为球状,粒径约 40 nm,尺寸均一,没有大颗粒的存在,且颗粒之间并没有出现团聚现象,这归功于 PVP 的作用。综上,尺寸均一的 Cu_2Se 纳米级颗粒已成功制备,接下来进行 Cu_2Se 墨水的配置。

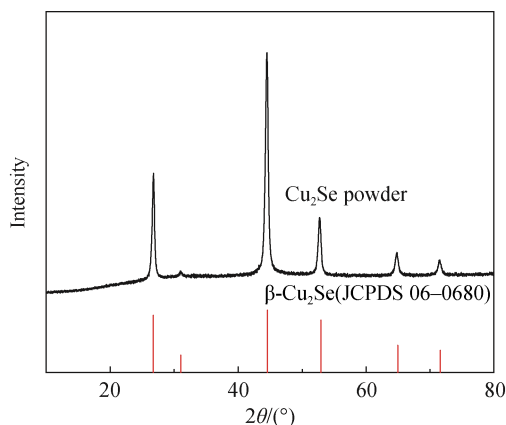


图 7 湿法制备 Cu_2Se 粉体的 XRD 谱
Fig. 7 XRD patterns of Cu_2Se powder synthesized by wet chemical method

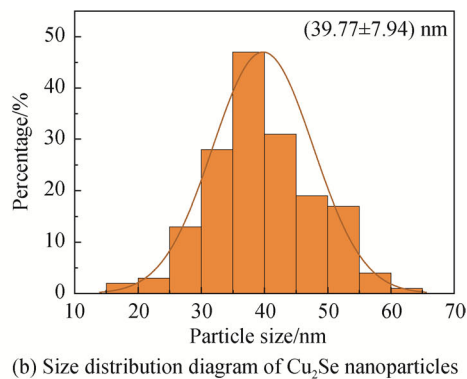
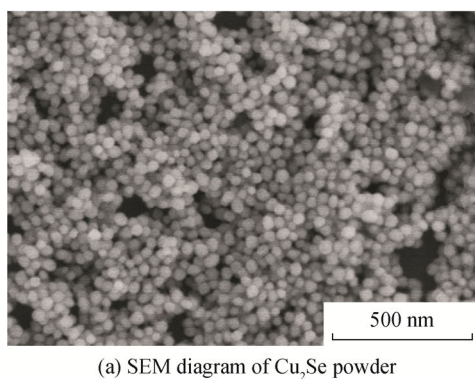
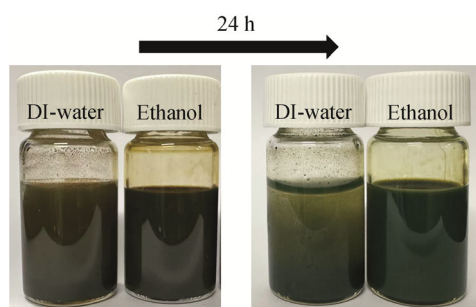


图 8 湿法制备的 Cu_2Se 粉体
Fig. 8 Cu_2Se powder synthesized by wet chemical method

2.3 分散剂对 Cu_2Se 墨水溶液的影响

图9为湿法合成的 Cu_2Se 粉体分散在去离子水、乙醇中配置墨水的分散效果。在进行超声分散后可以看出都具有良好的分散性，再放置 24 h 后明显看出在水中的 Cu_2Se 粉体出现了沉降现象，而 Cu_2Se -乙醇墨水仍保留着良好的分散性。造成这样差异的原因可能是： Cu_2Se 粉体表面包裹的一层有机配体，如图 10 所示，它来源于合成过程中所添加的 PVP，PVP 与溶剂之间存在相溶性，而乙醇对 PVP 的溶解度较大，使得 Cu_2Se 粉体颗粒在乙醇中稳定分散，且 PVP 提供的空间位阻效应避免了纳米颗粒团聚，进一步提高了体系的稳定性。因此，采用乙醇作为墨水分散剂。



DI-water is deionized water.

图 9 湿法制备 Cu_2Se 粉体在不同分散剂溶液中的分散性和稳定性

Fig. 9 Dispersion and stability of Cu_2Se powder synthesized by wet chemical method in different dispersant solutions

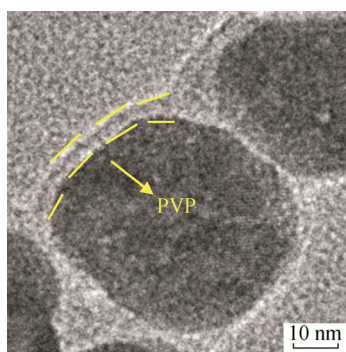


图 10 Cu_2Se 纳米颗粒的 TEM 照片

Fig. 10 TEM image of Cu_2Se nanoparticles

3 结论

为制备适于喷墨打印的 Cu_2Se 墨水，探讨了 3 种制备 Cu_2Se 纳米粉体的方法。在 2 种水热合成法中，发现增加反应过程中水合肼和 PVP 的用量有助于合成小尺寸的 Cu_2Se 纳米粉体。然而，这一方法未能有效解决粉体团聚的问题。为此，转向湿法合成法，并成功制备出粒径均一且不团聚的纳米级

Cu_2Se 颗粒，优异的分散性和稳定性主要归功于颗粒表面包覆的聚乙烯吡咯烷酮，这不仅提高了颗粒在乙醇中的溶解性，还有效防止了颗粒之间的聚集。通过这种方式，成功制备出适合喷墨打印的 Cu_2Se 墨水。这为后续开发高性能 Cu_2Se 热电薄膜及其微型器件提供了坚实的基础。

