Ag/AgCl-LaCO₃OH纳米棒可见光催化净化NO的性能增强及反应机理

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摘要 采用化学沉淀法制备三元Ag/AgCl-LaCO₃OH纳米棒光催化剂. 将Ag/AgCl引入LaCO₃OH(LCO)纳米棒后, 可同时实现光吸收范围紫外光区拓展至可见光吸收和光生载流子的高效分离. 可见光照射下, 金属Ag单质等离子共振(SPR)效应诱导电荷-空穴有效分离, 使其热电子传输至LCO样品缺陷能级. 随后表面O₂捕获光生电子产生超氧自由基·O₂⁻, 该自由基对氧化NO过程起主导作用. 空穴可以迁移至AgCl表面与Cl⁻相互作用转化Cl⁰, 直接参与氧化NO后再还原为Cl⁻, Cl⁻再与Ag⁺结合生成AgCl, 有效避免了AgCl的光腐蚀. 优化过后的Ag/AgCl-LaCO₃OH纳米棒复合材料的可见光净化NO去除率高达54.0%, 远高于纯的LCO(3.1%)和Ag/AgCl(8.0%)的可见光催化性能. 利用原位红外光谱实时动态监测Ag/AgCl-LaCO₃OH光催化氧化NO的反应过程, 结合自由基捕获结果, 从分子层面揭示其反应机理, 并提出Ag/AgCl-LaCO₃OH光催化性能增强机制. 本研究结果深入对等离子体基半导体复合材料光催化反应机理及环境净化应用提供新的认识.

关键词 SPR效应, Ag/AgCl, 可见光催化, 原位红外光谱, 反应机理

光催化技术可将丰富的太阳能进行转化, 在净化环境污染物和开发清洁能源等方面体现出巨大的潜力^[1]. 其中TiO₂作为一种传统的光催化剂被广泛研究, 但由于其较宽的禁带宽度限制了TiO₂的可见光催化性能及应用. 研究者通过一系列研究方法如元素掺杂、半导体复合以及光敏化等将其光响应范围拓展至可见光, 同时提高其光催化性能^[2-5]. 光催化性能主要取决于催化剂光吸收效率^[6]、载流子分离效率、氧化还原反应效率^[7]. 近年来, 二、三元复合光催化材料引起了人们的广泛兴趣, 这些复合材料具有宽光谱吸收、高

效载流子分离以及良好的化学稳定等特点, 表现出优异的光催化性能^[8].

最近, 研究者报道了基于稀土La系半导体材料, 如La₂Ti₃O₇, LaFeO₃, LaTaO₄和LaOF等. 该类材料具有合适的能带结构和良好的光化学性质^[9-12], 展示了高效的光催化产氢效率. LaCO₃OH(LCO)是稀土(La系)碱式碳酸盐家族的重要成员, 作为发光材料被广泛研究. LCO半导体材料具有合适的能带结构, 从而使其具备光催化制氢和氧化污染物的能力. 2013年, Pan等人^[13]首次报道了LCO作为光催化剂在紫外光照射下的产氢性能,

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其效率是锐钛矿TiO₂的3倍. Wang等人^[14]原位制备了Z型异质结g-C₃N₄/LaCO₃OH, 通过调控界面电子传递, 展现高效净化NO的光催化活性. Patil等人^[15]合成了Ag₃PO₄/LaCO₃OH@GO异质结催化剂, 实现可见光照射下对亚甲基蓝的高效光催化降解活性. 但是LCO带隙为4.1 eV, 是一种宽带隙半导体材料, 不能被可见光激发, 只能利用太阳光谱中少部分紫外光, 其较低的量子效率、可见光利用率等缺点极大地限制了LCO的光催化效率. 因此, 在能带结构匹配的前提下, 引入助催化剂与宽带隙的LCO复合, 可以将其光吸收范围拓展至可见光区, 使改性后的LCO可利用丰富的太阳能净化环境污染物质.

