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铋基宽光谱响应光催化材料的研究进展

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摘　要

在污水处理中，基于半导体光催化法的高级氧化技术(AOPs)由于其高效、节能、可循环利用的优点而被广泛研究。然而大多数光催化剂仅能被紫外光激发，为了进一步利用光能节约能源，开发宽光谱响应的光催化剂显得尤为重要。众多光催化剂中，铋基光催化剂其特殊的能带结构使其具有良好的可见光甚至近红外光响应。本文重点概述了具有宽光谱响应的铋基光催化剂的制备方法，并系统地归纳了其改性手段及其在环境污染物去除方面的催化活性性能，最后对该类具有宽光谱响应的铋基光催化剂的发展方向进行了展望。

关键词

铋基光催化剂，近红外，宽光谱响应，废水处理

Research Progress in Bismuth-Based Photocatalysts with Wide Spectral Response

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Abstract

Advanced oxidation technology (AOPs) based on semiconductor photocatalysis has been widely

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studied in wastewater treatment due to its advantages of high efficiency, energy saving and recycling. However, most photocatalysts can only be excited by ultraviolet light. It is crucial to develop photocatalysts with wide spectral response to further expand the light response range and save energy. Among many photocatalysts, bismuth-based photocatalysts have good response upon visible and even near-infrared light due to its special energy band structure. In this paper, the synthesis of bismuth-based photocatalysts with wide spectral response is given in outline, and the modification methods and their catalytic performance in the removal of environmental pollutants are systematically summarized. Finally, the development direction of bismuth-based photocatalysts with wide spectral response is prospected.

Keywords

Bismuth-Based Photocatalysts, Near-Infrared Light, Wide Spectral Response, Wastewater Treatment

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1. 引言

随着当今社会的发展，工业化进程的加快，废水的大量排放会造成严重的环境污染。尽管现有的 Fenton 氧化、UV/H_2O_2 氧化以及臭氧氧化等 AOPs 工艺已经十分成熟，且被广泛应用于实际污水处理当中，但仍然存在诸多问题[1] [2] [3]。例如，针对多环芳烃、多溴联苯醚等含卤素的难降解有机物，传统 AOPs 的去除能力有限[4]。自 1972 年 Fujishima 和 Honda 成功利用半导体催化剂 TiO_2 实现光解水反应以来，半导体光催化技术逐渐成为治理环境污染的热点研究方向[5]。

众所周知，太阳光谱中紫外光所占的比例仅为 4%，可见光和近红外光所占比例高达 95%，然而大多数光催化剂仅能被紫外光激发。为了进一步利用光能节约能源，开发宽光谱响应的光催化剂显得尤为重要，尤其是具有近红外光响应的光催化剂。一方面近红外光响应的光催化剂能更容易被激发，进行一系列催化反应，另一方面由于近红外光具有强穿透力，在实际水处理中可以一定程度上克服浊度对材料吸光性能的影响。

众多光催化剂中，铋基光催化剂由于其特殊的能带结构使其具有良好的可见光甚至近红外光响应[6]。同时其良好的稳定性、低生物毒性、较高的光催化活性使其在水环境污染治理方面显示出良好的应用前景[7] [8] [9]。大部分铋基光催化剂都具有可见光响应，少部分具有近红外响应。当材料的禁带宽度较小，激发价带电子所需光子的最低能量则相对较低。光子所处波长越大，能量越低。因此，一般能被近红外光激发的光催化剂都属于窄带系半导体。目前已报道的具有宽光谱响应的铋基光催化剂主要分为两类，一是由于合成过程中温度、酸碱性等的变化而形成本征缺陷导致材料具有较大的吸光范围，二是通过掺杂、构筑异质结等改性手段进一步提升材料的吸光范围。

鉴于此，笔者概述了具有宽光谱响应的铋基光催化剂的制备方法，并系统地归纳了其改性手段及其在环境污染物去除方面的催化性能，最后对该类具有宽光谱响应的铋基光催化剂的发展方向进行了展望。

