

SnS₂ 光催化材料研究进展

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摘 要 作为典型的金属硫化物半导体结构材料,SnS₂ 因其凭借丰富的边缘结构、巨大的比表面积、良好的化学稳定性和可调控禁带宽度(~2.5eV)等特点,近年来在光催化领域备受关注。结合近年来国内外 SnS₂ 材料在光催化领域的研究进展,综述了 SnS₂ 的结构、制备方法及其光催化研究,特别关注了近年来 SnS₂ 材料与其他材料在二元或三元复合光催化领域的研究现状,并对今后光催化 SnS₂ 领域的进一步研究前景提出了展望。

关键词 SnS₂,层状材料,光催化,研究进展

Research progress of SnS₂ photocatalytic material

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Abstract Tin disulfide (SnS₂) is a typical semi-conductor material of metal sulfide. With its virtue characteristics of layered structure and suitable band gap width (~2.5eV),SnS₂ has attracted much attention in the fields of photocatalysis. With research progress of SnS₂ materials in the field of photocatalysis, the structure, preparation methods and photocatalysis of SnS₂ were summarized. Finally, a prospect for the further development of photocatalytic SnS₂ was provided.

Key words SnS₂,layered material,photocatalysis,research progress

因其可将部分太阳光能量转化为化学能的特性,光催化技术被视为解决当今新能源开发和环境污染问题的研究热点^[1]。目前,光催化技术研究包括光催化制氢^[2]、光催化降解污染物^[3-4]及光催化有机化合物合成^[5]等。光催化领域的研究重点之一是如何制备出具有生态环境友好型、光催化性能高的光催化材料。

根据文献报道,从光催化研究的结构角度,目前呈现不同的纳米材料结构有量子点^[6-7]、纳米线^[8-9]、纳米片^[10-12]和多形貌^[13-17]等。这些结构具有纳米量子尺度效应和良好的比表面积等特点,成为众多研究者关注的焦点。与其他维度的纳米材料相比,二维纳米材料如石墨烯^[18]、g-C₃N₄ 纳米材料^[1]、层状金属硫化物纳米材料^[19-22]、ZnO 纳米材料^[23]、黑

磷(BP)^[24]等,由于具有特殊的物理化学结构及特殊的催化反应活性等优势,受到越来越多学者的关注。

在金属二硫化物中,SnS₂ 过渡金属化合物材料具有特殊的二维结构和光电特性^[25-28]。SnS₂ 晶体是六方 CdI₂ 型体系,内部原子间经共价键方式构成“汉堡包”结构,层间通过弱的分子间作用力结合。正因为如此,其结构具有介于二维和三维之间的特性,具有一定的各向异性和光电特性,属于 n 型半导体,其禁带宽度为~2.5eV^[29-30]。因为 SnS₂ 材料在可见光响应区域对应的禁带宽度能较好地利用太阳光,有相关文献报道其在光催化领域具有一定的研究开发价值,并在近年来取得了一定的研究进展^[31-32]。

作为光催化材料,SnS₂ 光催化材料有如下几大

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优点:(1)SnS₂ 是一种禁带宽度可调控的半导体材料,能吸收可见光频率的光子,提高可见光的利用效率;(2)其导带(CB)和价带(VB)的边缘电位^[31](-0.27eV,+2.21eV)比多数光敏半导体高,在作为助催化剂材料时,半导体材料与 CB SnS₂ 边缘之间的电位差促使电子从半导体转移至 SnS₂,这将使更多的导带电子迁移,从而促进电子-空穴对的分离^[25];(3)SnS₂ 材料具有一定可调的比表面积,能吸附更多的反应物分子;(4)SnS₂ 材料边缘结构复杂,有很多的不饱和键。一般而言,为提高光催化效率,主要是从材料界面有效反应比表面积、光谱响应的范围、光生载流子分离传输效率等方面研究。根据文献报道^[29-30,32-38],SnS₂ 光催化材料的研究大都集中在控制形貌结构、元素掺杂或复合异质结协同光催化方面,探讨如何提高光催化性能。