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Preparation and Characterization of Cu₂Se Ink for Inkjet Printing

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Extended Abstract

Introduction With the rapid development of portable and wearable microelectronics, flexible thermoelectric materials have attracted much attention due to their ability to enable self-powered devices via utilizing the temperature difference between the skin and the environment. However, the scarcity of tellurium resources and its high toxicity pose some challenges to the commercial application of tellurium-based thermoelectric materials. It is thus critical to develop high-performance, low-cost, and non-toxic alternatives for flexible thermoelectric films. Copper(I) selenide (*i.e.*, Cu₂Se), as a representative liquid-like thermoelectric material, has attracted recent attention. Cu₂Se is an intrinsic p-type semiconductor composed of abundant, low-cost, and non-toxic elements, thus offering significant advantages in the field of sustainable energy. The existing studies report the fabrication of high-performance Cu₂Se thin films using conventional preparation techniques. However, these processes face significant limitations in pattern refinement and miniaturization, hindering their application in the fabrication of micro-thermoelectric devices. Inkjet printing technology, as a low-cost, efficient, and high-precision digital printing process, offers a promising solution to these challenges. This technique enables the preparation of complex patterns without masks or templates and is suitable for a variety of substrate materials. Therefore, this study was to prepare Cu₂Se nanopowders and explore their dispersion properties in different solvents to develop Cu₂Se inks suitable for inkjet printing technology, thereby offering insights into the preparation of flexible thermoelectric films and their application in next-generation wearable devices.

Methods Cu₂Se nanoparticles were synthesized by the following methods. In method 1 (*i.e.*, hydrothermal method), 5 mmol copper chloride, 2.5 mmol selenium powder, 0.05 mol sodium hydroxide were mixed with 50 mL deionized water, and continuously stirred at room temperature for 20 min, and then a certain amount of hydrazine hydrate solution was added, and the mixture was transferred to 100 mL PPL–stainless steel autoclave. Subsequently, the sealed autoclave reactor was heated at 180 °C for 20 h and then naturally cooled to room temperature. The precipitate at the bottom of the reactor was centrifuged at 10 000 r/min and washed with ethanol and

distilled water for several times to obtain Cu_2Se powder. In method 2 (*i.e.*, hydrothermal method), 1 mmol of selenium dioxide and 2 mmol of copper acetate were mixed with 65 mL of deionized water, and then stirred at room temperature until there was no sediment. Afterwards, hydrazine hydrate was slowly added and stirred for 10 min. The mixture was transferred to 100 mL PPL–stainless steel autoclave, and then the sealed autoclave reactor was heated at 180 °C for 24 h. After cooling to room temperature, the resulting sediment was collected and centrifugally cleaned. The content of hydrazine hydrate was changed by the control variable method in the synthesis process to investigate its effect on the morphology. In method 3 (*i.e.*, wet synthesis), 1.54 g polyvinylpyrrolidone (PVP) was dispersed in 77 mL deionized water, followed by 1.92 mmol selenium dioxide (9.6 mL) and 11.52 mmol ascorbic acid (28.8 mL) solutions and stirred for 15 min. Afterwards, 3.84 mmol cupric sulfate pentahydrate (9.6 mL) and 15.36 mmol -ascorbic acid (38.4 mL) solution were added successively. The solution was magnetically stirred at room temperature for 16 h. After washing with deionized water for several times, Cu_2Se core–shell nanoparticles were collected by centrifugation at 11 000 r/min.

For Cu_2Se ink configuration, the prepared Cu_2Se powder was dispersed in deionized water and ethanol by an ultrasonic dispersion method. After ultrasonic treatment for 1 h, the dispersion effect was analyzed.

Results and discussion Cu_2Se nanoparticles are prepared by the three methods, and the crystal structure of the synthesized products is verified by the XRD patterns. The morphology and size of Cu_2Se particles prepared by different methods are different. In method 1, Cu_2Se powder prepared under alkaline conditions has a flake structure with a particle size of more than 10 μm , which does not meet the size requirements of inkjet printing. In method 2, under the influence of different contents of hydrazine hydrate, the synthesized powders show a large irregular flake structure (~500 nm) and small granular structure, and the particle size does not decrease significantly. The particle size of the powder is reduced when PVP is introduced into the subsequent synthesis process, indicating that the particles do not continue to grow into sheets during the synthesis process due to the coating of PVP, but remain small and irregular nanoparticles, and the particles are still agglomerated, which can cause a nozzle clogging in the subsequent printing process. In method 3, Cu_2Se particles synthesized by the wet method are spherical with a particle size of approximately 40 nm, and uniform in sizes without particle agglomeration, which can meet the requirements of material size for inkjet printing.

Cu_2Se particles synthesized by the wet method and dispersed under ultrasound in ethanol show a well-dispersion, and the particles in ink do not settle significantly after placing for a period of time, showing a good stability and suitable for inkjet printing.

Conclusions Cu_2Se particles were prepared by the three methods for Cu_2Se ink suitable for inkjet printing, respectively, and nano-sized particles of Cu_2Se with uniform particle size and non-agglomeration were prepared by the wet method. The effective dispersion and stability of Cu_2Se particles were mainly attributed to the coating of PVP on the surface of the particles, improving the solubility of the particles in ethanol, effectively preventing the particle aggregation. This study could provide a foundation for the subsequent development of high-performance Cu_2Se thermoelectric thin films and their microdevices.

Keywords copper(I) selenide; inkjet printing; thermoelectric; ink