

可见光诱导 Ag/AgX 等离子体光催化净化 NO 的性能与机理

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摘要 贵金属纳米颗粒的表面等离子共振效应使之在可见光区表现出显著的特征吸收. 在可见光的诱导下, 银/卤化银(Ag/AgX, X=Cl, Br, I)复合物在污染物净化中表现出了优良的光催化性能. 本研究采用室温沉淀法制备了Ag/AgX等离子体光催化剂, 对催化剂的微结构和光学性质进行了表征分析. 将制备的Ag/AgX应用于光催化净化空气中NO, Ag/AgCl因具有更强的等离子体效应和更高的电荷分离效率而表现出较高的光催化性能. 运用原位红外光谱动态监测了Ag/AgCl光催化净化NO的反应过程, 从分子层面揭示了Ag/AgCl等离子体可见光催化氧化NO的反应机理. 本研究为贵金属基等离子体光催化剂的作用机理及空气净化应用提供了新的认识.

关键词 Ag/AgX, 等离子共振, 光催化, NO 净化, 可见光, 原位红外

半导体光催化技术可以直接利用太阳能降解环境污染物和分解水, 将低密度的太阳光能转化为高密度的化学能和电能, 在净化环境污染物和开发清洁能源等方面具有巨大的应用潜力^[1~4]. 经过多年研究, 国内外学者在提高光催化效率、拓展光响应范围等问题上取得了许多重要突破^[5~8]. 当前研究较多的是对传统TiO₂光催化材料进行掺杂、半导体复合、光敏化改性和加氢处理等改性^[9~12]. 另一方面, 研究者设计研发了各种新型可见光响应的光催化材料, 如铋系光催化剂, 包括Bi₂WO₆^[13], BiMoO₆^[14], (BiO)₂CO₃^[15]和无金属C₃N₄^[16]等.

最近研究表明, 贵金属纳米粒子因表面等离子效应诱导而具备光催化性能, 被应用在环境污染物

净化和光解水制氢等领域. 表面等离子体是指金属表面沿着金属和介质界面传播的电子疏密波, 它能够被电子或光波激发, 在纳米金属表面场强最大, 在垂直于界面方向呈指数衰减. 当等离子体内部受到入射光的电磁扰动时, 金属表面一些区域电荷分布不均产生静电回复力, 使其电荷分布发生偶极振荡, 当电磁波的频率和等离子体振荡频率相同时, 就会形成表面等离子体共振(surface plasmon resonance, SPR). 这种共振在宏观上表现为金属纳米粒子对光的吸收^[17].

在等离子体光催化领域, 研究者关注最多的是基于银/卤化银(Ag/AgX, X=Cl, Br, I)的系列光催化体系. 比如, Huang课题组^[18,19]利用钼酸银和HCl或HBr

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Chen P, Liu H J, Dong F, et al. Performance and mechanism of visible-light-induced plasmonic photocatalytic purification of NO with Ag/AgX (in Chinese). Chin Sci Bull, 2016, 61: 3482–3489, doi: 10.1360/N972016-00887

之间的离子交换,制备出了AgCl和AgBr.通过光致还原,获得了高效、稳定的表面等离子体催化材料Ag@AgX(X=Cl, Br).近年来,研究者围绕Ag/AgX这类新型光催化材料的制备、污染物降解等方面开展了大量的研究工作,取得了丰硕成果^[20,21].但是,目前Ag/AgX等离子共振光催化主要应用于光解水产氢和降解水体污染物,而应用于空气污染物去除的报道较少,需要进行进一步探索,以扩展Ag/AgX的应用领域.此外,Ag/AgX等离子体光催化净化空气中NO的反应机理未见报道.

本研究采用室温沉淀法制备了Ag/AgX(X=Cl, Br, I)系列等离子体光催化剂,并将其应用于净化空气中NO污染物.对催化剂的微结构和光学性质进行了表征分析,研究结果表明,Ag/AgCl因具有更强的SPR吸收和更高的光生电荷分离效率而表现出最佳的光催化性能.首次运用原位红外光谱揭示了可见光诱导的Ag/AgCl等离子体光催化氧化NO的反应机理,研究结果深化了对Ag/AgX光催化机理及环境净化应用的认识.

