综论

钙钛矿型光催化材料的应用现状及进展

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摘要：光催化技术和光芬顿技术是解决环境污染和能源短缺问题的有效手段，而光催化剂是其研究核心。钙钛矿材料因其在光催化能量转换和环境净化方面的潜力而成为新型光催化材料的研究热点。该文综述了钙钛矿型光催化剂的特性、活性影响因素和新型钙钛矿光催化材料的发展现状，归纳了该材料在染料废水处理、氨氮废水处理、金属离子氧化还原、大气污染物净化和土壤有机物及重金属去除中的应用进展，并对其在实际应用中面临的挑战及未来发展方向进行了讨论。最后指出钙钛矿型光催化剂目前发展面临的关键问题在于节能绿色制备方法的开发、新型复合钙钛矿材料尤其是高比表面积钙钛矿基体材料的研发和针对钙钛矿材料特性的反应器的建造。

关键词：钙钛矿型光催化剂；ABX_3；光催化；光芬顿技术；进展

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Status quo and progress of perovskite-type photocatalysts

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Abstract: Photocatalysis and photo-Fenton technology, with photocatalyst the research core, are effective means for solving the problems of environmental pollution and energy shortage. Perovskite materials, showing great potential in photocatalytic energy conversion and environmental purification, have become a research hotspot in the field of new photocatalytic material development. Herein, The characteristics, activity influencing factors and status quo of perovskite-type photocatalysts were firstly reviewed, followed by summarization on the application progress of perovskite-type photocatalysts in dye wastewater treatment, ammonia nitrogen wastewater treatment, metal ion redox, atmospheric pollutant purification and soil organic matter and heavy metal removal and discussions on the challenges and future development directions in practical applications. Finally, it was suggested that development of energy-saving green preparation methods, research of new composite perovskite-type photocatalysts, especially perovskite matrix materials with high specific surface areas, and construction of reactors based on the characteristics of perovskite-type photocatalysts were key development directions.

Key words: perovskite-type photocatalysts; ABX_3; photocatalysis; photo-Fenton technology; progress

近年来，全球能源危机和环境污染问题突出，对 人类社会造成重大影响[1]。各种新兴难降解污染物

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的出现使以生物处理和化学处理为代表的传统方法面临失效的危险，光催化技术和光芬顿技术因具有高效和环境友好的双重优势而逐渐成为研究热点[2-3]。两种技术是在光催化剂、光辐射和氧化剂等条件下产生强氧化性的自由基，进而实现无选择性地氧化大部分有机污染物，其研究核心为光催化剂[4-5]。金属氧化物、氮化物、磷化物、硫化物、非金属和铋系等光催化材料被广泛研究，但其存在成本高、不可再生、比表面积小、光吸收能力差、光吸收范围窄、载流子分离效率和光催化活性低等问题，这促使研究者继续寻找低成本、稳定和高效的光催化剂[6-10]。

钙钛矿型材料具有与天然钙钛矿（$CaTiO_3$）相同的晶体结构（图 1a），其化学通式为 ABX_3，A 为碱土或稀土金属离子，B 为过渡金属离子，X 为原子半径较小的阴离子[11-12]。通过元素的替换和掺杂可以调控钙钛矿型材料的催化性能，A 位和 B 位都可被相同或不同价态离子取代，用 $A_{1-x}A'_xB_{1-y}B'_yX_{3+\delta}$ 表示[13]。元素周期表中绝大部分元素都能组成稳定的钙钛矿结构[14]。钙钛矿材料具有光、电、磁等物理特性以及氧化还原性、催化活性等化学性质，已经广泛应用于催化领域[15-16]。

近年来，研究者发现钙钛矿型材料具备优异的电子结构，利于电子激发和迁移，可将光响应段向可见光区移动，所以钙钛矿型材料作为光催化剂对太阳光具有极高的利用率[17]。同时，通过晶格畸变可以强烈影响钙钛矿型材料的光生电荷载流子的分离，进而避免复合过程[18]。所以，钙钛矿型材料作为新型光催化剂的潜力逐步得到重视。

钙钛矿型材料的光催化原理与传统光催化材料相似。在可见光或紫外光照射下，钙钛矿产生光生电子和空穴，光生电子和空穴在内部电场力的作用下分离并分别转移到导带（CB）和价带（VB），这些电荷与表面吸附的氧气和氧化物发生反应，产生具有强氧化性的自由基，进而实现污染物的降解（图 1b）[19-20]。

本文综述了钙钛矿型光催化剂的活性影响因素、新型钙钛矿光催化材料的发展现状以及钙钛矿材料在光催化领域的应用现状，并对其目前面临的问题及未来发展方向进行了展望（图 2）。

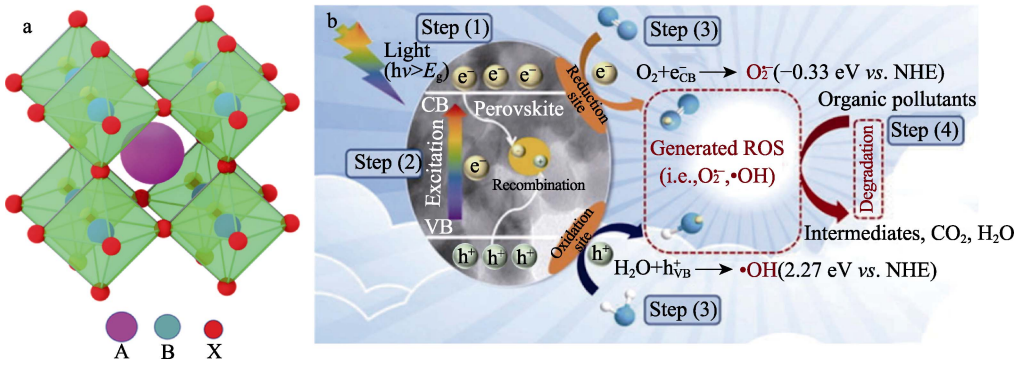

图 1　钙钛矿材料的晶体结构（a）；钙钛矿光催化剂降解污染物机理（b）[20]