2. 铋基宽光谱响应光催化剂的合成

2.1. 水热法

水热法是目前制备宽光谱响应铋基光催化剂十分普遍的方法。以水为溶剂时，反应前驱体在高温条件下逐渐发生晶相的转变，通过控制温度、反应时长及体系 pH 等条件可以得到具有宽光谱响应的铋基

光催化剂。Wanjun Wang 等人[10]以铋酸钠为前驱体，进行高温水热反应，得到具有本征缺陷的 Bi_2O_4，其光吸收边可以达到 620 nm。第一性原理计算表明其全充满的 Bi^{3+}中 Bi6s 带和空的 Bi^{5+}中 Bi6s 带使其具有较窄的禁带宽度，从而更容易被长波长范围的光子激发。Jun Li 等人[6]通过水热法在碱性条件下高温还原铋酸钠，得到了具有 Bi^{3+}和 Bi^{5+}混合价态的 BiO_{2-x}，其光吸收范围可以达到 851 nm。

除了具有混合价态的铋基材料具有较宽的光响应范围外，一些三价铋盐也具有优异的近红外光响应能力。例如 Huanchun Wang 等人[11]通过水热法在碱性条件下得到了具有近红外响应的 $NaBiS_2$，其吸收边可以达到 1000 nm。通过改变原料，还可以得到具有近红外吸收的 BiCuSO，其吸收边高达 1140 nm [12]。

2.2. 其他方法

除了水热法，还可以通过溶剂热法、煅烧法得到具有宽光谱响应的铋基光催化剂。与水热法不同的是，这两种方法通常是在完整晶体中引入阴离子缺陷或阳离子缺陷制造缺陷能级，从而达到缩短带隙，扩展光响应范围的目的。Jian Tian 等人[13]以乙二醇为溶剂，高温反应后得到富氧空位的 Bi_2WO_6 纳米片。Bi_2WO_6 中的氧空位可以提高费米能级，减小带边，允许在近红外激发下发生带间跃迁生成载流子。ChadeLv 等人[14]在氧气氛围下高温高压煅烧 $Bi_4V_2O_{11}$ 初生纤维制备了 Bi^{5+}自掺杂的 $Bi_4V_2O_{11}$，紫外－可见漫反射光谱表明其吸收边可以达到 580 nm。相关催化剂的制备方法及其光学性质见表 1。

Table 1. Preparation of bismuth-based photocatalysts with wide spectral response
表 1. 宽光谱响应铋基光催化剂的制备相关研究

催化剂	合成方法	禁带宽度/eV	吸收边/nm	参考文献
BiO_{2-x}	一步水热法	1.49	851	[6]
Bi_2O_4	一步水热法	1.86	620	[10]
BiCuSO	一步水热法	1.08	1140	[12]
$NaBiS_2$	一步水热法	1.02	1000	[11]
Bi_2WO_6	溶剂热法	-	>1800	[13]
$Bi_4V_2O_{11}$	煅烧法	2.15	580	[14]

3. 铋基宽光谱响应光催化剂的改性

影响光催化剂效率的因素主要包括催化剂的光吸收能力、载流子的分离和传输效率以及载流子在固液界面的传输效率[15] [16]。半导体光催化剂的吸收范围和转换效率影响光的吸收能力，而禁带宽度又是影响半导体光催化剂光吸收范围的决定性因素。当半导体材料的带隙值越小，其价带电子越容易被光子激发，产生电子－空穴对。接下来，未发生复合的空穴和光生电子会迁移到半导体表面的活性位点，并对吸附在半导体表面的污染物进行氧化或还原，使污染物矿化。针对上述四个关键因素，研究者们提出了许多方法来进一步提升铋基宽光谱响应光催化剂的催化性能。本节归纳了现有的关于宽光谱响应的铋基光催化剂的改性方式及其在近红外光下的催化降解有机污染物方面的相关研究(表 2)。