1 实验

(i) 方法. 分别称取氯化钾0.373 g, 溴化钾0.595 g和碘化钾0.830 g放于有磁力搅拌子的250 mL烧杯中,各加入去离子水70 mL,搅拌至溶解.分别称取硝酸银固体0.849 g于3个放有磁力搅拌子的100 mL烧杯中,加入去离子水30 mL,搅拌至溶解.把配好的硝酸银溶液分别对应滴加至氯化钾、溴化钾和碘化钾溶液中,搅拌30 min.最后将所得固体样品用水、乙醇各洗2次,于60℃烘箱中烘干备用.

(ii) 表征方法. 采用X射线衍射分析样品的晶体结构(XRD, model D/max RA, Rigaku Co., 日本);扫描电子显微镜分析样品的微观形貌(SEM, JEOL model JSM-64900, 日本);紫外-可见漫反射光谱(UV-vis DRS, UV2550PC, SHIMADZU, 日本)和荧光光谱(PL, F-7000, HITACHI, 日本)分析样品的光学性质.

(iii) 光催化活性测试. 样品的气相光催化性能通过在连续流反应器中去除低浓度NO进行评价.称取样品0.2 g于小烧杯中,各加入30 mL去离子水,超声分散5 min后,转移至直径为12 cm的玻璃圆盘中,60℃下烘干备用.采用标准空气和质量浓度为125 mg/m³的NO标准气体配置低浓度NO污染物,调节空

气流速为2.4 L/min, NO流速为15 mL/min,混合后NO浓度约为625 μg/m³,通入光催化反应器中.将负载有催化剂的玻璃圆盘放置于5.4 L长方体(30 cm×15 cm×12 cm)光催化反应器内,反应器上表面盖上石英玻璃密封,石英玻璃上方放置150 W金属卤化物灯光源,光源前加滤光片将波长小于420 nm的紫外光过滤.将浓度约为625 μg/m³的NO通入反应器内,反应器出口连接到NO_x分析仪(42i-TL, Thermo Scientific, 美国),待NO浓度稳定后,打开光源,NO_x分析仪每隔1 min进行采样检测并记录.按照下式计算光照后NO浓度随时间的变化率 η :

$$\eta = C/C_0 \times 100\%,$$

式中, C_0 为开灯前反应器内NO平衡浓度, C 为开灯后反应器内NO实测浓度.

(iv) 光催化净化NO的原位红外实验. 使用原位红外光谱仪(TENSO II FTIR, Bruker, 德国)进行测量分析,红外光谱仪配备了一个红外漫反射室(Harrick, 德国),其具有3个窗口,包括2个进行红外测量的KBr窗口和1个用可见光源(MVL-210, 日本)进行光照的石英窗口.催化剂床层深度为3 mm,包含了2.4 mm惰性SiO₂支撑层和SiO₂顶部的0.6 mm光催化剂层,气体流量为50 mL/min.催化剂样品在红外漫反射室内进行预处理去除碳氢化合物、H₂O和CO₂.然后将反应混合物(50 μg/m³ NO, 50%占比的He气)通入红外漫反射室.当He通入30 min后,改变气路引入NO气流时催化剂开始进行NO吸附.红外扫描范围4000~600 cm⁻¹且平均扫描64次, KBr用于测量背景光谱.

2 结果与讨论

2.1 晶体结构分析

采用XRD分析样品物相.将图1中Ag/AgX的XRD图谱与银(JCPDS No. 65-2871)、氯化银(JCPDS No. 31-1238)、溴化银(JCPDS No. 6-438)和碘化银(JCPDS No. 9-374)相对比^[22],可以发现,Ag/AgCl中包含立方相氯化银,Ag/AgBr包含立方相溴化银,Ag/AgI包含立方相碘化银.但是样品中银的衍射峰不明显,原因可能是银在样品中的含量较小.除此之外,没有其他物质的衍射峰出现.另外,Ag/AgCl与Ag/AgBr的衍射峰尖锐且明显强于Ag/AgI,说明Ag/AgCl与Ag/AgBr的结晶度比Ag/AgI高.