Fig. 1　Crystal structure of perovskites (a); Mechanism of degradation of pollutants by perovskite photocatalyst (b)[20]

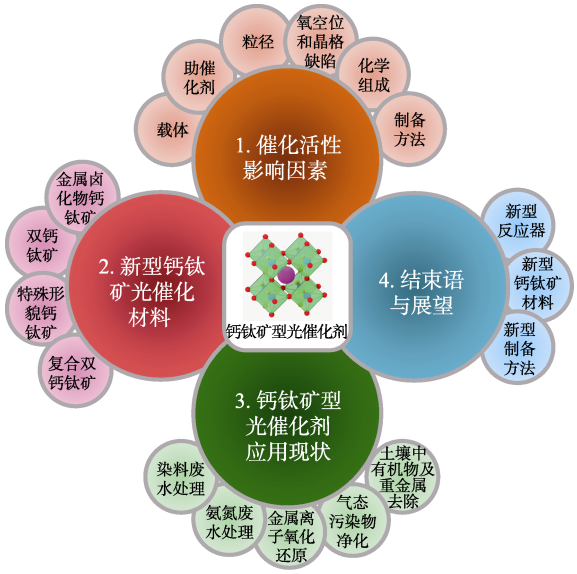

图 2　钙钛矿型光催化剂研究进展总图

Fig. 2　Overview of research progress of perovskite photocatalysts

1　催化活性影响因素

钙钛矿型光催化剂的制备方法、化学组成、氧空位浓度和晶格缺陷等因素在催化反应过程中起到重要作用[21]。

1.1　制备方法

制备方法直接影响钙钛矿的光学、电子性能和比表面积等性质，从而影响材料的光响应范围和载流子复合效率[22]。钙钛矿的制备方法有固相反应法、溶胶-凝胶法、化学沉淀法和水热合成法等[23]。固相反应法是钙钛矿制备的经典工艺，但已无法满足现阶段对钙钛矿纯度和晶粒尺寸的要求，所以目前溶胶-凝胶法、共沉淀法和水热合成法受到更多关注[24]。CHIEN 等[25]分别采用共沉淀法、水热合成法和溶胶-凝胶法制备 $BiFeO_3$ 用于光催化降解苯酚。结果表明，3 种方法制备的钙钛矿晶体结构、光学

和电学性质均有显著差异，其中溶胶-凝胶法制备的样品具有最高光催化活性。

上述传统制备方法虽已经发展成熟，但仍面临一系列问题，一些改进方法也正在发展中。传统制备方法往往面临团聚和烧结的问题，这导致钙钛矿产物比表面积严重受限，进而影响其催化性能，超声辅助、微波辅助和对前驱体采取冷冻干燥等手段可以在一定程度上改善上述问题[26-27]。YOUSEFI 等[28]对比了普通共沉淀法、微波辅助共沉淀法和超声波辅助共沉淀法制备的 $La_{0.75}Sr_{0.25}MnO_3$。结果表明，微波和超声波显著抑制了钙钛矿颗粒的烧结和团聚，有助于提高产物的均匀性并缩短反应周期。HUANG 等[29]采用冷冻干燥辅助共沉淀法制备 $La_{0.6}Sr_{0.4}MnO_3$。结果表明，与普通共沉淀法制备的产物相比，冷冻干燥显著提升了沉淀物的颗粒均匀性并大幅降低了结晶温度。

1.2 化学组成

光催化剂的禁带宽度越小，可吸收的光波长范围越大，催化所需能量越低，活性就越高[30]。在钙钛矿晶格中，B 位离子的 3*d* 轨道和 X 的 2*p* 轨道构成导带和价带，钙钛矿的禁带宽度主要与 A—X 和 B—X 的电负性差值有关[31]。因此，化学组成显著影响钙钛矿的光催化性能。

1.2.1 A 位离子电负性和电子结构影响催化材料的光催化活性

A 位离子电负性越大，与之配位的 X 原子极化作用越强，进而使 X_{2p} 电子云变形加大，所以 X 原子从 2*p* 至 3*d* 的电荷转移能减小，即激发电子从价带跃迁至导带所需能量降低，光波长变长，因而钙钛矿型光催化剂的活性随之提高[32-33]。QU 等[34]合成 $AMnO_3$（A=Gd、Tb、Dy）并对比系列催化剂的光催化性能。结果表明，$AMnO_3$ 的催化活性随 A 位离子的电负性增加而增加。CAI 等[35]合成了 $ATiO_3$（A=Ba、Pb、Sr）。结果表明，$PbTiO_3$ 光催化活性最高，这可能是由于 $PbTiO_3$ 具有更为优异的电子结构和更高的电荷分离效率。