1 SnS₂ 材料的制备

近年来,多形貌结构 SnS₂ 材料在多个领域受到广泛的研究与应用。其制备方法趋于多样化,其中固相反应法、溶剂(水)热法、化学气相沉积法(CVD)和喷雾热解法等方法常用的材料制备方法。

1.1 固相反应法

固相反应法就是反应物均呈固态形式,反应后直接生成所需产品的方法。其主要特点是无需溶剂、设备简单、反应易控、应用简单。如 Kiruthigaa 等^[39]通过固相法在 300℃ 下成功合成了尺度在 426~725nm 的纳米 SnS₂,形貌呈微球状,其禁带宽度为 3.41eV,并在紫外光下能很好地降解 Reactive Red 120 染料。Hou 等^[40]以硫脲和 SnCl₂·2H₂O 为原料,通过固相法在 170℃ 下反应 2h,成功制备了多孔花瓣状 SnS₂ 材料,并在可见光下 25min 几乎完全将 Cr⁶⁺ 还原。

1.2 溶剂(水)热法

溶剂(水)热法是一种进行材料合成与形貌控制的热点方法。据文献报道,该法在制备 SnS₂ 材料方面进行了大量的工作,并成功获得了多种不同形貌结构、不同尺度的 SnS₂ 纳米材料。如 Zhang 等^[41]将四氯化锡、硫代乙酰胺与柠檬酸混合,通过水热反应在不同温度(130~170℃)和不同反应时间(6~24h)条件下调控获得了一系列尺度可控的 SnS₂ 纳米材料,且禁带宽度在 2.20~2.30eV,研究发现在 150℃ 下反应 12h 制备的 SnS₂ 纳米材料在可见光下

降解 Cr⁶⁺ 的效果最好;Xia 等^[42]以 SnCl₂·2H₂O、硫粉和 Na₂S₂O₃·5H₂O 为原料,通过十六烷基三甲基溴化铵(CTAB)微乳法一步水热获得了形貌为空心微球的 SnS₂ 材料,并从实验结果出发,提出了一种基于气泡模板、自组装和后续壳层演化的机理过程;Liu 等^[43]以乙二醇为溶剂,硫脲和 SnCl₄·5H₂O 为原料,通过微波辅助溶剂热法在 180℃ 下反应 12h,成功获得了类康乃馨花状结构三维纳米材料,并通过可见光催化性能测试测得对罗丹明 B(RhB)降解拟一阶速率常数为 0.7836h⁻¹,4h 降解基本完全,对苯酚降解拟一阶速率常数为 0.2475h⁻¹,4h 降解达 60%。

1.3 CVD

作为半导体领域最为广泛的制备技术,CVD 是利用含有薄膜元素的一种或几种气相化合物或单质,在衬底表面上进行化学反应生成薄膜的方法。如 Su 等^[44]在此制备方法上,通过籽晶诱导生长的思路,成功获得了高品质的 SnS₂ 薄层晶体,表征分析厚度在 20nm 左右,光电流响应时间~5μs;Huang 等^[45]通过两步 CVD 法在碳布上成功生长出了 SnS₂ 纳米片,通过测试发现该材料在真空条件下受 473nm 激光照射敏感响应时间为 22ms,可作为良好的光电探测材料,可被应用在光电晶体管上。Li 等^[46]采用 CVD 法,以 S 和 Sn 粉为反应物, SiO₂/Si 为衬底,在 410~525℃ 下能够成功生长出二维 SnS₂ 纳米薄片和花状 SnS₂,其带隙约为 2.20eV,并对其纳米薄片和花状形貌生长进行了机理讨论。Chen 等^[47]报道了将 SnCl₄·5H₂O 和 S 粉作为原料,通过简易 CVD 的方法,在 FTO 导电胶上 450℃ 下生长出了形貌均一的 SnS₂ 六角纳米薄片,其薄片大小在 2~5μm,厚度约在 20nm,且在电压 5eV 下表现出良好的电流密度 3.68mA/cm²。