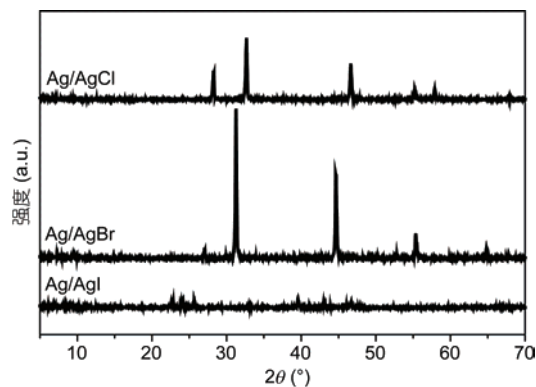


图1 Ag/AgX的XRD图谱

Figure 1 XRD patterns of Ag/AgX samples

2.2 形貌分析

从图2(a)~(c)观察可知, Ag/AgCl与Ag/AgBr的表面形貌成多面体状, Ag/AgCl的形态比Ag/AgBr更加规则, 两个样品比表面积均为 $1.3 \text{ cm}^2/\text{g}$, 在其表面能够比较明显观察到一些细小银颗粒的分布, 且银颗粒分布紧密且较均匀. Ag/AgI为无规则颗粒, 在其表面未能观察到明显的银颗粒, 其比表面积为 $1.2 \text{ cm}^2/\text{g}$. 由上可知, 不同卤素离子的加入对复合光催化剂的形貌产生了显著影响. Ag/AgCl和Ag/AgBr的形态较规则且表面Ag颗粒较多, 会表现出较强的等离子共振效应, 而AgI表面Ag颗粒较少. 样品表面Ag颗粒的产生来自于自然光照下AgX表面 Ag^+ 被光生电子还原.

2.3 光学性质

紫外可见光漫反射图(图3)可知, Ag/AgX样品对紫外-可见光的吸收峰特征是不同的. 3个样品在 $300\sim 400 \text{ nm}$ 处有明显吸收, 在 $500\sim 550 \text{ nm}$ 处均出现明显的吸收峰. 文献[23~25]表明, 500 nm 左右的吸收

峰归属于纳米银的SPR吸收. Ag的尺寸大小对等离子体效应影响较大. Zhang等人^[26]报道指出, Ag的吸收峰随着它的尺寸增大而偏移, 并且变宽. 本研究中, Ag/AgX样品的等离子体吸收峰的偏移源于Ag颗粒大小的不同. 另外, Ag/AgCl和Ag/AgBr在 $500\sim 550 \text{ nm}$ 的吸收峰明显强于Ag/AgI的吸收峰, 且Ag/AgCl的吸收峰最强. 这表明Ag/AgCl样品中Ag颗粒生成量最高, 且Ag和AgCl之间的相互作用力更强. 从热稳定性上看, AgCl应该最稳定, AgI最不稳定. AgCl的等离子共振效应最强的原因可能是AgCl对光更敏感, 因此诱导了更多Ag颗粒的生成, 这与SEM(图2)观察的结果是一致的. 增强的SPR效应会促进催化剂活性的增强. 因此, Ag/AgCl较Ag/AgBr和Ag/AgI应具有更高的光催化活性.

催化剂的电子-空穴分离效率是影响光催化性能的重要影响因素之一^[27]. 只有分离的光生电子和空穴才能参与后续的光催化反应. 图4是Ag/AgX的荧光光谱图. 从图中可知, 样品的PL峰主要出现在可见光区 $435\sim 500 \text{ nm}$ 处, 3个样品均在 $\sim 475 \text{ nm}$ 处出现1个发射峰, 且Ag/AgI, Ag/AgBr, Ag/AgCl的发射峰强度依次降低. 该处Ag/AgCl的PL峰强度最低, 表明Ag/AgCl的电子-空穴复合分离效率最高, 这可能预示着Ag/AgCl具有最佳的光催化活性.