1.2.2 B 位离子半径大小、电子结构和电负性等影响催化材料的光催化活性

在钙钛矿型化合物中，B 位离子半径越小，电负性越大，禁带宽度越小，电子更易于被激发，因此催化活性越高[36]。此外，B 位离子位于钙钛矿晶格结构中心，其 5 条简并轨道可分裂为能量高的轨道（e_g）和能量低的轨道（t_{2g}），当 e_g 和 t_{2g} 上的电子处于不饱和状态时，费米能级升高，电子逸出功减小，电子更易被激发，所以此时钙钛矿的光催化活性也相应地处于较高水平[37]。JÁCOME-ACATITLA 等[38]合成 $LaMO_3$（M=Fe、Co、Mn）用于光催化降解 4-氯苯酚。结果表明，$LaMnO_3$ 在 1~2 eV 之间发生电子跃迁，呈现最大吸光度，进而表现出最高光催化活性。YIN 等[39]制备了 $LaMn_{1-x}B_xO_{3+\delta}$（B=Fe、Co、Ni）用于光催化析氢。结果表明，Ni 的掺杂可以最大程度上促进氧空位的形成以及氧离子的传导，同时 Ni 具有最多的 *d* 电子数，*d* 电子数越多导带能级越低，电子跃迁到导带而被激发所需的能量也就越低，所以当以 Ni 为 B 位掺杂离子时催化活性最高。

1.3 氧空位和晶格缺陷

氧空位和晶格缺陷对钙钛矿型光催化剂的性能具有重要影响。钙钛矿型光催化剂产生氧空位的途径有两种：一种是不同金属离子部分取代 A 位和 B 位阳离子形成掺杂型钙钛矿，为保证钙钛矿晶体结构不变，根据电中性原则而产生氧空位；另一种是在 H_2 或 N_2 等还原性气氛中进行退火处理，在晶体内形成氧空位[40-41]。氧空位可以吸收部分氧物种，而这部分氧物种因其具有极高的反应活性而对催化过程产生积极影响[42]。另外，对钙钛矿的 A、B 或 X 位进行掺杂时，会使钙钛矿晶格结构发生畸变，间接增强催化剂晶格氧的活性和迁移性，进而提高其光催化活性[43]。LI 等[44]制备了 $La_xCa_{1-x}FeO_3$ 用于光催化水产氢。结果表明，Ca 的掺杂显著提升了材料表面的氧空位含量，影响了金属的电子不对称化学状态，提高了催化位点的活性。WU 等[45]制备了 $SrTi_xMn_{1-x}O_3$ 用于光催化 H_2O 还原 CO_2。结果表明，Mn^{4+}取代了 Ti^{3+}进入钙钛矿晶格导致大量氧空位的产生，材料的光催化活性随掺杂量的上升出现先升高后降低的趋势，这可能是因为氧空位的存在有利于光吸收起始点向可见光区移动，但随掺杂量的增加，界面电子和空穴的转移受到抑制。因此，将钙钛矿型光催化剂中氧空位和晶格缺陷的量控制在一定范围内才能使其呈现出优良的催化性能。

1.4 粒径

粒径越小，催化剂的比表面积越大、禁带宽度越宽、光生电荷载流子迁移到表面的路径越短，越有利于光生空穴和电子的氧化还原能力的提升和光诱导的电荷载流子快速到达催化剂表面并被捕获以引发光化学反应，因此，催化活性越高[46-48]。当粒径小于 10 nm 时会产生量子尺寸效应，使得禁带宽度增大，进而使空穴/电子对获得更强的氧化还原能力[49]。PARIDA 等[50]制备不同粒径的 $LaFeO_3$ 用于光催化水产氢。结果表明，500 ℃活化的 $LaFeO_3$ 具有最小的粒径和最大的比表面积，同时达到最高产氢效率，证实了钙钛矿的光催化活性随粒径的减小而升高。WIRANWETCHAYAN 等[51]采用微波等离子体法合成 $LaFeO_3$ 用于光催化降解罗丹明 B。结果表明，当粒径由 58 nm 下降到 27 nm 时，光催化活性

提高 20.1%。

1.5　助催化剂

助催化剂能够促进光生电荷向助催化剂转移，进而提升电子捕获性能，同时对光催化剂的带隙具有重要影响[52-53]。常见的助催化剂主要有贵金属类（Au、Ag 和 Pt 等的单质或氧化物）、稀土类（CeO_2 和 ZrO_2 等）、过渡金属类（CuO、NiO 和 MnO_2 等）和非金属类（石墨烯）[54-56]。

贵金属可产生局域等离子体共振效应，提高钙钛矿的光响应范围，同时其具有较低的费米能级，可有效抑制电子/空穴对的复合[57]。相比于 Au、Pt 和 Pd 等，Ag 因其成本较低而成为研究重点。CARRASCO-JAIM 等[58]制备了 $Ag/AgTaO_3$ 用于光催化产氢。结果表明，Ag 表面的等离子体共振效应抑制了电子/空穴对的复合，进而显著改善了钙钛矿的光催化性能。

稀土金属具有多电子组态，能够通过导带和价带进行氧化还原反应，进而显著提升钙钛矿光催化剂的活性[59]。Ce 是含量最为丰富的稀土元素，其中，CeO_2 表面存在大量氧空位，具有优异的电子转移能力和储氧能力[60]。QIAN 等[61]制备了 $CeO_2/NaNbO_3$ 用于光催化降解废水中的抗生素和染料。结果表明，$CeO_2/NaNbO_3$ 在紫外光和可见光下均呈现比 $NaNbO_3$ 更高的光催化活性，这主要归因于光生电子和空穴的高分离率和光生电荷在界面区域的高迁移率。