3.1. 构筑缺陷

构筑缺陷是一种扩展光吸收范围的有效方法。在宽光谱响应的铋基催化剂中，常见的缺陷类型有氧空位、铋空位以及缺陷簇。材料表面元素空位的形成除了可以起到调控能带的作用，还可以对表界面反应产生一定的影响[17] [18]。Jun Li 等人[6]通过超声剥离的方法制备了 BiO_{2-x} 单层片，相比于多层 BiO_{2-x}，单层超薄片中缺陷簇的形成使其具有更宽的吸收边，导致材料在近红外光下具有更优的光催化性能。

Hongli Sun 等人[19]通过溶剂热法制备了只具有氧空位的 BiO_{2-x} 纳米球，该纳米球在可见光下具有较好的催化活性，但在近红外光下活性低于具有缺陷簇的 BiO_{2-x}。

Table 2. Study on degradation of organic pollutants by bismuth-based photocatalyst with wide spectral response under near infrared light
表 2. 宽光谱响应铋基光催化剂在近红外光下降解有机污染物相关研究

材料	改性方法	降解物及浓度	去除率(近红外下)	参考文献
Bi_2WO_6	-	甲基橙(20 mg/L)	58% (2 h)	[13]
$BiO_{2-x}/Bi_2O_{2.75}$	异质结	Rhb (10 mg/L)	90% (2 h)	[21]
Bi_2O_4-Bi_4O_7-BiO_{2-x}	异质结	双酚 A (40 mg/L)	48% (1 h)	[23]
C 量子点-$Bi_2O_2CO_3$	表面修饰	环丙沙星(10 mg/L)	50% (6 h)	[31]
石墨烯量子点-BiO_{2-x}	表面修饰	四环素(10 mg/L)	85% (2 h)	[32]
Ni^{2+}掺杂 BiO_{2-x}	元素掺杂	Rhb (10 mg/L)	85% (7 h)	[33]
C 掺杂 BiO_{2-x}	元素掺杂	甲基橙(10 mg/L)	100% (3 h)	[34]
Yb^{3+}/Er^{3+}共掺杂 $Bi_4O_5I_2$	元素掺杂	Rhb (10 mg/L)	45% (1.5 h)	[38]

3.2. 构建异质结

构建异质结在提升铋基本征半导体性能方面被广泛应用。典型的异质结类型有 n-n 型、p-n 型、Z 型、S 型等。Junxiu Wang 等人[20]通过离子刻蚀法制备了 Bi_2O_4/BiOClp-n 异质结材料，异质结的形成使光生电子更多的聚集在 Bi_2O_4 导带，进一步增强了材料活化分子氧产生超氧自由基的作用。Min Wang 等人[21]通过水热法制备了 $BiO_{2-x}/Bi_2O_{2.75}$ Z 型异质结材料，氧空缺在 Z 型异质结中起着高效传输电子的作用，有效的促进了载流子在催化剂内部的分离与迁移，进而提升了光催化活性。Dehua Xia 等人[22]在 Bi_2O_4 表面原位沉积 Fe_3O_4，得到了 Bi_2O_4/Fe_3O_4 异质结复合材料，Fe_3O_4 得电子后可以有效的活化分子氧生成超氧自由基，从而进一步提升材料的降解活性。YuefaJia 等人[23]通过一锅水热法制备了 Bi_2O_4-Bi_4O_7-BiO_{2-x} 三元复合材料。这种三元复合材料无论是在可见光还是近红外光下，其降解有机物的活性都大大增强。此外，还有许多相关材料的异质结被报道，例如 Bi_2O_4/BiO_{2-x} 异质结[24]、BiO_{2-x}/Ag_3PO_4/CNT 异质结[25]、$NaBiO_3/BiO_{2-x}$ 异质结[26]、$KBiO_3$/BiOX (X = Cl, Br, I)异质结[27]等。

目前关于 S 型异质结(Step-scheme)的报道较少，主要集中于超薄材料的复合。例如 Fu 等人[28]通过静电自组装法制备了 2D/2D WO_3/g-C_3N_4 材料并用于光解水产氢，较大的接触界面有效的促进了界面电子转移，S 型异质结的形成加快了无用载流子的复合，同时促进了有用载流子的分离。在宽光谱响应铋基材料的设计中也可以考虑通过构建这种异质结来进一步提升材料的活性。