2.4 可见光催化活性分析

以空气中NO为目标污染物, 考察Ag/AgX样品在可见光照射下的光催化活性, 结果如图5所示. 从图中可知, Ag/AgBr和Ag/AgI光催化活性均较低, 光照 30 min 时对NO的去除效率分别为9.8%和6.3%. 值得注意的是, Ag/AgCl却表现出较好的催化活性, 对NO的去除效率为25.0%. 研究发现, 催化剂的光催化活性与Ag的等离子体吸收强度有密切联系^[28]. 结合

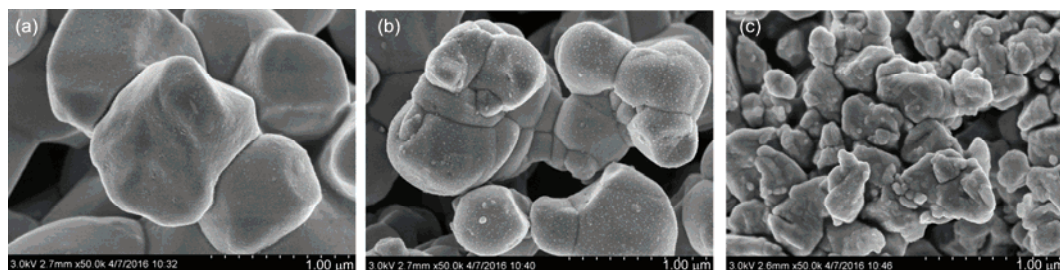


图2 Ag/AgX的SEM图. (a) Ag/AgCl; (b) Ag/AgBr; (c) Ag/AgI

Figure 2 SEM images of Ag/AgX samples. (a) Ag/AgCl; (b) Ag/AgBr; (c) Ag/AgI

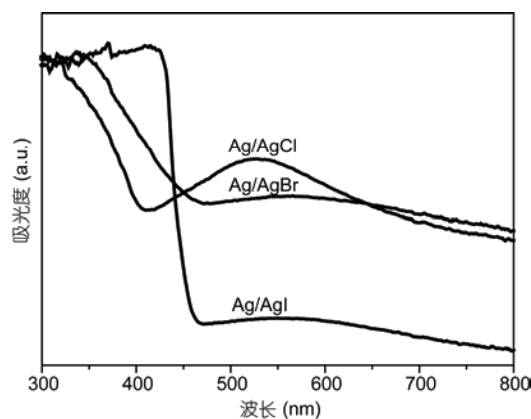


图3 Ag/AgX的UV-Vis DRS图
Figure 3 UV-Vis DRS of Ag/AgX samples

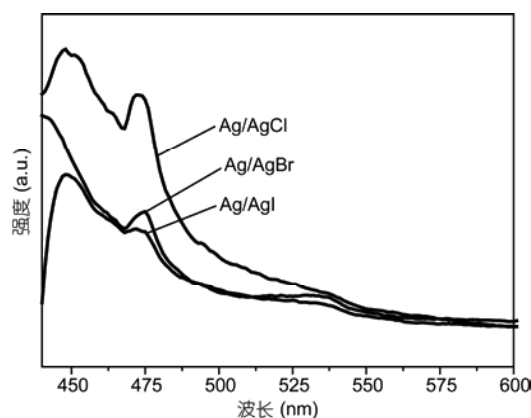


图4 Ag/AgX的荧光光谱图
Figure 4 Photoluminescence spectra of Ag/AgX

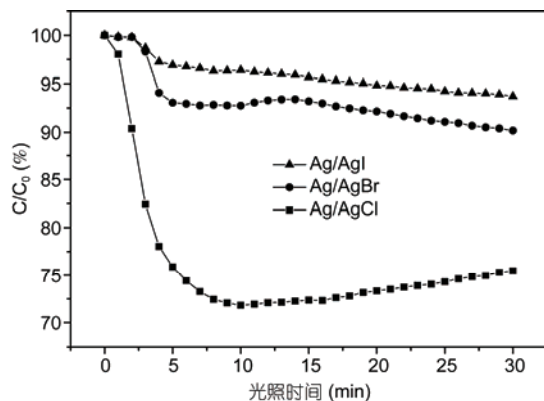


图5 Ag/AgX可见光催化净化低浓度NO曲线
Figure 5 Visible light photocatalytic activity of Ag/AgX for low-concentration NO removal