过渡金属元素存在多种价态，掺杂进钙钛矿结构中可使其晶格畸变，产生光生载流子捕获阱，从而抑制电子与空穴的复合[62]。Cu 储量丰富、价格低廉，具有较高的能带边缘拓展能力，其中，CuO 带隙窄，光生电子更容易发生跃迁[63]。AHMADI 等[64]制备了 $SrTiO_3$/CuO 用于光催化降解罗丹明 B。结果表明，CuO 的添加可使钙钛矿导带中的激发电子转移到 CuO 导带，显著降低光生电子与空穴的复合效率。

还原石墨烯（rGO）具有量子隧道效应和高电子传输效率，已经成为优良的钙钛矿助催化剂[65]。LI 等[66]制备了 $LaCoO_3$/凹凸棒石黏土（ATP）/还原石墨烯（rGO）用于光催化还原 NO。结果表明，rGO 作为 ATP 和 $LaCoO_3$ 之间的优良电子传输介质，实现了间接 *Z* 型电子转移，从而显著提高了复合材料的电荷分离效率和氧化还原能力。

1.6　载体

将钙钛矿型光催化材料分散在多孔材料表面，不仅可以提升其比表面积，暴露更多活性位点，另外，载体与钙钛矿之间的相互作用也可提高钙钛矿的光催化活性[67]。PENG 等[68]通过溶胶-凝胶法在蒙脱石（MMT）表面沉积 $LaFeO_3$ 纳米颗粒。结果表明，$LaFeO_3$/MMT 表现出优异的吸附性能和可见光催化活性，这归因于较大的比表面积和丰富的羟基基团，丰富的羟基基团可以捕获光生空穴产生羟基自由基并降低电子/空穴对的复合效率。CHEN 等[69]通过溶胶-凝胶法在木质素-生物炭上负载 $LaFeO_3$。结果表明，载体的引入会使钙钛矿暴露更多活性位点，进而提升催化剂与反应物分子之间的接触效率，提高了催化活性。

2　新型钙钛矿光催化材料

近年来，金属卤化物钙钛矿、双钙钛矿、特殊形貌钙钛矿和复合钙钛矿等新型钙钛矿光催化材料受到研究人员的青睐，其应用价值也得到了广泛认同[70]。钙钛矿型光催化剂发展情况如图 3 所示。

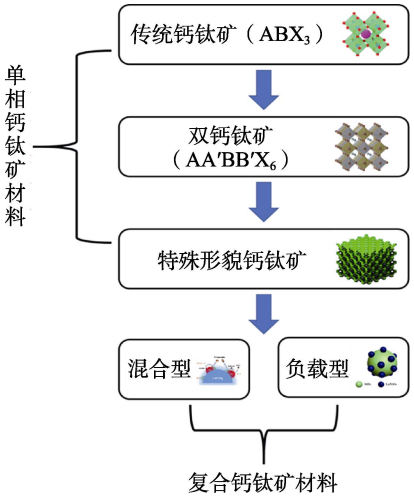

图 3　钙钛矿型光催化材料的发展情况

Fig. 3　Development of perovskite-type photocatalysts

2.1　金属卤化物钙钛矿

金属卤化物钙钛矿因具有高量子效率、强光致发光、可调节带隙、长载流子寿命等优点，并且其储量丰富，成本低廉而成为新兴光催化材料[71]。WANG 等[72]制备了 $MAPbI_3$ 用于光催化水产氢。结果表明，该材料具有优异的光生电荷载流子分离和可见光催化水产氢能力。但金属卤化物钙钛矿稳定性较差并且其表面存在缺陷，环境中的紫外线、氧气和温度等因素会使其光催化活性大幅度降低[73]。可采用组分工程增强其晶体结构稳定性，或采用界面工程构建异质结，促进光生载流子的分离和迁移效率，提高其光催化活性[74]。GUAN 等[75]采用光辅助法和离子交换法合成 I^- 由壳层到核心浓度逐渐减小的 $CsPbBr_{3-x}I_x$/Pt。由于 I^- 浓度的梯度分布，该材料具有带隙漏斗结构，该结构增强了光生载流子从核心到壳层的转移，从而产生了优异的光催化性能。WU 等[76]采用光还原法合成 $MAPbI_3$/rGO。结果表明，与 $MAPbI_3$ 相比，$MAPbI_3$/rGO 的光致发光强度

急剧下降，表明 $MAPbI_3$ 中的光电子被有效地转移到 rGO 中，导致电荷重组减少，进而提升钙钛矿的光催化活性。

2.2　双钙钛矿

双钙钛矿化学通式为 $AA'BB'X_6$，其中 A′为碱金属或稀土阳离子，如锂和镧等，B′为过渡金属或稀土元素，如钨和钌等[77]。相较于单钙钛矿，双钙钛矿具有元素组成和晶体结构丰富、原子环境复杂以及组成空间宽广等优势，因此，其成为单钙钛矿光催化材料的新兴替代品[78]。WU 等[79]采用热注入法制备无铅全无机钙钛矿 $Cs_2AgBiBr_6$（图 4）用于光催化降解 NO。结果表明，所制备的双钙钛矿在可见光照射下对 NO 的去除率达到了 97%，同时可以在空气中保持两个多月的结构稳定。

目前双钙钛矿光催化材料存在以下问题：（1）量子产率低；（2）热稳定性差；（3）催化活性不高[80-81]。有文献报道可通过掺杂和复合等方法减小带隙，改变晶体结构，抑制电子/空穴对的复合来增强其光催化活性[82-83]。