3.3. 表面修饰

表面修饰是通过改变表面电荷转移路径来提升光催化剂的催化活性的另一种改性手段。对于宽带隙铋基半导体而言，表面存在的大量缺陷一方面使其能被波长范围更广的光子激发，另一方面也可能成为电子－空穴对的复合中心，从而降低表面载流子的利用率。研究发现，无机非金属离子的修饰对光催化剂的表界面性质产生显著影响，增强表面反应[29]。Ping Chen 等人[30]通过水热法制备了磷酸盐修饰的 Bi_2O_4 用于水体中磺胺嘧啶的降解。磷酸盐的修饰一方面提高了材料对磺胺嘧啶的吸附能力，另一方面提高了材料中光生载流子的分离效率，从而提高了表面反应效率。除了采用无机非金属离子进行表面修饰，量子点也因为其显著的量子尺寸效应而被广泛应用。Xin Hu 等人[31]通过水热法制备了 C 量子点修饰的

$Bi_2O_2CO_3$用于水体中环丙沙星的去除。研究发现，C 量子点可以通过上转换效应使 $Bi_2O_2CO_3$在可见光及近红外区域的光响应性显著增强。Fei Chen 等人[32]将氮掺杂的石墨烯量子点负载在 BiO_{2-x}上，量子点的上转换效应使材料的光响应范围提升至 895 nm。并且量子点可以作为活性中心进一步提高 BiO_{2-x}活化分子氧生成·O_2^-的能力。

3.4. 元素掺杂

将外来元素掺杂进催化剂晶体内部，可以调控催化剂的能带结构和电子迁移能力，进一步提高材料的光响应范围，从而达到提高光催化剂催化活性的目的。Jun Li 等人[33]通过掺杂过渡金属 Ni^{2+}离子，进一步提升了 BiO_{2-x}材料的光响应范围。研究发现，Ni^{2+}掺杂使 BiO_{2-x}中形成了新的杂质能级，进一步减小了材料的带隙宽度，从而使载流子更容易被近红外光区的光子激发而分离。Yueshuang Mao 等人[34]以氮化碳为 C 源制备了 C 掺杂的 BiO_{2-x}。理论计算表明，C 的引入增强了局域电场，进而促进了电子－空穴分离，同时也促进了载流子迁移至材料表面进一步发生反应。不仅如此，掺杂 C 与表面 O 空位还可协同增强材料活化分子氧的能力，进一步提升材料的催化性能。另外，还可以通过稀土离子的掺杂来提高光催化性能[35] [36] [37]。例如，Yb^{3+}/Er^{3+}共掺杂使得 $Bi_4O_5I_2$的光响应范围从可见光区扩展至近红外光区，稀土离子的掺杂不仅调控了能带结构，还可以通过稀土离子特有的上转换效应使材料间接利用近红外光[38]。

4. 结语与展望

具有宽光谱响应的铋基光催化剂在光催化降解有机污染物方面具有良好的应用前景，并且在近红外光利用领域也取得了一定的发展。当前，对于具有宽光谱响应的铋基光催化剂的研究呈现多元化的趋势，越来越多的光催化剂被开发和应用。但是，对于合成机理及近红外光响应机理方面的研究还比较薄弱。因此，未来对于具有宽光谱响应的铋基光催化材料还应该在以下几大方面进行深入研究。

1) 深入研究合成机制。进行合成方法创新，进一步丰富具有近红外响应的光催化剂的种类和改性手段，进一步提升近红外光下光催化剂的催化活性。

2) 深入研究催化机制。针对特定污染物进行降解，并深入研究降解机理。加深对近红外光下有机污染物光催化降解的环境归趋、降解产物毒副作用的认识。

3) 深入研究抗光腐蚀性能。目前已报道的具有近红外响应的铋基光催化剂都存在光稳定性差的问题，这将影响光催化剂的循环使用性能，未来可以针对提升材料抗光腐蚀性能进行深入研究。

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