空心玻璃微珠/ ZnIn_2S_4 纳米复合微球的制备及性能

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摘要 以空心玻璃微珠为载体, 通过水热法实现了六方相型 ZnIn_2S_4 在空心玻璃微珠表面的可控自组装, 从而制备出空心玻璃微珠/ ZnIn_2S_4 核壳复合微球. 采用X射线衍射(XRD)、扫描电子显微镜(SEM)、紫外-可见漫反射光谱(UV-Vis)、光电子能谱分析(XPS)技术对复合微球的表征, 研究了微珠表面活化处理对表面包覆 ZnIn_2S_4 晶体结构、形貌、光学性质及催化性能的影响. 结果表明, 空心玻璃微珠分别通过硅烷偶联剂 γ -氨丙基三乙氧基硅烷(KH550)和双氧水活化预处理后, 其表面负载 ZnIn_2S_4 更为均匀, 呈层状纳米花瓣结构, 并对有机污染物罗丹明B(RhB)有着良好的降解效果.

关键词 可见光催化, ZnIn_2S_4 , 空心玻璃微珠, 核壳结构, 可控自组装

近年来, 以半导体光催化剂为代表的异相光催化技术在环境修复领域尤其水体修复领域受到众多学者的关注^[1-5], 其中, 金属硫化物由于其具有较窄的带隙和对可见光较强的吸收能力, 被认为是最具有发展前景的光催化剂之一. ZnIn_2S_4 属于 AB_2X_4 家族的三元半导体金属硫化物^[6,7], 因其具有独特的光电性能^[8,9]和催化特性^[10]等诸多优点, 引起了学者的广泛关注. 但粉体 ZnIn_2S_4 易团聚、难分离的缺点使其光催化效率受到了限制, 尤其在流动体系中使用受很大限制^[11], 严重影响了其在光催化降解污染物和光催化解离水制氢等方面的应用. 因此如何将粉体催化剂负载于较大尺度的载体并保持其光催化活性成为新的研究热点.

漂浮型负载光催化剂由于可漂浮于水面且易于分离, 使得其不仅有效增强了催化剂与光接触面积而且克服了纳米粉体光催化剂在水中易团聚、难分离

的缺点, 并可以有效地减少光催化剂的用量. 空心玻璃微珠(HGM)^[12]因具有质轻、中空、分散性好、流动性好等特点, 常用做光催化的漂浮型载体. 对于空心玻璃微珠负载宽带隙 TiO_2 及其改性物的研究多有报道^[13-16], 如Chen等人^[7]通过物理吸附和热黏合的方法将 TiO_2 (Degussa, P25)颗粒成功负载在平均直径为80~100 μm 的空心玻璃微珠上, 并在水中和紫外光照条件下可以长期保持稳定, 孙智博等人^[15]采用溶胶-凝胶法制备了 Fe^{3+} , Gd^{3+} 共掺杂纳米 TiO_2 并成功负载于空心玻璃微珠表面等. 然而有对新型窄带隙半导体可见光催化剂, 如部分金属硫化物^[16]负载于空心玻璃微珠表面的研究鲜有报道.

本文采用水热法将 ZnIn_2S_4 通过自组装过程成功负载于空心玻璃微珠表面, 并且完好地保留了其纳米片层花瓣结构, 从而制备出HGM/ ZnIn_2S_4 核壳复合微球. 此外, 重点研究了微珠表面预处理条件对

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HGM/ZnIn₂S₄壳层的形貌及性能的影响。本研究为HGM/ZnIn₂S₄核壳结构的形成提供了一种简单、可控的途径。此外,该漂浮型可见光催化剂在模拟太阳光条件下,对染料废水罗丹明B(RhB)具有良好的催化降解性能。