近年来, 贵金属纳米粒子如Au, Ag, Pt, Cu等由于其表面等离子体共振(SPR)效应作为辅助催化剂, 可以表现出较强的可见光SPR吸收^[16,17]. 因此, 通过Ag/AgX (X=Cl, Br, I)与窄带隙或宽带隙半导体催化剂复合引起了人们极大的兴趣. 一方面金属单质作为光敏剂可增强催化剂的可见光吸收; 另一方面利用金属Ag单质的SPR效应可促进光生载流子的分离效率以提高光催化活性. 此外, 光产生空穴(h⁺)转移至AgCl表面将Cl⁻氧化成Cl⁰, Cl⁰作为活性物种将NO转化为NO₃⁻, 再次还原成Cl⁻. 这种Cl⁰与Cl⁻价态循环转换的方式能有效抑制AgCl的光腐蚀, 从而为Ag/AgCl提供等离子体诱导电荷分离的稳定性. 比如, Ag/AgX-BiOX(X=Cl, Br)^[18], Ag/AgCl-GO^[19], Ag/AgCl/TiO₂^[8], Ag/AgBr-Bi₂MoO₆^[20], Ag/AgCl-WO₃^[21]等复合材料都展示出优异的可见光活性. 因此, 可以利用Ag/AgCl作为辅助催化剂复合LaCO₃OH纳米棒, 从而实现太阳能高效的光催化效率.

本研究采用化学沉淀方法制备了三元Ag/AgCl-LaCO₃OH(Ag/AgCl-LCO)复合光催化剂. 结果表明, 与Ag/AgCl复合以后, LCO纳米棒可见光催化氧化NO的性能大幅度增强, 远高于Ag/AgCl和纯的LCO. Ag/AgCl-LCO体系中, 金属Ag单质的SPR效应在电子-空穴分离起到了关键作用, 同时将LCO的光响应范围从紫外光区拓宽至可见光区, 增强可见光吸收. 激发态热电子传输至LCO样品缺陷能级, 与表面O₂捕获的光生电子产生活性自由基·O₂⁻, 直接参与氧化NO反应. 此外, 利用原位红外光揭示了Ag/AgCl-LCO复合材料的光催化氧化NO的反应过程, 结合中间产物分析和自由基捕获ESR信号结果, 提出了Ag/AgCl-LCO复合样品光催化净化NO的反应机理, 深入对等离子体基半导体功能材料光催化反应机理及环境净化应用提供新的认识.

1 实验

(i) LCO催化剂制备. 本实验所用化学试剂均为分析纯. 称取1.083 g La(NO₃)₃·6H₂O于250 mL烧杯1中, 加去离子水至120 mL; 将烧杯1放至磁力搅拌器上搅拌均匀; 同时逐滴滴加15 mL浓氨水, 调节pH约为9~11, 搅拌30 min. 将烧杯放至油浴锅里100°C油浴, 向量筒通入CO₂, 流量为1.1 L/min, 通气时间30 min. 上述溶液标记为A溶液(理论产量0.54 g).

(ii) Ag/AgCl-LCO复合材料的制备. 称取一定量的0.031 g AgNO₃·5H₂O和0.01 g NaCl(AgCl:LCO摩尔比为15%)分别溶解在30 mL去离子水的烧杯2和烧杯3中, 均匀搅拌30 min. 然后先将烧杯2中的AgNO₃溶液逐滴加入A溶液, 再将烧杯3中的NaCl溶液逐滴加入A溶液, 磁力搅拌30 min. 最后, 将样品进行清洗(水、醇洗各3次), 然后离心、烘干(60°C), 得到最终产物, 标记为Ag/AgCl-LCO-15; 按照相同条件下, 将制备含有摩尔之比30, 50, 75, 100的AgCl溶液逐滴加入LCO溶液中, 得到的最终产物分别标记为Ag/AgCl-LCO-30, Ag/AgCl-LCO-50, Ag/AgCl-LCO-75和Ag/AgCl-LCO-100.

(iii) 催化剂的表征. 采用X射线衍射仪(XRD, Model D/max RA, Rigaku Co., 日本)分析样品的晶体结构. X射线光电子能谱(XPS, Thermo ESCALAB 250, 美国)分析样品的化学组成. 扫描电子显微镜(SEM, JEOL model JSM-6490, 日本)表征样品的形貌结构. N₂吸附-脱附仪(ASAP 2020, 美国)测定样品的比表面积(BET)和孔结构. 紫外-可见漫反射(UV-vis DRS, UV2550PC, Shimadzu)和荧光光谱(PL, F-7000, Hitachi, 日本)分析样品的光学性质.

