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压电效应在过硫酸盐高级氧化技术中的应用与展望

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摘要 基于过硫酸盐氧化的高级氧化技术(persulfate-based advanced oxidation processes, PS-AOPs), 作为一类新型高级氧化技术, 被广泛应用于去除水中难降解有机污染物. 然而, 过硫酸盐氧化技术需要一个活化过程, 而目前的主流活化方法(如紫外活化、微波活化、热活化和过渡金属离子活化)需要大量的能耗或物耗. 近年来, 基于压电效应, 研究人员利用介电材料其固有的压电特性, 可以实现将机械能转化为化学能, 并成功应用于过硫酸盐活化过程中. 该活化方法具备利用自然界中绿色可再生机械力, 包括风、潮汐、水流等潜力, 是一类新型绿色、清洁的过硫酸盐活化技术. 本文围绕这一技术, 深入总结了压电/PS-AOPs这一新兴技术的基本原理、催化剂调控、机械力来源与潜在应用场景, 为推动这类新技术在水处理中的进一步应用提供理论和技术支撑.

关键词 过硫酸盐氧化, 压电效应, 压电活化, 水处理, 有机污染物

随着化工产品在农业、畜牧业、医药行业等行业的大量使用, 各种难降解有机污染物大量流入水环境中, 对人类健康和生态安全构成了极大的威胁[1]. 高级氧化技术(AOPs), 能够产生强氧化性的自由基物种, 快速将有机污染物降解成低毒性的小分子或者CO_2和H_2O[2~4], 被作为去除水中有机污染物的有效手段之一. 近年来, 基于过硫酸盐高级氧化技术(PS-AOPs), 由于其众多优势而备受关注[5~8]. 与传统的芬顿技术相比, PS-AOPs具备: (1) 较低的运输成本及安全风险; (2) 丰富多样的活化方法; (3) 对pH和环境介质等操作参数的依赖性较小; (4) 更高的氧化电位($E^0(SO_4^{\bullet-}/SO_4^{2-})=+(2.60-3.10)V_{NHE}>E^0(HO^\bullet/OH^-)=+(1.90-2.70)V_{NHE}$). PS在AOPs中的使用可以追溯到21世纪初, Dionysiou团队[5]于2003年首次发现了钴离子可高效活化过一硫酸盐, 去除有机污染物. 在PS-AOPs过程中, 主要是通过活化过硫酸盐(过一硫酸盐, PMS; 过二硫酸盐, PDS)的过氧键, 形成强氧化性的硫酸根自由基并引发其他链式反应, 氧化难降解有机污染物. 然而, 现有的PS活化方法(如紫外线(UV)、微波、热和过渡金属活化等)需要大量的能耗或物耗, 严重限制了PS-AOPs的实际应用[9]. 因此, 我们需要寻求一类绿色环保且具备低耗高效的PS活化技术, 以高效去除水中的难降解有机污染物.

压电效应是指非中心对称的介电材料在受到机械应力或压力时表现出内部极化, 进而在其表面产生极化电荷的现象[10~12]. 压电效应源于晶体结构的各向异性, 当压电材料受到外部应力或应变作用时, 促使晶格内的原子发生位移, 这会导致阳离子和阴离子中心的位置不匹配, 从而产生本征偶极矩. 这些偶极矩在晶胞内的有序叠加会产生宏观的极化电场, 通常称为压电势. 该压电势由固定且非湮灭的离子电荷产生, 这些丰富的束缚电荷可以有效催化各种反应, 包括能源转换

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和废水净化等[13~15]. 自2020年朱明山团队率先利用钛酸钡作为压电催化剂, 在超声应力作用下其表面的压电电荷可以实现PMS中的O–O键活化, 实现PS的活化过程[16], 各种压电材料和压电方式被研究人员开发出并应用于PS-AOPs中, 在污染物降解[9,17~52]、废水资源化利用[53~58]、水源杀菌消毒[59~62]等领域形成一类新兴的研究热点. 除此之外, 压电效应以其独特的内在特征, 即具备将环境机械能(如风、潮汐、水流、声音和大气力)转化为化学能, 一类新型的绿色环保且低耗高效的PS活化方法.

本综述围绕压电效应在PS-AOPs中的应用为研究背景, 详细阐述了压电/PS-AOPs的基本原理、压电材料分类及其调控、机械力来源和潜在应用场景. 随后, 评估了该新兴高级氧化技术作为发展新一代水处理技术的应用潜力, 并进一步对该技术的未来发展轨迹提出展望, 从而为推动水污染控制化学其减污降碳协同增效这一目标的发展提供理论和技术支撑.