1.4 喷雾热解法

喷雾热解过程是将各反应物按化学计量比形成前驱液,通过雾化后,由载气引入高温反应炉,在炉中瞬间蒸发溶剂、沉淀溶质,通过干燥、热分解、烧结与烧成等物理化学过程,最终获得超细目标粉体。据相关文献报道,在制备 SnS₂ 材料方面已有应用。如 Vijayakumar 等^[48]采用此方法,通过 SnS₂ 与 N,N-二甲基硫脲为原料,在 348~423K 下成功制备出六角 SnS₂ 薄片状颗粒,研究发现光吸收波长在 400~800nm 范围内,其禁带宽度为~2.75eV,其电阻率在 1.48×10³~0.55×10³Ω·cm 范围;Kumar

等^[49]以四氯化锡、硫脲和酒精(水和酒精体积比为1:3)混合形成溶液,通过此技术在300℃下成功制得了SnS₂材料,研究发现其形貌平均尺寸为60nm,禁带宽度为2.72eV,形成薄膜的透光率达98%。Anitha等^[50]以氯化锡和硫脲为原料,在175~275℃下成功合成了花瓣状SnS₂薄膜材料,通过分析表明其优先定向沿(001)面,禁带宽度在3.26~2.7eV,250℃下合成的SnS₂薄膜材料所获得的电阻率最小(21.9Ω·cm)。Arulanantham等^[51]研究了在325℃下不同硫浓度对喷雾热解SnS₂薄膜物理化学性能的影响,随着硫浓度(0.8mol/L、0.9mol/L、1.0mol/L)增大,获得的SnS₂薄膜颗粒粒径变大(分别为23nm、27nm、40nm),电阻率从 $1.4 \times 10^2 \Omega \cdot \text{cm}$ 增大到 $3.01 \times 10^2 \Omega \cdot \text{cm}$ 。

此外,据文献报道,SnS₂材料的制备方法还有很多,如化学沉淀法^[52]、原子层沉积法^[53]和真空热蒸发法^[54]等。随着材料制备方法的不断开发与研究,众多新型制备方法正被逐步用于制备不同形貌的SnS₂材料中。

2 SnS₂及其复合物在光催化中的应用

如何增大SnS₂材料比表面积、扩展光谱响应的范围、提高光生载流子分离传输效率等问题,是该材料关注的重点。添加微量的助催化剂抑制载流子对复合是常见的光催化性能的提高研究手段^[33-34]。根据文献报道,一是对SnS₂单元改性,主要是通过控制形貌结构和元素掺杂改性,来提高光催化性能;二是通过有机或无机化合物与SnS₂形成二元或多元复合异质结,通过光催化协同效应来提高光催化性能。

2.1 SnS₂单元改性方面

根据文献报道,当前SnS₂单元改性主要是从材料自身的形貌控制、尺度控制、元素掺杂、晶格空位等方面提高光催化性能。如Zhang等^[55]以二硫化硒与单质硫粉作反应源,采用水热法得到花瓣形的SnS₂,测试表明与P25型TiO₂相比,花瓣形状的SnS₂在太阳光下60min甲基橙降解完全,而P25型TiO₂只有1.4%。分析认为花瓣型的SnS₂比表面积较大,并提供了良好的吸附场所,而且提高了SnS₂材料光生电子-空穴对的分离效率。Zhao等^[56]以四氯化锡、三氯化铬和硫脲为原料,通过水热法成功合成了不同量Cr掺杂的SnS₂纳米化状光催化材料,表征分析发现,Cr成功进入到SnS₂晶格

中,且结晶度良好,测试表明掺杂摩尔比5%含量的Cr光催化性能是SnS₂的2.9倍。Liu等^[57]通过控制合成温度和反应时间,制备出不同尺度、不同形貌的SnS₂样品,通过光催化测试比较发现,当材料制备的制度为120℃×3h,反应后制得的SnS₂效果最好。Sun等^[58]采用甲酰胺液体对体相六边形SnS₂材料进行插层剥离,成功获得了单层SnS₂,表征发现,剥离得到的单层SnS₂的厚度相当于约3个原子厚度,与TiO₂对太阳光吸收率为7%相比,其光催化性能测试发现其对太阳光的吸收率达到38.7%。