(iv) 光催化活性评估. 室温下通过监测连续流反应器中气相NO的浓度来对光催化活性进行评价. 将0.2 g样品超声分散在直径为12 cm的玻璃圆盘中, 60°C下烘干, 自然冷却后放入容积为4.5 L(30 cm×15 cm×10 cm)的矩形反应器中心, 反应器上面覆盖1层石英玻璃, 1个150 W的商业卤钨灯垂直安置在反应器上方20 cm处, 其光照强度为0.16 W/cm². 对于可见光催化活性测试, 采用滤光片去除光束中小于420 nm的紫外光. 采用标准空气和原始浓度为100 ppm(1 ppm=1 mg/m³)的NO标准气体来配置低浓度的NO. 调节空气流速为2.4 L/min, NO气体流速为15 mL/min, 通过三通阀将空气流和NO气流混合, 得到初始浓度为600 ppb(1 ppb=1 µg/m³)的NO. 将稀释后的NO通入反应器中,

待NO浓度稳定后开灯. NO_x分析仪(Thermo Scientific, 42i-TL, 美国)每隔1 min进行采样检测并记录NO, NO₂以及NO_x(NO和NO₂)的浓度.

NO的去除率(η)可用下式计算:

$$\eta(\%) = (1 - C/C_0) \times 100\%, \quad (1)$$

式中, C 代表开灯后反应器出口处的NO浓度, C_0 代表开灯前达到吸附解吸平衡时的NO浓度.

(v) 光催化净化NO的原位红外表征. 原位红外测试仪器是由Tensor II FTIR分光仪(Bruker)配备原位反射反应仓(Harrick)组成. 一定量的光催化剂装载与原位反应仓内. 首先用氦气(50 mL/min)以及热处理去除残留在催化剂上的碳水化合物、水和二氧化碳. 将处理后的实时红外谱线作为背景. 然后, 反应气体(50 mL/min NO和50 mL/min O₂混合)通入反应仓内. 吸附20 min后, 用可见光照射催化剂60 min. 在吸附和反应阶段, 每隔2 min记录一次红外光谱数据. 红外扫描范围为4000~600 cm⁻¹. 其中, 800~2200 cm⁻¹可用作分析后解释Ag/AgCl-LCO吸附和光催化氧化NO的过程.

2 结果与分析

2.1 晶相结构与微观结构分析

图1为样品Ag/AgCl, LCO和Ag/AgCl-LCO的XRD

图和XPS图谱. 由图1(a)可知, LCO和AgCl的衍射峰分别对应于正交晶相的LaCO₃OH(PDF No. 49-0981)和立方晶相的AgCl(PDF No. 31-1238). 在复合催化剂中, 位于 $2\theta=27.82^\circ$, 32.24° 和 46.25° 的衍射峰分别归属于AgCl的(111), (200)和(220)晶面. Ag/AgCl-LCO复合样品中, LCO的衍射峰和晶格参数没有变化. 金属Ag单质含量低和分散性高^[8,17,18,22], 因此在Ag/AgCl-LCO复合材料中未检测出金属Ag单质的特征衍射峰.

为进一步证明Ag/AgCl-LCO复合材料中Ag单质存在及其他元素的化学态, 通过X射线光电子能谱(XPS)对样品进行表征. 图1(b)~(f)为Ag/AgCl-LCO样品的XPS图谱. 图1(b)表明Ag/AgCl-LCO含有La, C, O, H, Ag和Cl元素. 图1(c)中结合能为835.3和852.0 eV的特征峰(3d⁰ 4f⁰配位结构)归属于La 3d_{5/2}和La 3d_{3/2}, 其振荡峰(3d⁰ 4f¹配位结构, 结合能位于838.8和855.3 eV)归属于La³⁺^[13,23]. 图1(d)显示结合能为367.6和373.6 eV的特征峰分别归属于AgCl中的Ag 3d_{5/2}和Ag 3d_{3/2}. 值得注意的是, 结合能为367.5和373.5 eV处的峰可归属于AgCl中的Ag⁺, 而367.9和373.9 eV结合能归因于金属Ag单质, 说明部分的Ag⁺还原为Ag⁰^[24]. 因此, 可以确定复合催化剂含有一定量的Ag单质, 这是由光致还原造成^[21,22,25-27]. 从图1(e)可知, 在198.1和199.7 eV的结合能分别归于Cl 2p_{3/2}和Cl 2p_{1/2}. 图1(f)中C 1s的结合能为