1 压电/PS-AOPs的概述

压电/PS-AOPs作为一类新兴的高级氧化技术, 本文从基本原理、压电材料及其改性的方法、机械力的来源和应用场景等方面进行全面的概述.

1.1 基本原理

压电/PS-AOPs的核心在于PS分子的活化. PS的活化通常遵循两种不同的反应途径: 自由基途径和非自由基途径[7,63~65]. 本质上, PS(包括PMS和PDS)活化涉及电子的获得或损失, 通过相应的还原或氧化反应导致各种活性物种的产生. 而压电材料在受到机械应力或压力时会导致材料内部极化, 进而在其表面产生极化电荷. 这些丰富的束缚电荷可以被用来有效地活化PS[11,13,14,66]. 如图1所示, 压电材料受外力激发产生局部电荷, 通过电子转移反应可以实现PS过氧化物键的断裂, 从而产生多种活性物质, 包括主要活性物种($HO^{\bullet}$和$SO_4^{\bullet-}$)和次要活性物种($O_2^{\bullet-}$、$^1O_2$和e^-). 这些活性物种具有杰出的氧化能力, 可以有效去除废水中的有机污染物[67~69].

如前所述, 压电材料通过压电效应产生的局部电荷在活化PMS和PDS中的O–O键时发挥着关键作用. 具体来说, 当压电材料受到外部机械力或应变时会引起晶格内原子的位移, 从而导致阳离子和阴离子中心的位置不匹配. 这种原子位置的位移会诱导偶极矩的产生, 当偶极矩有序叠加时就可以产生宏观的极化电场. 压电极化电荷形成的电场可以促进PS激活, 并且这种电场还可以在外力作用下驱动极化电子(e^-)和空穴(h^+)对向相反的方向迁移(式(1)). 电子倾向于与HSO_5^-反应生成$HO^{\bullet}$(式(2))和$SO_4^{\bullet-}$(式(3)); 或者与$S_2O_8^{2-}$反应生成$SO_4^{\bullet-}$(式(4)). 同时, 空穴与HSO_5^-反应生成$SO_5^{\bullet-}$(式(5)); 两分子的$SO_5^{\bullet-}$可以形成一分子$^1O_2$和一分子$SO_4^{\bullet-}$(式(6)). 另一方面, 少量的压电电荷还可以与水分子反应生成少量的$HO^{\bullet}$(式(7))、与氧气反应生成$O_2^{\bullet-}$(式(8)). 以上过程产生的$O_2^{\bullet-}$还可以与$HO^{\bullet}$反应生成$^1O_2$(式(9)). 具体的反应方程式如下:

$$\text{压电材料} + \text{机械力} / \text{应变} \rightarrow e^- + h^+ \quad (1)$$

$$HSO_5^- + e^- \rightarrow HO^{\bullet} + SO_4^{2-} \quad (2)$$

$$HSO_5^- + e^- \rightarrow OH^- + SO_4^{\bullet-} \quad (3)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (4)$$

$$HSO_5^- + h^+ \rightarrow H^+ + SO_5^{\bullet-} \quad (5)$$

$$2SO_5^{\bullet-} \rightarrow {}^1O_2 + 2SO_4^{\bullet-} \quad (6)$$

$$H_2O + h^+ \rightarrow H^+ + HO^{\bullet} \quad (7)$$

$$O_2 + e^- \rightarrow O_2^{\bullet-} \quad (8)$$

$$O_2^{\bullet-} + HO^{\bullet} \rightarrow OH^- + {}^1O_2 \quad (9)$$

近年来, 压电/PS-AOPs在废水处理及环境修复中

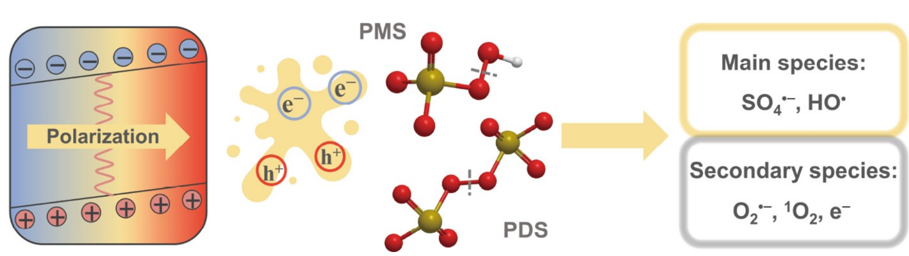

图 1 (网络版彩色)压电/PS-AOPs的基本原理示意图
Figure 1 (Color online) The diagram of the mechanism for piezoelectric PS-AOPs