图3和5可知, 催化剂的光催化活性随着SPR吸收增强而提高. 原因是纳米Ag具有较强的等离子体效应, 而使其具有更强的可见光吸收能力, 且增强的SPR效

应可以激发产生更多的载流子参与光催化反应. 结合图4和5可知, 催化剂的光催化活性与催化剂的电子-空穴分离效率有关, 分离效率越高则催化活性越好. 可见光诱导的Ag/AgX等离子体光催化活性随着催化剂中Ag的SPR吸收增强和电子-空穴分离效率的提高而提高. 从图3和4可知, Ag/AgCl的SPR最强, 且电子-空穴分离效率最高, 因此Ag/AgCl具备最佳的光催化性能. 文献[29,30]报道, 在相同活性测定条件下, C_3N_4 和BiOBr可见光催化NO去除率分别为22.0%和21.3%. 比较发现, Ag/AgCl具备更优异的光催化性能. 值得注意的是, 原位红外监测表明(图6), 反应10 min后, 反应产物逐渐在催化剂表面积累, 占据了催化剂表面部分活性点位, 因此催化剂的活性有所下降, 导致出口NO浓度随时间变化有所升高.

2.5 原位红外光谱分析

通过原位红外光谱的分析可以准确地监测Ag/AgX光催化氧化NO的反应过程. 图6是Ag/AgCl在可见光照射下光催化氧化NO的原位红外光谱图, 表明在可见光照射和通入50 ppm NO的稳定状态下, 红外光谱曲线随时间的演变过程. 957 cm^{-1} 吸收峰归属于 $\nu(\text{NO})$ ^[31], 且其强度随着可见光照射时间逐渐减弱, 表明NO从Ag/AgCl的表面解吸而进一步转化; $1060\sim 1010\text{ cm}^{-1}$ 吸收峰归属于硝酸盐, 可能是双配位基 $\nu(\text{NO}_3^-)$ 或者单配位基的亚硝酸盐物质 $\nu(\text{NO}_2^-)$ ^[32~34]. 在 1280 和 1520 cm^{-1} 处的吸收峰可能是硝基化合物或

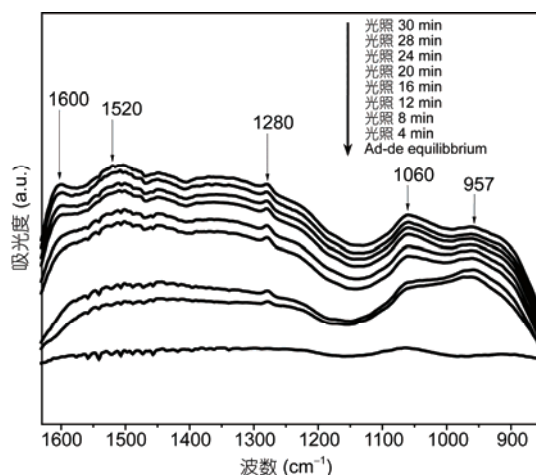


图6 Ag/AgCl可见光催化氧化NO的原位红外光谱图
Figure 6 In situ FT-IR spectra for photocatalytic NO oxidation over Ag/AgCl under visible-light irradiation

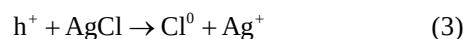
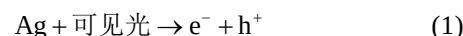
是单配位基硝酸盐 $\nu(\text{NO}_3^-)$; $1600\sim 1550\text{ cm}^{-1}$ 处的吸收峰是双配位基硝酸盐 $\nu(\text{NO}_3^-)$ ^[35]. 值得注意的是, 957 cm^{-1} 吸收峰的强度随着可见光照射时间逐渐减弱, 同时 $1060, 1280, 1520$ 和 1600 cm^{-1} 的吸收峰强度明显随着时间增加, 表明有活性基团诱导NO转化为硝酸盐相关的物种. 吸收峰强度的改变直接说明了催化剂光催化氧化NO的反应过程, 同时也进一步证实了Ag/AgCl在可见光诱导下的等离子体光催化活性.