图1 样品的XRD(a)和XPS(b)~(f)图谱. (a) XRD; (b) 全谱; (c) La 3d; (d) Ag 3d; (e) Cl 2p; (f) C 1s

Figure 1 XRD spectra of all the samples (a) and XPS spectra of Ag/AgCl-LCO sample (b)~(f). (a) XRD; (b) survey spectra; (c) La 3d; (d) Ag 3d; (e) Cl 2p; (f) C 1s

284.8和289.8 eV, 前者归因于表面碳污染, 后者归因于碳酸盐^[28,29].

图2为样品的SEM, HRTEM图和EDS图谱. 从图2(a)中可以看出纯的LCO为纳米棒状结构. 如图2(b)和(c)所示, 复合了Ag/AgCl以后, 催化剂仍然具有纳米棒状结构. 由于金属Ag单质分散高、含量少, 未直接观察到颗粒状金属Ag单质. 图2(d)为Ag/AgCl-LCO-75样品的透射电子显微镜图(TEM). 如图2(d)所示, AgCl附着生长在LCO纳米棒表面. 从图2(e)(放大版图像见图S2)中可以观察到晶格间距为0.277和0.56 nm的晶格条纹所对应的LCO样品的(011)和(111)晶面对应, 而AgCl(200)和(220)晶面对应的晶格间距为0.144和0.37 nm. 图2(f)为Ag/AgCl-LCO-75的EDS能谱图. 从图2(f)中可知, Ag/AgCl-LCO复合材料由La, C, O, Cl, Ag元素组成, 同时相对量化地说明了各元素组成的含量. 值得注意的是Ag元素与Cl元素的原子百分比值为1.28, 说明AgCl中的Ag⁺被部分还原为金属Ag单质. 这可以归因于催化剂在制备过程受到光照, 引起的Ag⁺的光还原程. 因此, 该结果进一步证实Ag/AgCl在LaCO₃OH纳米棒表面共存, 这与XRD, XPS分析结果相一致.

图S1为Ag/AgCl-LCO-X(10, 15, 30, 50, 75和100)的

N₂吸附-脱附等温线(图S1(a))和相应的孔径分布曲线(图S1(b)). 根据Brunauer-Deming-Deming-Teller(BDDT)分类, 上述样品均属于第IV类等温线, 表明样品中有介孔的存在(图S1(a)). 吸附-脱附等温线中滞回环为H₃型(按IUPAC分类), 表明有裂缝孔的存在, 这是由于纳米棒/纳米片堆叠造成的, 与SEM的结构相一致(图2). 从孔径分布曲线(图S1(b))中可知, 样品Ag/AgCl-LCO-X(X=15, 30, 50, 70, 100)的孔径范围为10~150 nm, 其样品的孔径为75nm(表S1). 随着Ag/AgCl比例提高, Ag/AgCl-LCO复合材料的比表面积从15.0 m²/g减少至7.0 m²/g, 孔容从0.073 cm³/g减少至0.036 cm³/g. 因此, 复合材料比表面积和孔容逐渐减小, 是由于Ag/AgCl部分填充了LCO的孔道. 值得注意的是, 结合后续分析结果可知, Ag/AgCl-LCO-X(X=15, 30, 50, 75, 100)复合材料比表面积和孔容依次减小, 但复合样品有良好的光催化活性, 这说明比表面积和多孔结构不是提高光催化活性的关键因素.