1 实验

(i) 主要原料及试剂。七水合硫酸锌(ZnSO₄·7H₂O, 分析纯)、四水合氯化铟(InCl₃·4H₂O, 分析纯)均购自国药集团化学试剂有限公司;硫代乙酰胺(TAA)购自天津市科密欧化学试剂有限公司;空心玻璃微球(直径15~75 μm, 表观密度0.4 kg/m³)购自中钢集团马鞍山矿院新材料科技有限公司;γ-氨丙基三乙氧基硅烷(KH550)购自东市鼎海有限公司;无水乙醇(99.8%), 市售;罗丹明B(RhB, 分析纯)购自天津市科密欧化学试剂有限公司。

(ii) 空心玻璃微珠的处理。粗化处理^[18,20]: 配制1 L氢氧化钠(40 g/L)、碳酸钠(10 g/L)和硅酸钠(5 g/L)的混合液并加热至90℃, 称取空心玻璃微珠10 g于上述溶液中, 采用机械搅拌方法使空心微珠在混合液中充分分散, 1 h后取上层漂浮微珠做抽滤干燥处理。取上述空心玻璃微珠置于1 mol/L的氢氧化钠溶液中, 磁力搅拌下加热至80℃, 1 h后用去离子水洗涤直至中性, 减压抽滤后做干燥处理, 即得粗化后空心玻璃微珠。

活化处理^[21]: 配置双氧水酸性溶液(体积比: H₂O₂/H₂SO₄=1:7), 将粗化干燥后的空心玻璃微珠(5 g)置于上述溶液, 磁力搅拌条件下加热至80℃, 30 min后取出, 静置冷却后水洗过滤至中性, 放入烘箱内做干燥处理, 即得双氧水活化处理后空心玻璃微珠。

硅烷偶联处理^[19,20,22]: 将乙醇和水按体积比为9:1配制成300 mL乙醇溶液, 用该溶液稀释1%(硅烷偶联剂与粗化的空心玻璃微珠质量比)硅烷偶联剂KH550, 将粗化干燥后的空心玻璃微珠(10 g)置于硅烷-乙醇水溶液, 磁力搅拌条件下加热至80℃, 反应2 h后冷却至室温。取上层空心玻璃微珠用无水乙醇减压抽滤清洗, 以去除玻璃微珠表面残余的偶联剂。最后将抽滤后的空心玻璃微珠放入烘箱内做干燥处理, 即得硅烷偶联处理后空心玻璃微珠。

(iii) HGM/ZnIn₂S₄复合微球的制备。称取0.441 g ZnSO₄·7H₂O, 0.9363 g InCl₃·3H₂O溶于30 mL

去离子水中, 再加入过量的TAA后继续磁力搅拌直至完全溶解, 得到无色澄清前驱液A。向A溶液中分别加入未做任何处理、经粗化、活化和硅烷偶联处理后的空心玻璃微珠, 继续磁力搅拌0.5 h, 然后将溶液转移至100 mL内衬为聚四氟乙烯的反应釜中, 于160℃水热反应16 h, 自然冷却至室温。经离心分离, 取上层悬浮物过滤, 干燥后即可得到经不同方法处理后制得的包覆ZnIn₂S₄的空心玻璃微珠复合材料, 标记为HGM/ZnIn₂S₄。

(iv) 催化剂的表征与分析。采用X射线衍射仪(XRD)对HGM/ZnIn₂S₄的晶相结构进行分析, 测试在日本株式会社理UltimanIV型X射线衍射仪上完成, 以Cu为靶源, 管电流为40 mA, 管电压为40 kV, 扫描范围为10°~80°, 扫描速度为8°/min; 采用光电子能谱分析(XPS)对样品所含元素与化学状态进行分析, 测试在美国热电公司K-Alpha型X射线光电子能谱仪上进行; 采用扫描电子显微镜(SEM)观察催化剂形貌, 在日立场发射SEM SU8000上对HGM/ZnIn₂S₄的表观形貌进行分析, 扫描电压1.0 kV; 采用日立UV-3900紫外-可见漫反射光谱对样品进行光谱分析, 催化剂粉末在装有积分球的U-4100紫外可见近红外光谱仪上进行, 扫描范围为300~1000 nm, 扫描速度为600 nm/min, 测量分度为1 nm, 狭缝宽度2 nm。