2.2 SnS₂二元复合异质结

据已有文献报道,提高光催化性能的一个手段就是通过物理化学制备方法,进行SnS₂复合异质结。而进行复合异质结的形式也有很多种,如量子点修饰、二维层状复合、核壳结构复合、三维结构复合、聚合物复合等。如Liu等^[59]采用简单的原位水热离子交换法制备了一种新型的可见光驱动Ag₂S/SnS₂复合光催化剂。在去除甲基橙(MO)和铬(VI)方面,Ag₂S/SnS₂复合材料较纯SnS₂具有更好的光催化活性,在可见光照射下,1% Ag₂S/SnS₂异质结材料光催化降解最好。Song等^[60]通过水热法合成的六方SnS₂与超薄纳米片2Dg-C₃N₄复合,形成了2D/2D z型光催化复合异质结。研究表明5% 2D SnS₂/g-C₃N₄表现最佳,照射60min后去除RhB 94.8%,较单纯2D g-C₃N₄提高了42.1%。Fan等^[61]制备了SnO₂@SnS₂包裹核壳纳米棒,壳层厚度约为3.5nm。在可见光下,与纯SnS₂纳米材料相比,核壳纳米棒具有更好的光催化活性。Luo等^[37]采用简单水热法成功合成了直接Z型LaFeO₃/SnS₂复合异质结光催化材料,通过可见光降解四环素(TC)测试研究发现,LaFeO₃(10.0%)/SnS₂的降解效果最好,降解速率分别为SnS₂和LaFeO₃的3.5倍和2.2倍。Xu等^[62]首次采用原位聚合法合成了聚吡咯(PPy)改性的SnS₂纳米六方片材料,测试结果表明,15-PPy/SnS₂复合材料不仅在可见光区(>420nm)具有良好的光催化性能,而且在近红外区(>760nm)也有较大的光催化性能改善。

2.3 SnS₂的三元复合异质结

近年来,三元化合物作为光催化剂的研究受到部分研究者的关注。三元复合光催化材料可以进一步增强光生载流子的分离与迁移能力,提高光催化

活性^[63]。如 Deng 等^[34]通过水热法成功制备了花瓣形 Ag-Ag₂O-SnS₂ 三元结构纳米复合异质结光催化材料,与二元复合物 Ag-SnS₂ 和 Ag₂O-SnS₂ 相比,Ag-Ag₂O-SnS₂ 在紫外-可见光区域具有更高的光吸收效率,同时在光催化降解 RhB 的降解速率和降解稳定性上,Ag-Ag₂O-SnS₂ 都具备优异的特性。机理研究发现,单质 Ag 介于 Ag₂O 和 SnS₂ 之间,如导体连接,当 Ag₂O 受光照产生电子迁移时,电子会迅速经过 Ag 流向 SnS₂ 光致空穴,形成相互湮灭,而 Ag₂O 光致空穴与 SnS₂ 光生电子因能级差甚远,难以复合。因此实现光生电子-空穴对的分离与迁移,从而具有良好的光催化性能。

3 结语与展望

SnS₂ 材料由于具有可见光响应的禁带宽度和优良的电子传输性能,通过自身材料改性或复合异质结可形成良好的光催化性能,被广泛应用于光催化领域。尽管在光催化领域,SnS₂ 材料已取得了部分研究进展,但还有很多值得研究者深入的地方,主要表现在以下几个方面:一是 SnS₂ 材料结构的可控制备和层数调控方面还有很多研究发展的空间。二是 SnS₂ 材料与其他材料的复合方法也有待优化。目前最多的是原位生长法、水热法和条件混合法。条件混合法过程简单,表界面效应、形貌、电子-空穴对分离与降解机理探究仍是重点方向。三是如何将 SnS₂ 材料光催化响应区向近红外区迁移仍是研究的方向。尽管利用 SnS₂/半导体复合异质结能在可见光区取得一定的进展研究,而向近红外区的利用率不佳,研究者可通过改性该材料,使其向近红外光光催化迁移,以获得全波段太阳光良好的催化效率。

通过综述近年来 SnS₂ 作为光催化材料的研究发展与现状,从材料组成结构、制备及光催化研究 3 个角度,总结了 SnS₂ 材料制备及光催化研究方面的内容,并讨论了提高 SnS₂ 基光催化性能的几种形式。总之,新型 SnS₂ 光催化材料因其自身优势,将成为当下光催化研究的热点。

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