的应用引发了研究人员越来越多的关注，相关的研究也呈现出逐年增长的趋势(图2)[9,16,18,61,70]．例如，夏德华团队[24]采用水热法合成了$BaTiO_3$纳米颗粒和纳米线并将其用作压电催化剂激活PS以产生活性物种用于降解布洛芬(IBP)．结果显示在超声作用下，$BaTiO_3$纳米线/PS体系表现出比$BaTiO_3$纳米颗粒/PS更快速的IBP降解速率．王文辉课题组[25]合成了一种新型压电催化剂$Bi_2Fe_4O_9$纳米片, 该催化剂被证明可以通过压电催化显著提高PDS的活化效率, 其优越的催化性能得益于作为活性位点的Fe^{2+}为PDS捐赠电子以生成活性物种，同时压电电子又可以加速Fe^{2+}的再生. 朱明山课题组[32]使用双刷型结构的ZnO介观晶体(TB-ZnO)作为压电材料, 在超声作用下活化PMS降解IBP. 结果表明，TB-ZnO中氧空位和有序介孔结构的存在促进了电子转移，降低了反应势垒, 从而促进了PMS的有效活化以降解IBP.

1.2　压电材料及其改性

目前，已有多种压电材料被证明可用于PS的压电激活(图3)．$BaTiO_3$作为研究最广泛的催化剂[16,18,19,24,26,30,33,34,39,43,44,59]，于2020年首次成功在超声作用下成功实现压电活化PS降解苯并噻唑，为后续压电/PS-AOPs的大量研究奠定了基础[16]．此外，其他压电材料也被报道用于PS活化，如ZnO[29,32,35,60,70]、MoS_2[20,21,23,31,37,38,45,47,55,57,58]、$BiVO_4$[42]、$Bi_2Fe_4O_9$[25,41]、$SrBi_2B_2O_7$[28,36]、氮化碳[27,40]和层状双氢氧化物[22]等.

然而，当前的压电催化剂仍然存在机械能收集能力弱、表面积小和电子转移速率缓慢等缺点，因此其进一步的广泛应用仍然存在各种挑战．为了克服这些困难，通过材料改性或修饰用以提高压电激活PS的能力，如形貌调控[24]、贵金属负载[59]、单原子锚定[9]、元素掺杂[22,29,30,44,58]、缺陷工程[20,37,70]和杂化构建[18,55]等手段, 逐渐被研究人员开发出来. 这些调控方法可以优化催化剂的结构和性质，从而提高其在PS活化过程中的压电响应和催化活性．例如，夏德华团队[59]利用Ag掺杂的$BaTiO_3$用于压电活化PDS生成$SO_4^{\bullet-}$和$HO^{\bullet}$, 应用于高效去除大肠杆菌. 又如, 朱明山课题组[18]构建$BaTiO_3/MoS_2$压电异质结用于PMS的压电活化及抗生素奥硝唑(ORZ)的高效去除.

1.3　机械力的来源

压电材料产生的极化电场可以通过外部机械力来调控, 并驱动催化反应. 目前已经报道用于压电催化活化PS的外部机械力包括超声、搅拌和水流等．超声和搅拌是目前用于压电催化最主要的机械力来源，它们需要消耗从外界输入的能源, 比如电能. 超声属于高频机械力, 而搅拌属于低频的机械力. 水流则是自然界中微弱的机械力，用于压电催化时不需要其他外部能源的消耗, 能自给自足. 当微弱的机械力以有效的方式施加到压电材料上时就会导致材料晶格内原子的位移, 从而诱导偶极矩的产生．而当偶极矩有序叠加时就可以产生宏观的极化电场．在机械力持续不断的作用下, 极化电子(e^-)和空穴(h^+)对会向相反的方向迁移，在这个过程中PS可以得到或失去电子发生相应的氧化或还原反应从而被压电催化活化生成一系列活性物种．水流驱动力被报道成功用于引发压电催化反应，使得自然界中其他的弱机械力(例如风、潮汐、声音和大气力)被寄予厚望，在未来应用于压电催化活化PS，以实现环境净化(图4).