(v) 催化剂光催化降解RhB活性评价。以RhB水溶液模拟污水来评价该催化剂的光催化活性。将0.05 g复合空心微球及500 mL浓度0.03 g/L的RhB溶液置于带有冷却夹套的玻璃容器中, 采用500 W氙灯(PL-X500C, 北京普林塞斯科技有限公司)作光源, 溶液表面光强为1000 W/m²。光催化反应前, 磁力搅拌下暗反应0.5 h以确保达到吸附平衡后开启光源, 并持续磁力搅拌。反应液间隔设定定时取样, 取样后样品通过0.22 μm水系膜, 以消除溶液纳米复合微球对吸光度的影响, 使用UV-2600型紫外可见光光度计检测其吸光度, 然后通过吸光度-浓度标准曲线换算RhB浓度并计算降解率。

2 结果与讨论

2.1 样品的形貌

图1为经不同方法处理后制得的ZnIn₂S₄包覆空心玻璃微珠的SEM图。由图1(a)可以看出, 未做任何处理的微珠表面ZnIn₂S₄生长不牢固、易脱落, 仅以微

图1 不同方法处理HGM制得的HGM/ZnIn₂S₄复合微球的SEM图。(a) 未经任何处理;(b) 碱洗;(c) 活化;(d) 硅烷偶联

Figure 1 SEM diagram of HGM/ZnIn₂S₄ composite microspheres with HGM by different methods: (a) without any treatment; (b) alkali washing; (c) activation; (d) silane coupling

珠作为模型,单独生长成ZnIn₂S₄层片;用碱洗粗化处理的微珠表面有少许ZnIn₂S₄生长,但负载极为不均匀并伴随裂缝出现(图1(b)).由图1(c), (d)可以看出,经双氧水和硅烷偶联KH550处理后,空心玻璃微珠表面ZnIn₂S₄生长均匀,且由许多轮廓清晰的纳米尺寸的薄片组成,薄片之间交错连接在一起,呈现出花瓣状形貌.双氧水和KH550预处理都不同程度地增加了空心玻璃微珠表面的官能团,使得ZnIn₂S₄前驱体更易在其表面形成化合键,从而利于ZnIn₂S₄的生长,具体分析见后文生长机理分析部分.

2.2 样品相结构

结合上述SEM结果,利用XRD检测经活化和硅烷偶联KH550处理后所负载的ZnIn₂S₄的相结构和结晶度,结果如图2所示.可以看出,未经任何处理的空心玻璃微珠出现了SiO₂的非晶态衍射峰,这是由于空心玻璃微珠主要由SiO₂组成.采用两种处理方法所负载的ZnIn₂S₄样品的衍射峰形状总体上大致相同.其中,经硅烷偶联KH550处理后,其衍射峰分别位于21.6°, 27.7°, 39.8°, 47.2°, 52.4°, 55.6°和75.7°,分别对应于ZnIn₂S₄的(006), (102), (108), (112), (116), (202)和(213)晶面(ICSD-JCPDS No. 01-072-0773),且所有衍射峰均可归属于六方相晶型的ZnIn₂S₄.此外,

图2 (网络版彩色)不同预处理方法所制样品的XRD图。(a) 硅烷偶联处理;(b) 活化处理;(c) 空心玻璃微珠基体

Figure 2 (Color online) XRD patterns of the different samples with pretreatment by alkali washing (a), activation (b), and hollow glass bead substrate (c)

并没有发现ZnS, In₂S₃及其他杂质衍射峰的存在,因此可以推断出空心微珠表面所负载的是为单一的六方相型ZnIn₂S₄.与硅烷偶联处理结果相比,经双氧水活化后所负载ZnIn₂S₄出现了比较细小的(104)晶面衍射峰,这可能与空心玻璃微珠表面羟基化有关.此外,经硅烷偶联处理后表面ZnIn₂S₄的衍射峰强度均大于双氧水活化预处理的,说明经硅烷偶联处理后表面ZnIn₂S₄晶型较好.故以下均以硅烷偶联KH550

处理后制得的 ZnIn_2S_4 包覆空心玻璃微珠为研究对象做讨论.