2.2 光学性质分析

图3为AgCl, LCO和Ag/AgCl-LCO的紫外-可见漫反射光谱. 如图3所示, LCO在紫外光区(200~250 nm)有明

图2 LCO, Ag/AgCl-LCO-15和Ag/AgCl-LCO-75的SEM, HRTEM和EDS图谱. (a) LCO; (b) Ag/AgCl-LCO-15; (c) Ag/AgCl-LCO-75; (d), (e) Ag/AgCl-LCO-75 HRTEM; (f) Ag/AgCl-LCO-75 EDS

Figure 2 SEM (a, b, c) and TEM (d, e) images of LCO and Ag/AgCl-LCO samples and EDS spectra (f) of Ag/AgCl-LCO sample

图3 AgCl, LCO和Ag/AgCl-LCO的UV-vis DRS图
Figure 3 UV-vis DRS of Ag/AgCl, LCO and Ag/AgCl-LCO sample

显吸收,可见光区没有光吸收。但是Ag/AgCl和Ag/AgCl-LCO复合材料在紫外(200~400 nm)-可见光(470~600 nm)均有明显吸收。其中,500 nm左右的吸收峰归属于金属Ag单质的SPR吸收^[30-32]。对比于纯的LCO,改性后Ag/AgCl-LCO复合材料光吸收带边红移,拓宽至可见光吸收范围。由此可见,Ag/AgCl的引入可以实现Ag/AgCl-LCO复合光催化剂可见光吸收能力的提升。

2.3 可见光催化性能评估与机理图

图4为LCO, Ag/AgCl, Ag/AgCl-LCO- X ($X=15, 30, 50, 75, 100$)可见光催化净化NO活性图。如4(a)图所示,纯的LCO样品的禁带宽度较大,不能被可见光激发,其可见光活性可以忽略。Ag/AgCl对NO的去除率为18.0%,这归因于Ag单质的SPR效应,使其在可见光下表现出一定的活性^[33]。当Ag/AgCl含量逐渐提高,复合催化的活性随之提高,Ag/AgCl-LCO-75可见光条件下对NO去除率提高至54.0%,明显高于Ag/AgCl和LCO。结合图3, 4(b)和表S1分析结果可知,Ag/AgCl-LCO-75复合样品可见光活性增强与其可见光吸收效率和电荷分离密的提升相关。通过UV-vis DRS结果可知,Ag/AgCl-LCO-75复合样品光响应范围从紫外光拓展至可见光区,从而增强了催化剂的光吸收能力^[34,35]。同时,Ag中光激发诱导产生的热电子倾向于跃迁至LCO中的缺陷能级,LCO中的缺陷能级可通过黑暗条件下的归属于氧缺陷的EPR信号峰($g=1.996$)得以证明(图4(b))^[36,37]。在可见光照射下,LCO的EPR信号显著增强,表明光照条件下光生载流子的移动性增强,因此,Ag/AgCl与LCO的复合可以实现光生载流子的有效分离进而提高光催化性能。

为进一步测定光催化反应过程中的主要活性物种,采用DMPO捕获ESR自由基信号。图4(c)~(e)为Ag/AgCl-LCO-75样品在光照下 e^- , $\cdot O_2^-$ 和 $\cdot OH$ 的生成趋势谱图。如图4(c)所示,黑暗条件下显著的自由电子捕获信号随着光照时间增加明显减弱,这说明Ag/AgCl-LCO-75在光激发后生成大量的活性物种 $\cdot O_2^-$ 消耗了自由电子,这与随着光照时间推移增强的关于活性物种 $\cdot O_2^-$ 的ESR图谱(图4(d))增加趋势结果相匹配。此外,光生空穴(h^+)转移至AgCl表面将 Cl^- 氧化成 Cl^0 , Cl^0 与 OH^- 作用产生活性自由基 $\cdot OH$ ^[31,38-41];同时 Cl^0 作为活性物种,直接参与氧化污染物反应过程;这种 Cl^0 与 Cl^- 价态相互转化方式,一方面有效避免光腐蚀催化剂,另一方面为活性基团 $\cdot OH$ 产生提供可靠的稳定性。