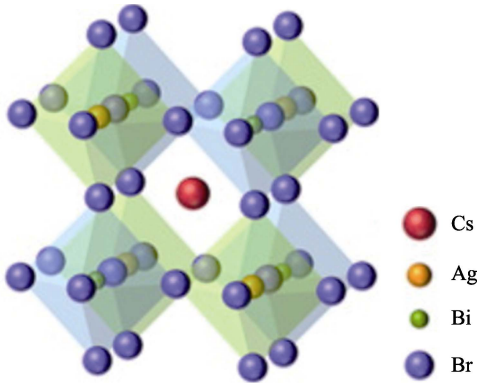

图 4　$Cs_2AgBiBr_6$ 的结构示意图[79]

Fig. 4　Structure diagram of $Cs_2AgBiBr_6$[79]

2.3　特殊形貌钙钛矿

近年来，一些具备三维有序大孔（3DOM）、空心微球、带状多孔和晶体管状等结构的特殊形貌钙钛矿材料因具有光生电子/空穴对复合率低、比表面积大及光能利用率高等优点而被广泛研究[84-85]。3DOM 材料的三维有序空间结构表现出明显的光子带隙效应和慢光子效应，当入射光波长与 3DOM 材料的阻带边缘重叠时，光捕获效率和光催化性能会显著提高[86-87]。TANG 等[88]制备 $3DOMAu\text{-}CsPbBr_3$ 并将其用于光催化还原 CO_2，制备流程及产物结构如图 5 所示（PS 为聚苯乙烯）。结果表明，与块体钙钛矿相比，3DOM 结构改善了材料的集光效果，$3DOMAu\text{-}CsPbBr_3$ 的光催化电子消耗率提高了 2.6 倍，极大地提高了光捕获和载流子转移能力，从而改善了光催化性能。

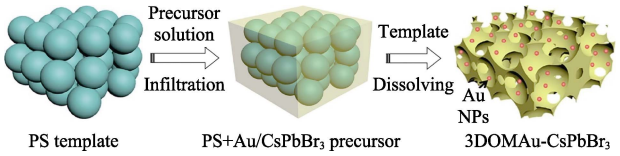

图 5　$3DOMAu\text{-}CsPbBr_3$ 的制备过程及产物结构[88]

Fig. 5　Preparation process and product structure of $3DOMAu\text{-}CsPbBr_3$[88]

2.4　复合钙钛矿

金属氧化物、二氧化硅和碳基材料等可与钙钛矿光催化材料组合在一起，提高比表面积，形成异质结，促进电荷分离，进而提高光催化活性[89-90]。石墨烯具有比其他材料更合适的能级分布，在可见光和近红外区域具有良好的光透过性，因此，成为近年来的研究热点[91]。CHEN 等[92]制备了 $CsPbBr_3$-半导体氧化石墨烯（GO）用于光催化还原 CO_2。结果表明，GO 的添加使电荷分离效率显著提高，进而提升 $CsPbBr_3$-GO 的可见光催化活性。VENKATESH 等[93]制备了 $rGO/BaSnO_3$ 用于光催化降解有机染料。结果表明，rGO 的加入促进了电子转移，有效抑制了电子/空穴的复合。

3　钙钛矿型光催化剂应用现状

与传统光催化材料相比，钙钛矿材料具有优异的光学和导电性能，能够促进光生电子/空穴对的分离，提高其光响应范围和强度[94]。因此，钙钛矿型光催化剂被广泛应用于多种污染物的去除，其应用现状如图 6 所示。

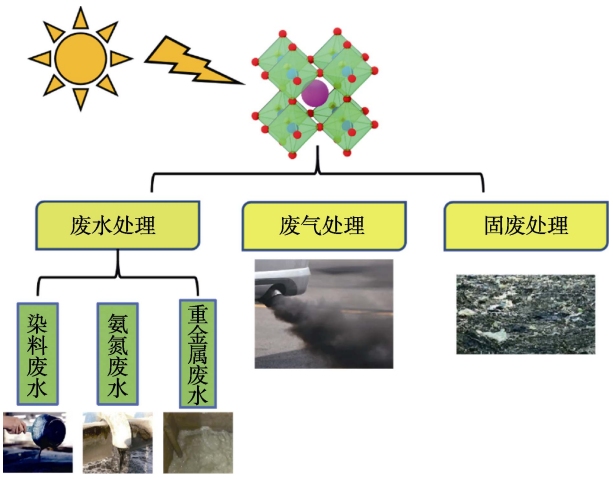

图 6　钙钛矿型光催化剂的应用现状

Fig. 6　Application status of perovskite-type photocatalysts

3.1　染料废水处理

染料废水具有高色度、高化学需氧量、高毒性、高稳定性、种类繁多且结构复杂等诸多特点，光催化和光芬顿技术由于氧化能力强且成本可控，被广

泛用作染料废水的处理[95-96]。近年来，有色化合物抗紫外和抗氧化能力逐渐加强，所以开发具有高可见光活性的光催化剂是一个重要课题[97]。

钙钛矿材料具备适当的电子结构，可将光响应段向可见光区移动，因此其对可见光的利用效率较高[98]。MATHIARASU 等[99]制备了 $La_{0.5}Ca_{0.5}TiO_3$ 用于光催化降解活性黄 145。结果表明，$La_{0.5}Ca_{0.5}TiO_3$ 在紫外光范围内实现了光催化降解，其降解机理如图 7a 所示。为了提高紫外光利用率 KARAMI 等[100]制备了具有纳米结构的 $CsPbI_3$ 用于光催化降解甲基紫。结果表明，$CsPbI_3$ 带隙较窄，从而在可见光范围内取得较高的催化降解效率，其降解机理如图 7b 所示。