2.3 XPS分析

为了进一步研究制备的HGM/ ZnIn_2S_4 复合微球表面 ZnIn_2S_4 的化学价态及元素组成, 本文对硅烷偶联KH550处理后的样品进行XPS分析, 结果如图3所示. 图3为HGM/ ZnIn_2S_4 纳米复合微球的全谱图及其组成元素的高分辨谱图, 从图中可以观察到Zn 2p, In 3d, S 2p, C 1s, O 1s, Si 2p的特征峰存在, 其中C和O元素可能来自样品表面的污染和仪器本身的干扰. 其中, Si元素来自空心玻璃微珠基体, O元素也可能来自空心玻璃微珠基体. 从图中可知, Zn 2p_{3/2}和Zn 2p_{1/2}的主峰位置分别位于1022.3和1045.5 eV, 表明 ZnIn_2S_4 壳中Zn离子的化学价态为+2价^[23], In 3d_{5/2}和In 3d_{3/2}的主峰位置分别位于445和452.6 eV, 表明In离子的化学价态为+3价^[24], 而162.1 eV处则对应的是S 2p的特征峰, 表明了S离子的化学价态为+2价^[23]. 通过XPS半定量结果可以得出Zn:In:S=1:2.1:4.0, 与纯 ZnIn_2S_4 元素理论比基本吻合. 因此结合上述

XRD图谱和XPS图谱结果可知制备的产物为纯相 ZnIn_2S_4 .

2.4 样品的光学性能

本文通过表征不同样品的UV-Vis漫反射光谱来研究负载前后 ZnIn_2S_4 的能级结构及光吸收性能, 图4为纯 ZnIn_2S_4 与HGM/ ZnIn_2S_4 复合微球的紫外-可见吸收光谱图. 纯 ZnIn_2S_4 微球及HGM/ ZnIn_2S_4 复合微球在从紫外到可见光范围均有明显吸收, 并在450~550 nm波长范围内出现陡峭的吸收带边. 与纯 ZnIn_2S_4 微球相比, HGM/ ZnIn_2S_4 复合微球在可见光范围内均表现出更强的吸光强度, 并且吸收边发生轻微红移. 可能原因是由于 ZnIn_2S_4 花瓣结构在空心玻璃微珠表面负载较均匀, 且HGM/ ZnIn_2S_4 分散性较好. 通过切线法作切线可得样品纯 ZnIn_2S_4 微球及HGM/ ZnIn_2S_4 的光吸收阈值 λ_g 分别约为519.19和523.5 nm. 利用公式 $E_g = hc/\lambda_g$ (h 为普朗克常数, c 为光速)换算可得 ZnIn_2S_4 和HGM/ ZnIn_2S_4 的带隙分别为2.39和2.37 eV. 由此可知样品中HGM与 ZnIn_2S_4 之间发生相互作用使得 ZnIn_2S_4 的禁带宽度变小, 从而提高了复合光催化剂

图3 ZnIn_2S_4 /HGM的XPS全谱图(a)及Zn(b), In(c), S(d)元素的高分辨谱图

Figure 3 XPS spectra of ZnIn_2S_4 /HGM sample (a) and high resolution scan of Zn (b), In (c), S (d)

图4 (网络版彩色)样品紫外可见漫反射光谱图。(a) HGM/ZnIn₂S₄; (b) ZnIn₂S₄; (c) 空心玻璃微珠基体

Figure 4 (Color online) UV-Vis diffuse reflectance spectra of the samples. (a) HGM/ZnIn₂S₄; (b) ZnIn₂S₄; (c) hollow glass bead substrate