2.6 Ag/AgX光催化机理

对Ag/AgX光催化机理的理解主要包括2个过程. 一方面, 在可见光照射下, Ag/AgX表面的银纳米颗粒表现出等离子体共振吸收效应, 该吸收发生在可见光区. 因此, Ag/AgX体系表现出优良的可见光吸收性能. 这种吸收使银纳米颗粒的内部产生了光生电子空穴对, 电子迅速传递至银纳米颗粒的表面, 远离卤化银表面, 相反空穴则传递至卤化银表面. 银纳米颗粒表面的光生电子被氧气俘获, 通过链式反应生成超氧负离子. 另外, 传递至卤化银表面的空穴与卤素离子作用生成卤素原子, 该原子具有较强的氧化活性. 在此过程中, 卤素原子又被污染物还原成卤素负离子, 维持体系平衡^[18,19,36~38]. 另一方面, 研究者提出银纳米颗粒被光激发产生光生电子和空穴对, 电子迅速转移至卤化银的导带(conduction band, CB), 并被氧气俘获, 生成氧负离子或其他活性氧基团, 而空穴则直接参与氧化反应, 氧化污染物. 此过程中, 银离子则从污染物分子中获得电子而还原成金属银

原子, 维持整个体系平衡^[39~41]. 但是不同文献报道的Ag/AgX光催化材料在光照条件下的电荷分离、转移机制以及光催化活性不同, 因为Ag/AgX光催化材料具有不同的晶体结构以及催化形貌, 使得催化剂表面的银纳米颗粒的表面等离子共振吸收效应的强度不一. 综合以上催化机理分析和本研究表征结果, 提出了一个可能的反应机理, 如图7所示.

可见光照射下, Ag/AgCl表面的Ag纳米颗粒内部产生光生电子和空穴对, 光生电子迅速移动到Ag纳米颗粒表面被空气中的氧气, 产生 $\cdot\text{O}_2^-$; 活性基团 $\cdot\text{O}_2^-$ 与NO进行氧化还原反应, 使NO转化为 NO_3^- 等. 而空穴则移至AgCl表面与 Cl^- 结合生成 Cl^0 , Cl^0 具有较强的氧化性, 且 Cl^0 氧化了NO后转变成 Cl^- , 之后与 Ag^+ 结合又生成了AgCl. 因此, 光催化反应过程列为以下几步:



3 结论

采用室温直接沉淀法制备了Ag/AgX复合光催化剂, Ag/AgCl的可见光等离子体光催化性能优于Ag/AgBr和Ag/AgI. Ag/AgCl的形态规则且表面银颗