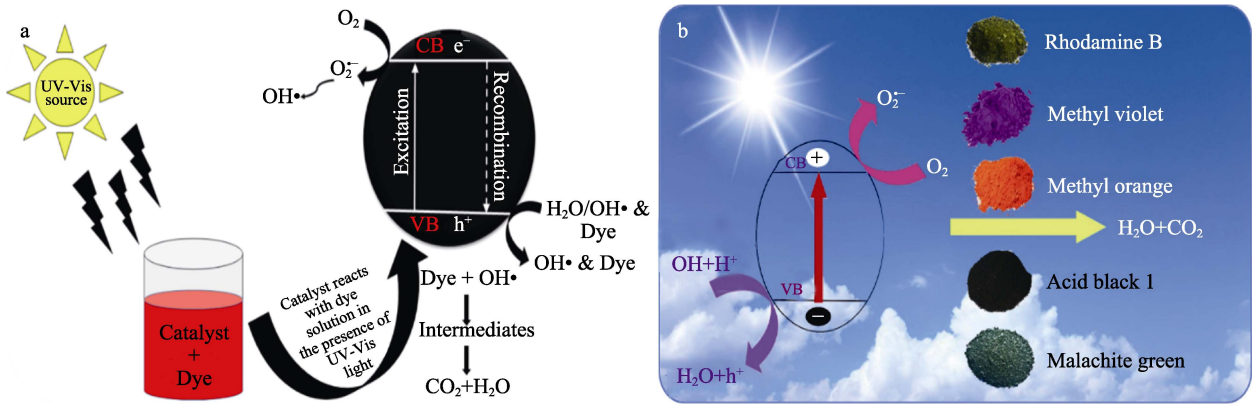

图 7　$La_{0.5}Ca_{0.5}TiO_3$ 光催化降解活性黄 145 染料机理（a）[99]；$CsPbI_3$ 光催化降解有机染料的机理（b）[100]

Fig. 7　Mechanism of photocatalytic degradation of reactive yellow 145 dye by $La_{0.5}Ca_{0.5}TiO_3$ (a)[99]; Mechanism of photocatalytic degradation of organic dyes by $CsPbI_3$ (b)[100]

3.2　氨氮废水处理

化学工业、农业生产和市政工程产生大量高氨氮废水，对人类和生态系统构成严重威胁[101]。目前的氨氮处理技术，如离子交换、生物化学法和吸附等存在反应条件苛刻和二次污染等问题[102]。光催化和光芬顿技术具有操作简单、能源成本低和几乎不产生污泥等二次固体废物的优势，已经成为潜在高氨氮废水处理的有效方法[103-104]。TiO_2 基光催化剂是目前用于处理氨氮废水的主要光催化材料[105]。TiO_2 基光催化剂的优势在于可以完全破坏 N—H 键，而对太阳光利用率低的问题仍然限制其在氨氮废水处理领域的应用[106]。

钙钛矿型光催化剂在氨氮废水处理中具有高活性和高选择性[107]。ZOU 等[108]制备石墨烯（rG）负载 $BiFeO_3$ 并用于光催化去除氨氮。结果表明，在可见光下，氨氮去除率达 91.2%，转化产物以 N_2 为主，催化剂循环使用 7 次后，活性未减退，其催化机理如图 8 所示。KHEN 等[109]制备 $LaFeO_3$/改性珍珠岩并用于光催化去除氨氮，该材料同样表现出高稳定性和高催化活性。

3.3　金属离子氧化还原

铬污染在污水治理中颇受关注。Cr^{6+}具有毒性高、氧化性强、致癌致畸和不可降解的特点[110]。光催化技术和光芬顿技术可将 Cr^{6+}转化为低毒的 Cr^{3+}，具有高效、安全和操作简单等优势，是一种具有潜力的含铬废水处理方法[111]。纳米零价铁具有低成本、高活性、大比表面积、强吸附能力和强还原能力，成为去除 Cr^{6+}的常用光催化材料，但其在实际应用中易氧化，难回收[112]。

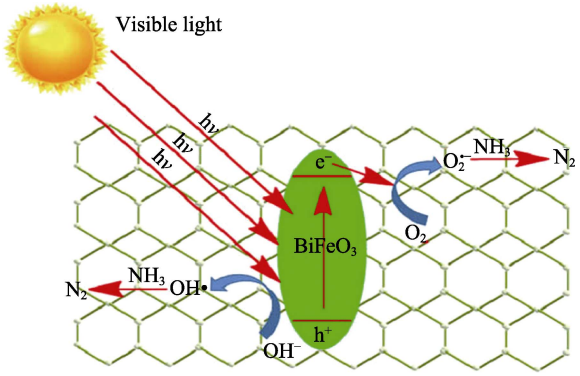

图 8　rG-$BiFeO_3$ 光催化剂降解 NH_3 反应机理[108]

Fig. 8　Reaction mechanism of rG-$BiFeO_3$ photocatalyst for NH_3 degradation[108]