对可见光的利用率。

2.5 负载前后空心玻璃微珠光催化降解RhB活性

KH550改性的空心玻璃微珠及HGM/ZnIn₂S₄复合微球可见光催化剂的光催化降解RhB结果如图5所示。从图5(a)可知,所制备的纳米复合空心微球对RhB有良好的光催化降解效果,在2 h内降解底物RhB可达99.7%。与不加催化剂降解相比,表明HGM/ZnIn₂S₄纳米复合微球对底物RhB的整个降解过程是光催化起作用而不是光降解导致的。此外,图5(a)可以说明偶联改性的空心玻璃微珠对RhB的脱色率很低,且仅发生在暗反应阶段,在光照条件下处于吸附-脱附平衡状态,RhB并未发生任何变化。从图5(b)可知,RhB起始最大吸收波长为553 nm,该峰随反应时间不断下降并发生蓝移,表明RhB已降解为其他物质。

图5 (网络版彩色)光催化降解RhB。(a) 光催化降解RhB的效率图;(b) RhB的吸收光谱图

Figure 5 (Color online) Photocatalytic degradation of RhB. (a) Photocatalytic degradation efficiency of RhB; (b) absorption spectrum of RhB

2.6 HGM/ZnIn₂S₄复合微球生长机制

HGM/ZnIn₂S₄复合微球的形成主要分为3个步骤:

(1) 空心玻璃微珠的处理; (2) ZnIn₂S₄在空心玻璃微珠表面的异相成核; (3) ZnIn₂S₄纳米片层在微核处的定向生长。其中在微珠处理阶段,由于玻璃微珠的主要成分为二氧化硅,经NaOH溶液处理后的空心玻璃微珠表面可形成少量Si-OH键^[19]。加入KH550对上述玻璃微珠进行进一步改性,由于KH550水解生成硅醇,极易与中空玻璃微珠表面的羟基结合脱水^[25],裸露在外侧的氨基及部分剩余羟基经无水乙醇溶液清洗后被去质子化从而带负电^[26],以利于下一阶段ZnIn₂S₄在空心玻璃微珠表面的异相成核。由于反应溶液中存在过量的TAA,使得其与溶液中的In³⁺离子及Zn²⁺离子容易螯合形成[In(TAA)_n]³⁺和[Zn(TAA)_n]³⁺,如式(1),(2)所示,并与空心玻璃微珠表面发生静电吸附,为ZnIn₂S₄的成核提供位点。随着反应体系温度逐步升高,螯合物中的TAA逐步解离,发生如式(1)与(2)中的逆向反应。当温度升至80℃时,溶液中的TAA发生水解释放出H₂S,如式(3)所示,并与游离的Zn²⁺和In³⁺发生反应,形成ZnIn₂S₄微核,其反应如式(4)所示。由于空心玻璃微珠表面较低,使得ZnIn₂S₄在玻璃微珠表面的异相成核较ZnIn₂S₄的均相成核更为容易。当ZnIn₂S₄微核形成后,随着反应的持续进行,ZnIn₂S₄纳米微核逐步定向沉积形成层状花瓣结构,继而制得表面负载均匀HGM/ZnIn₂S₄复合微球,其生长机理示意图如图6所示。

图6 (网络版彩色)空心玻璃微珠负载 ZnIn_2S_4 工艺图

Figure 6 (Color online) Process diagram of hollow glass bead load ZnIn_2S_4

3 结论

本文采用水热法将 ZnIn_2S_4 成功负载于空心玻璃微珠上,从而制备出 $\text{HGM}/\text{ZnIn}_2\text{S}_4$ 核壳结构,并研究了不同预处理方法对 ZnIn_2S_4 负载效果的影响。结果表明经KH550改性后的空心玻璃微珠表面 ZnIn_2S_4 生长均匀,呈纳米层状花瓣结构,从而为 ZnIn_2S_4 负载

于空心玻璃微珠上提供了一种简单、可靠的制备条件及工艺。该漂浮型可见光催化剂不仅保持了高的催化活性,而且还克服了微纳米状 ZnIn_2S_4 粉体在水中分散性差、易团聚等不足,在模拟太阳光辐射下也具有良好的催化降解性能,为进一步研究展示了良好的应用前景。此外,本文提出了 ZnIn_2S_4 在空心玻璃微珠表面定向自组装的可能机制和形成过程,为漂浮型可见光催化剂 $\text{HGM}/\text{ZnIn}_2\text{S}_4$ 在环境光催化领域的应用研究提供了新的方向。