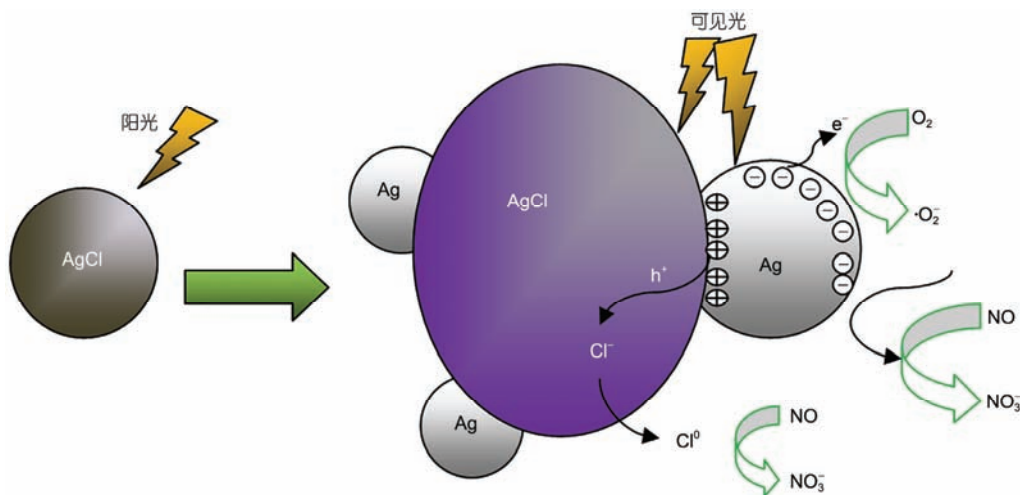


图7 (网络版彩色)Ag/AgCl光催化剂去除NO的光催化机理图

Figure 7 (Color online) Photocatalysis mechanism for purifying NO with Ag/AgCl photocatalyst

粒较多, 表现出了较强的等离子共振效应. Ag/AgCl 表现出更强的SPR效应且其光生电子空穴对的分离效率高, 使其在可见光下表现出对空气中NO优异的净化性能. 采用原位红外光谱揭示了Ag/AgCl等离子

体光催化氧化NO的反应机理. 可见光照射下, 吸附在催化剂表面的NO随着时间逐渐减少而转变为硝酸盐物种. 本研究对于深入认识Ag/AgX等离子体光催化机理及空气污染净化应用具有重要的科学意义.

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Performance and mechanism of visible-light-induced plasmonic photocatalytic purification of NO with Ag/AgX

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Photocatalysis technology could utilize solar energy for pollutants degradation and water splitting, displaying great potential in environmental remediation and clean energy development. Significant progresses have been made on promoting photocatalysis efficiency and extending light absorption range. Specific semiconductors and plasmonic metals can behave photocatalysts. Recently, the plasmonic photocatalysis with Ag/AgX (X=Cl, Br, I) has been received increasing research interests. The preparation and application of Ag/AgX plasmonic photocatalysts have extensively explored. However, the Ag/AgX plasmonic photocatalysts were mainly applied in water splitting and degradation of aqueous pollutants. The application of Ag/AgX in air purification has been rarely reported. Also, the mechanism of photocatalytic NO purification with Ag/AgX has never been revealed.

Noble metal nanoparticles showed obvious characteristic absorption in the visible light region due to surface plasmon resonance effect. Under the induction of visible light, silver/silver halide (Ag/AgX, X=Cl, Br, I) compounds shows excellent photocatalytic performance in the purification of pollutants. This research adopted the method of precipitation at room temperature to prepare Ag/AgX plasmonic photocatalyst. The formation of Ag metal on the AgX surface can be ascribed to the natural light illumination. The microstructure and optical properties of the as-prepared catalysts were characterized with XRD, SEM, UV-Vis DRS and PL techniques. The prepared Ag/AgX was applied in photocatalytic purification of ppb-level NO in the air. NO is one of the typical indoor and outdoor air pollutants. The results indicated that the Ag/AgCl showed higher visible light photocatalytic performance due to the strong surface plasmon resonance absorption and the high charge separation efficiency in comparison with Ag/AgBr and Ag/AgI. The process of photocatalytic NO purification with Ag/AgCl was dynamically monitored with *in situ* FT-IR equipped with an *in situ* diffuse-reflectance cell. The time-dependent evolution of IR peaks have been identified. The plasmonic visible light photocatalytic NO oxidation reaction mechanism with Ag/AgCl was revealed at molecular level. The reaction mechanism can be described as $\text{Ag} + \text{visible light} \rightarrow \text{e}^- + \text{h}^+$, $\text{e}^- + \text{O}_2 \rightarrow \cdot\text{O}_2$, $\text{h}^+ + \text{AgCl} \rightarrow \text{Cl}_0 + \text{Ag}^+$, $\cdot\text{O}_2 + \text{NO} \rightarrow \text{NO}_3^-$, $\text{Cl}_0 + \text{NO} \rightarrow \text{Cl}^- + \text{NO}_3^-$ and $\text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl}$. The present work could provide a new perspective in the understanding of the mechanism of noble metal based function plasmonic photocatalyst and air purification application.

silver/silver halide, plasmon, photocatalysis, NO purification, visible light, *in situ* FT-IR

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