钙钛矿型光催化剂具有优良的带隙和能带排列，在光辐射下可以产生强氧化性的电子以还原水中六价铬。此外，其稳定性和可回收性优良[113]。LEI 等[114]制备 $CaTiO_3/TiO_2$ 用于可见光下还原水中 Cr^{6+}。结果表明，在 400 ℃煅烧下，该材料表现出比其他催化剂更高的光催化活性。ANAND 等[115]制备 $Bi_{0.85}Ca_{0.15}FeO_3$ 用于还原水中 Cr^{6+}。结果表明，该材料具有高稳定性、高还原活性和强吸附性能，其催化机理如图 9 所示。

3.4　气态污染物净化

火力发电和钢铁冶炼等行业伴随着煤炭大量消耗，导致 CO_2、SO_2、NO_x 和挥发性有机物（VOCs）

等废气的排放，造成严重的环境污染[116]。光催化和光芬顿技术具有产生二次污染风险低和在温和条件下能够脱除 1.0×10^{-6} 数量级浓度的气态污染物等优势，成为环境友好型烟气净化技术[117]。尖晶石可形成异化效应，有利于气态分子的活化，且其晶格间距和费米能级处在活化气态分子最适宜的状态，从而有利于气态污染物的去除，但其结构受掺杂元素、反应条件、制备方法和制备过程等因素的影响较大，容易生成反尖晶石或混晶结构，从而导致催化活性降低[118-119]。

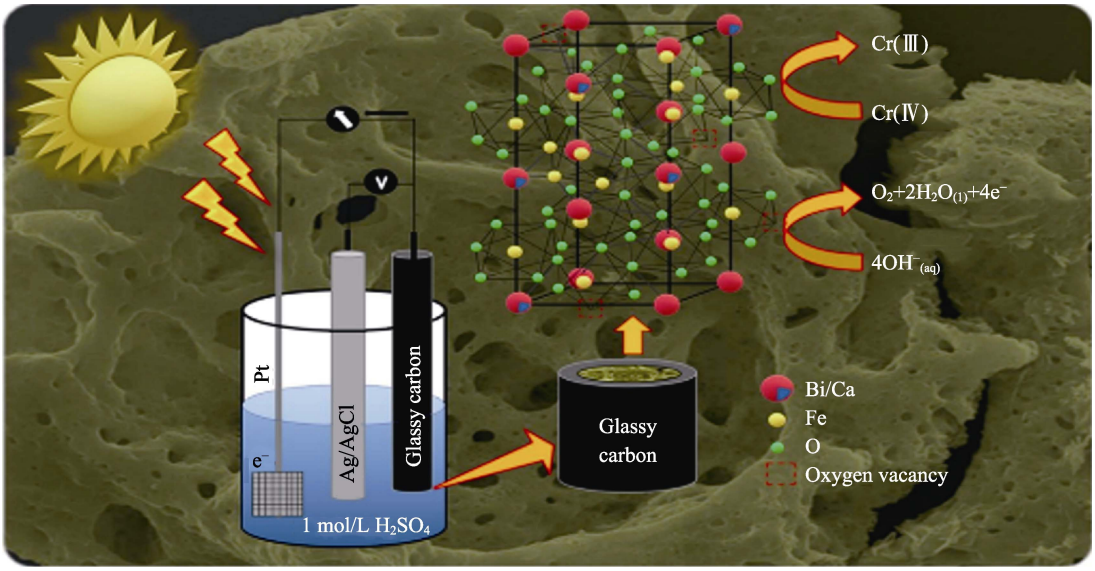

图 9　$Bi_{0.85}Ca_{0.15}FeO_3$ 的光催化机理图[115]

Fig. 9　Photocatalytic mechanism diagram of $Bi_{0.85}Ca_{0.15}FeO_3$[115]

钙钛矿型光催化剂可通过对 A、B 和 X 位进行掺杂，使得晶格结构畸变，降低带隙，进而提高催化剂的光催化活性[120]。ZHANG 等[121]制备了 $CaTi_{1-x}Mn_xO_{3-\delta}$ 用于光催化还原 NO。结果表明，TiO_2 组分可与矿渣中的碱土金属形成钙钛矿结构，导致其具有较强光响应能力，该催化剂在光辅助 NH_3 的选择性催化还原（NH_3-SCR）中 NO 去除效率达 93%以上。

将两种钙钛矿型光催化剂复合或与其他半导体材料形成异质结也可以促进光生载流子的迁移，进而提高光催化活性[122]。LI 等[123]制备碳量子点（CQDs）/$SmFeO_3$/凹凸棒石黏土（ATP）复合材料。结果表明，该材料在太阳光下实现了 NO 的高效降解，催化活性的增强归因于 *Z* 型异质结促进光生电子和空穴的分离（图 10）。

3.5　土壤中有机物及重金属去除

随着中国农业化进程加快，农药、化肥施用量的增加及污水灌溉等造成土壤有机物和重金属污染问题[124]。多环芳烃类有机物和重金属是土壤中主要存在的污染物，其具有毒性大、可富集、难治理、易转化和难降解的特点[125]。土壤是承载有机污染物及重金属的重要介质，而光催化和光芬顿技术能将土壤中难降解有机污染物矿化[126]。广泛使用的 TiO_2 光催化剂粉末在土壤中易聚集，易被雨水冲刷流失，另外其具有较大的禁带宽度和高载流子复合率，同时，还原产物容易吸附在 TiO_2 的表面，堵塞活性中心，从而导致催化剂失活[127-128]。