Ag/AgCl-LCO-75复合光催化剂的光催化机理图如图4(f)所示。Ag/AgCl-LCO-75复合样品中金属Ag单质的SPR效应与LCO氧缺陷结构诱导的高效电荷分离,极大地促进了活性物种的生成,进而实现NO的高效去除。Ag/AgCl-LCO-75样品可见光活性增强可归因于以下因素的协同作用:(1) Ag/AgCl-LCO复合材料将光吸收范围从紫外光区拓展至可见光区,增强了光能的捕获与利用,提高了光吸收效率;(2) 金属Ag单质可见光激发产生的热电子更容易跃迁至LCO的缺陷能级,表面吸附的 O_2 捕获光生电子(e^-),产生 $\cdot O_2^-$ 自由基,参与污染物氧化反应。光生空穴(h^+)转移至AgCl表面将 Cl^- 氧化成 Cl^0 , Cl^0 作为活性物种将NO转化为 NO_3^- ,或者 Cl^0 与 OH^- 反应生成 $\cdot OH$, Cl^0 再次还原成 Cl^- 从而避免了光腐蚀,产生的活性物种 $\cdot O_2^-$, Cl^0 和 $\cdot OH$ 参与氧化污染物的反应过程^[31,38]。其光催化氧化NO的反应步骤如下:

2.4 光催化反应机理的原位红外光谱研究

为进一步揭示Ag/AgCl-LCO-75复合催化剂的反应机理,利用原位红外光谱技术动态监测了NO吸附、光催化NO氧化过程中的中间产物与终产物。图5(a)和(b)

图4 样品的可见光活性及光催化氧化NO机理图谱。(a) LCO, Ag/AgCl, Ag/AgCl-LCO-X(X=15, 30, 50, 75, 100)样品的可见光催化活性图; (b) LCO的EPR图谱; (c)~(e) Ag/AgCl-LCO-75自由基图谱; (f) 光催化氧化NO机理图

Figure 4 Visible light photocatalytic activities of all the samples (a); solid state EPR spectra of LCO (b) and DMPO ESR spectra in dark and under visible-light ($\lambda \geq 420$ nm) for 15 min in methanol dispersion, respectively for e^- (c), $\cdot O_2^-$ (d) and aqueous dispersion for $\cdot OH$ (e) and photocatalysis mechanism of Ag/AgCl-LCO sample (f)

分别为LCO和Ag/AgCl-LCO-75样品NO吸附过程中的原位红外图谱。表1分别为样品NO吸附、光催化NO氧化过程中的相关物种的红外吸收峰归属情况汇总。纯的LCO样品对NO的吸附过程如图5(a)所示,在LCO样品表面可以检测出NO的吸收峰NO(1061 cm^{-1}), NO^- (1193 cm^{-1}), NO_2 (1372 cm^{-1})和 N_2O_3 (1294 cm^{-1})。这表明吸附态NO与氧缺陷处局域的电子发生还原反应转化为 NO^- (方程式(9))。同时, LCO样品表面的NO与 O_2 相互作用氧化生成 NO_2 , 少量的 NO_2 与NO生成 N_2O_3 (方程式(10)), 说明NO能稳定吸附在LCO样品表面。波长为 944 和 1012 cm^{-1} 处的吸收峰归属于硝酸盐或者双齿亚硝酸盐, 这可归因于LCO样品中的氧缺陷能将少量的NO氧化为硝酸盐。图5(b)为Ag/AgCl-LCO-75复合样品对NO吸附的原位红外图谱。如图5(b)所示,在Ag/AgCl-LCO-75复合材料表面检测到关于 NO^- (1180 cm^{-1}), NO_2^- (1274 cm^{-1}), NO_3^- (1057 和 1008 cm^{-1})的吸收峰,其吸附过程与LCO类似。但不同的是,出现了新的关于 NO_2^- 的吸收峰,这由于LCO样品中的氧缺陷能将少量的NO氧化为 NO_2^- , 极少部分的 NO_2^- 再被氧化为硝酸

盐(方程式(11), (12))。这表明复合光催化剂具有更强的氧化能力去除NO。据此,提出NO吸附过程中的中间产物和终产物的反应式(9)~(12):