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Summary for “空心玻璃微珠/ZnIn₂S₄ 纳米复合微球的制备及性能”

Preparation and characterization of visible light catalyst ZnIn₂S₄ coated on hollow glass microbeads

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Heterogeneous photocatalytic technology based on semiconductors has been considered to be a green technology for environmental remediation because it can use the solar energy. As a semiconductor visible light catalyst, ZnIn₂S₄ has attracted a lot of attention because of its narrow bandgap, strong absorption of visible light and unique catalytic properties. However, the disadvantages that the powders ZnIn₂S₄ are easy to aggregate and hard to separate make its photocatalytic efficiency limited. Besides, micro/nano powders are difficult to recycle, which tends to cause secondary pollution and increase the cost of photocatalysis inevitably. In order to solve the disadvantages of the powder photocatalysts, floating substrates hollow glass microspheres (HGMs) are used as supporters for the coating of powder photocatalysts. Hollow glass microspheres, which are commonly used as floating-type carrier for photocatalysts due to their favorable properties of high chemical stability, low cost, lightweight mass, low thermal conductivity, hollow spherical morphology, good dispersibility and fluidity, are considered one of the most suitable supporters, and their combination are expected to show higher light utilization and collection efficiencies. In this research, the visible light photocatalyst ZnIn₂S₄ was coated on HGMs through a hydrothermal method at 160°C, which obtained HGM/ZnIn₂S₄ composite microspheres. The crystal structure, morphology and optical properties of the obtained composite microspheres were characterized by measurements such as X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectrum (XPS) and UV-Vis diffuse reflectance spectra (UV-Vis). The optimized conditions of ZnIn₂S₄ film coated on hollow glass microspheres were investigated by different pretreatment methods such as alkali pretreatment, H₂O₂ activation and silane coupling modification. The results revealed that the activation of the HGMs through H₂O₂ and silane coupler agent KH550 showed better morphology of HGM/ZnIn₂S₄ composite microspheres with a nano-layered petal-like structure on the HGMs. Besides, HGM/ZnIn₂S₄ composite microspheres pretreated by silane coupling agent KH550 exhibited a higher hexagonal phase crystal structure compared with the H₂O₂ pretreated samples, and its band gap was estimated to be 2.37 eV from UV-vis absorbance spectrum, which showed that HGM/ZnIn₂S₄ composite microspheres exhibited good photocatalytic performance in the visible range. The HGM/ZnIn₂S₄ composite microspheres can not only maintain the high photocatalytic activity, but also overcome the disadvantages that nanoparticles powder are inclined to agglomeration in water. Furthermore, the degradation effect of Rhodamine B (RhB) under visible light were investigated through the as-prepared HGM/ZnIn₂S₄ composite microspheres. The results showed that the composite microspheres have good photocatalytic degradation effect on RhB, and the degradation of substrate RhB can reach 99.7% within 2 h. Finally, we proposed the possible growth mechanism of ZnIn₂S₄ film on HGMs and the formation of HGM/ZnIn₂S₄ composite microspheres. The precursor of ZnIn₂S₄ was firstly adsorbed on the surface of hollow glass microspheres by electrostatic adsorption. As the temperature of the reaction system was gradually increased, Zn(TAA)_n²⁺ and In(TAA)_n³⁺ generated at the same time can further combine *in situ* to yield numerous ZnIn₂S₄ nuclei. When the micronucleus of ZnIn₂S₄ was formed, the ZnIn₂S₄ nano-nucleus gradually deposited to form a layered petal structure, and then the HGM/ZnIn₂S₄ composite microspheres were prepared. The study showed a simple and reliable preparation condition and process for ZnIn₂S₄ coated on hollow glass microspheres, which provides a promising application on photocatalytic field of the as prepared floating HGM/ZnIn₂S₄ composite microspheres, and it will be beneficial to explore the coating mechanism of ZnIn₂S₄ on glass-based carrier material.

visible-light photocatalysis, ZnIn₂S₄, hollow glass beads, core-shell, controlled self-assembly

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