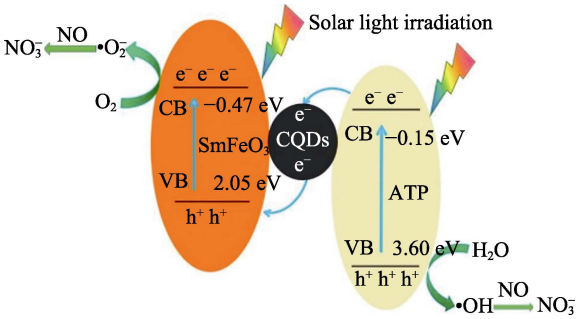

图 10　CQDs/$SmFeO_3$/ATP 作为催化剂光催化降解 NO 的机理[123]

Fig. 10　Mechanism of photocatalytic NO degradation using CQDs/$SmFeO_3$/ATP as catalyst[123]

钙钛矿型光催化剂具有强氧化还原能力和可直接利用太阳能的潜力，在修复土壤中有机物和重金属污染方面具有广阔应用前景。ARMAN 等[129]制备 $La_{0.85}Ce_{0.15}FeO_3$ 光催化降解土壤中的 Pb^{2+}。结果表明，该材料对 Pb^{2+} 的去除率达 99%且易于回收利用。HERNÁNDEZ-MORENO 等[130]制备 WO_3/$NaNbO_3$ 降解 2,4-二氯苯氧基乙酸除草剂。结果表明，该材料表现出低禁带宽度、低载流子复合率、比纯 WO_3 和 $NaNbO_3$ 更高的光催化活性，其催化机理见图 11。

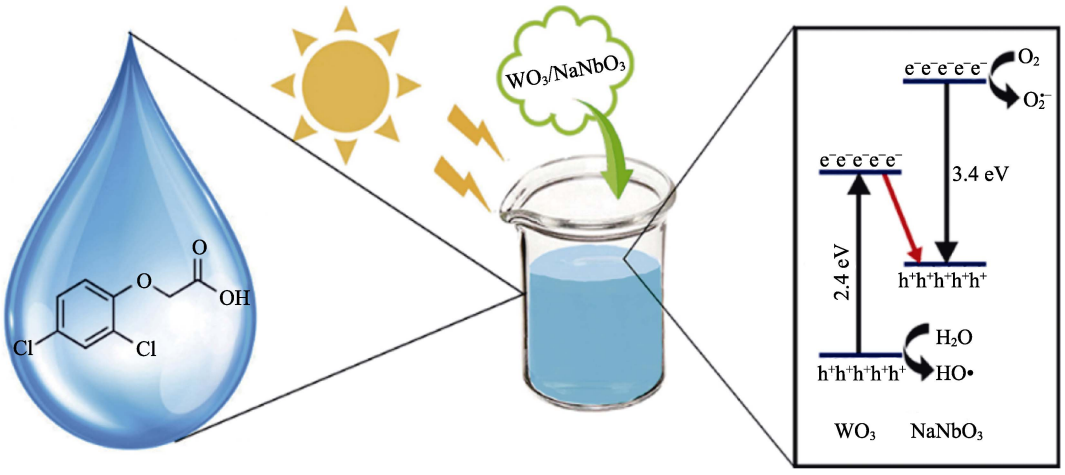

图 11　$WO_3/NaNbO_3$ 催化机理图[130]

Fig. 11　Diagram of catalytic mechanism of $WO_3/NaNbO_3$[130]

4　结束语与展望

大量钙钛矿材料已被用作光催化剂。钙钛矿丰富的空间结构为独特性能材料的产生提供了可能，从而产生了一系列具有独特性能的材料体系。本文总结了钙钛矿型光催化剂的活性影响因素、新型钙钛矿光催化材料的发展现状以及钙钛矿材料在光催化领域的应用现状。钙钛矿型光催化剂具有结构稳定，组成多样等优点，但目前研究还停留在实验室水平，面临诸多挑战。

（1）钙钛矿型光催化剂可通过溶胶-凝胶法、化学共沉淀法、水热法和固相反应法等制备而成，但其单独使用仍然存在比表面积小和颗粒聚集等问题，进而限制其应用。将几种制备工艺联合使用是未来的发展方向，并且研究者应着力于开发新的制备工艺。

（2）纯相钙钛矿型光催化剂面临巨大挑战，提高稳定性和可回收性是开发新型钙钛矿光催化剂的重点，研究钙钛矿在不同载体上的催化活性是值得关注的课题。

（3）钙钛矿型光催化剂在水、气和土壤中有机物及重金属去除等方面有了广泛应用，但大多集中在实验室水平。因此，应在未来的研究中建立现场验证的操作程序,以减轻光催化剂在实际应用中受到的影响。

基于此，作者认为，在今后的研究中，可从以下 3 点开展：首先是新型制备方法的开发，目前的钙钛矿制备方法多需要高温煅烧且产物存在聚集程度高等问题，所以开发节能绿色的制备方法是实现钙钛矿光催化材料工业应用的关键；其次是新型钙钛矿材料的开发，其中复合型钙钛矿材料将成为研究重点。然而，目前国内外研究者开发的新型催化剂往往具有稳定性差的问题，作者认为针对这个问题需要开发新型复合方法和新型高比表面积基体材料；最后，目前仍缺少针对钙钛矿型光催化剂特性的新型反应器，这也是限制该材料在工业中大规模应用的主要问题之一。无论如何钙钛矿型光催化剂仍具有极大的应用潜力，值得国内外研究者们继续关注。

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