图5(c)和(d)为LCO和Ag/AgCl-LCO-75样品光催化氧化NO过程中中间产物和终产物的原位红外图谱。当达到吸附平衡后,从图5(c)中可以观察关于 NO^- (1193 cm^{-1}), NO_2 (1372 cm^{-1}), N_2O_3 (1294 cm^{-1})和 NO_3^- (934 , 1012 和 1057 cm^{-1})吸附峰。当可见光照射20 min后,中间产物 N_2O_3 , NO_2 的吸收峰随着光照射时间推移均有明显增强,终产物 NO_3^- 的吸收峰除了在 1057 cm^{-1} 处有所增强,其他峰位没有变化,表明LCO样品较弱的可见光氧化还原能力使得NO大部分被氧化为 NO_2 和 N_2O_3 ,少量的NO氧化成 NO_3^- 或者单齿 NO_3^- 。图5(d)为Ag/AgCl-LCO-75光催化氧化NO图谱,如图5(d)可以观

图5 (网络版彩色)LCO(a)和Ag/AgCl-LCO-75(b)样品对NO吸附过程的原位红外谱图, LCO(c)和Ag/AgCl-LCO-75(d)样品在光照下NO反应过程的原位红外谱图

Figure 5 (Color online) The *in situ* FT-IR spectra of the adsorption process of NO + O₂ on the surface of LCO (a) and Ag/AgCl-LCO (b); the *in situ* FT-IR spectra of the photocatalytic oxidation of NO + O₂ on the surface of LCO (c) and Ag/AgCl-LCO (d) under visible-light irradiation

表1 LaCO₃OH, Ag/AgCl-LCO样品NO吸附、光催化NO氧化过程中原位红外吸收峰归属

Table 1 Assignments of the IR bands observed during NO oxidation processes over LCO and Ag/AgCl-LCO-75

波数(cm ⁻¹)	峰归属	文献
1061	NO	[42, 43]
1193, 1180, 1143, 1175	NO ⁻ /NOH	[43, 44]
1372	NO ₂	[42, 45]
1294	N ₂ O ₃	[44, 46, 47]
930~1030	单齿(NO ₃)	[42]
1274	NO ₂ ⁻	[47]
1060~1003, 1080~1010	双齿(NO ₃)	[46]

察到关于NO⁻(1143和1175 cm⁻¹), NO₂⁻(1274 cm⁻¹)和NO₃⁻(997和1057 cm⁻¹)的吸收峰。与纯的LCO不同的是, 在977 cm⁻¹处出现新的NO₃⁻吸收峰, 而1057 cm⁻¹处的NO₃⁻吸收峰有显著增强, 表明中间产物在光照条件下被直接氧化转化为单齿NO₃⁻(方程式(13),(14)), 不稳定的单齿NO₃⁻最后会转变成稳定的双齿NO₃⁻。因此,

复合光催化剂Ag/AgCl-LCO-75能使得污染物NO快速转化为终产物NO₃⁻的效率更高。这归因于缺陷能级将SPR效应热电子传递至LCO缺陷能级, 提高电子-空穴对分离。光催化剂表面活性物种(·O₂⁻, ·OH, Cl⁰和h⁺)的生成得到促进, 加快污染物到终产物的转化速率(方程式(15),(16))。终产物硝酸根富集在催化剂表面, 催化剂上积累的硝酸盐很容易通过水洗去除^[48]。在实际应用中, 硝酸盐可通过水洗雨水去除。根据以上监测NO吸附的中间产物和终产物, 推演NO反应过程:

3 结论

本研究通过化学沉淀法制备出具备高效的可见光响应的三元Ag/AgCl-LCO复合光催化剂。Ag/AgCl-

LCO-75复合样品中金属Ag单质的SPR效应和LCO氧缺陷结构诱导电荷高效分离,极大地促进了活性物种($\cdot\text{O}_2^-$, $\cdot\text{OH}$ 和 Cl^0)的生成,使其光催化氧化NO过程的氧化性更强.可见光照射下,Ag/AgCl的复合使得Ag/AgCl-LCO复合材料的光催化活性高达54.0%,远高于Ag/AgCl和纯的LCO的可见光性能.Ag/AgCl-LCO高效的

可见光催化性能可归因于拓展的光响应范围以及促进的光生载流子分离效率.此外,通过原位红外技术动态监测了光催化氧化NO的反应中间产物,并提出了Ag/AgCl-LCO光催化净化NO的反应机理,为深入研究等离子体基复合材料光催化机理及环境净化应用提供了新的思路.

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补充材料

图S1 Ag/AgCl-LCO-X(X=15, 30, 50, 70, 100)的N₂吸附-解吸等温线和孔径分布曲线

图S2 Ag/AgCl-LCO-75 HRTEM图

表S1 样品的比表面积、孔径以及NO去除率

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Summary for “Ag/AgCl-LaCO₃OH纳米棒可见光催化净化NO的性能增强及反应机理”

Enhanced visible light photocatalytic performance and reaction mechanism on Ag/AgCl-LaCO₃OH nanorods composite

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Air pollution has become a focused issue worldwide with the rapid development of industry. As one of the major air pollutants, nitric oxide (NO) could cause to serious atmospheric problems, such as acid rain, haze and photochemical smog. Photocatalysis as a green technology has received increasing attention, because it has represented greatly potential application over the late decades. As a novel photocatalyst, LaCO₃OH possesses relatively negative conduction band and positive valence band edges, which can be enable to sufficient potential for photocatalytic air decomposition. But the band gap of LaCO₃OH (4.1 eV) allows only a small portion of solar spectrum in the ultraviolet (UV) light region to be absorbed. To extend the light absorption spectra into the visible light region, the combination of narrow band gap Ag/AgCl with the wide band gap LaCO₃OH to build heterojunction could utilize abundant solar light. Noble metal nanoparticles (NPs) showed strong visible light absorption due to surface Plasmon resonance effect (SPR). In particular, silver NPs show SPR in the visible region, which has been utilized to develop efficient plasmonic photocatalysts.

In this study, a three-component Ag/AgCl-LaCO₃OH nanorod photocatalyst has been fabricated successfully through a chemical precipitation treatment and applied to photocatalytic NO removal. The as-prepared samples were characterized by XRD, SEM, TEM, XPS, UV-vis DRS, PL and ESR. The photocatalytic NO oxidation process was monitored by *in situ* DRIFTS. The results indicated that the visible-light harvesting and the photogenerated carrier separation can be enhanced simultaneously, which could result from introduction of Ag/AgCl into LaCO₃OH (LCO) nanorod photocatalyst. Under visible-light irradiation, the photogenerated electron-hole pairs separation is promoted by the plasma resonance (SPR) effect of the metallic Ag⁰. The hot electrons would be transferred to the defect level endowed by the oxygen vacancies of the LCO. Subsequently, the electron can be transferred to the surface of LCO, captured by O₂ to form ·O₂⁻ radicals, which plays a dominant role in the photocatalytic NO oxidation. In addition, the holes would be transferred to the surface of AgCl, and interact with Cl⁻ to transform Cl⁰, which can directly participate in the oxidation of NO. Furthermore, Cl⁰ can be reduced to Cl⁻ and react with Ag⁺ to forming AgCl, avoiding the photocorrosion of AgCl effectively. Meanwhile, the effect of the mol ratio of Ag/AgCl on the photocatalytic performance was also evaluated. The optimized Ag/AgCl-LCO (mol ratio at 75%) nanorods demonstrated a high NO removal ratio of 54.0%, which far exceeding that of the individual LCO (3.1%) or Ag/AgCl (18.0%) photocatalyst. Moreover, the *in situ* FT-IR spectra was used to dynamically monitor the intermediate toxic by-products, in combination with the active species, and further reveal the mechanism of photocatalytic NO oxidation from the molecular level. The reaction mechanism can be described as Ag + visible light → e⁻ + h⁺, e⁻ + O₂ → ·O₂⁻, h⁺ + AgCl → Cl⁰ + Ag⁺, ·O₂⁻ + NO → NO₃⁻, Cl⁰ + NO → NO₃⁻ + Cl⁻, NO + 2·OH → NO₂ + H₂O, NO₂ + ·OH → NO₃⁻ + H⁺ and Cl⁻ + Ag⁺ → AgCl. The present work could provide navel perspectives for advancing the photocatalysis efficiency, offer a new insight of the photocatalytic reaction mechanism and promote large-scale environmental decontamination applications of plasma-based semiconductor composites.

Ag, LaCO₃OH, surface plasmon resonance, visible-light photocatalysis, *in situ* FT-IR

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