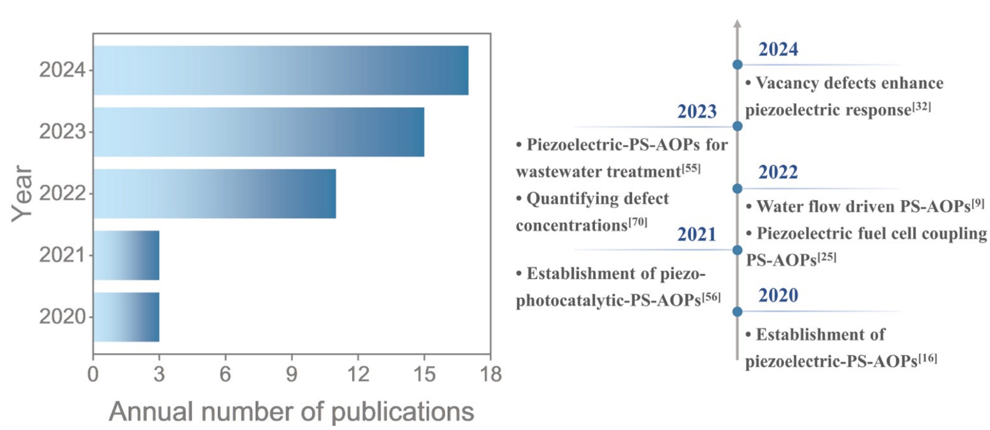

图 2　(网络版彩色)压电/PS-AOPs的出版物数量
Figure 2　(Color online) Number of publications on piezoelectric/PS-AOPs per year

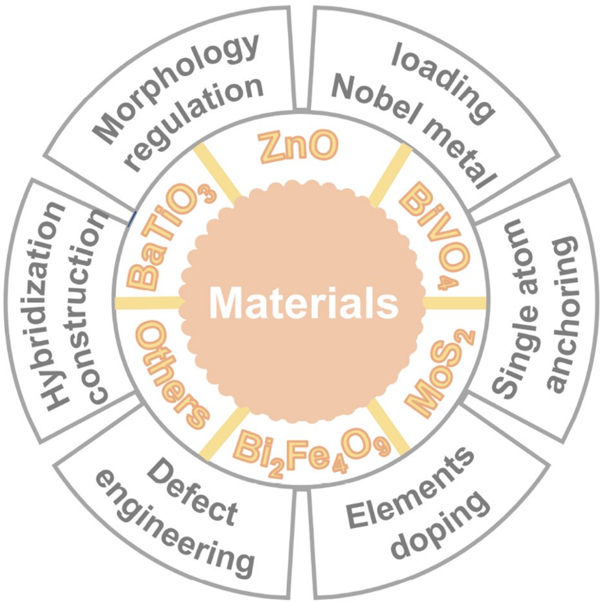

图 3 (网络版彩色)压电材料的分类及改性方法
Figure 3 (Color online) Classification and modification methods of piezoelectric materials

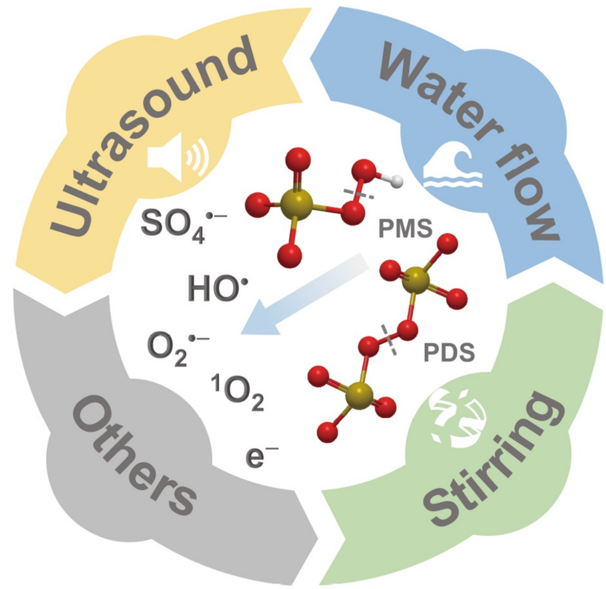

图 4 (网络版彩色)压电激活PS的机械力来源
Figure 4 (Color online) The source of mechanical force for piezo-electrically activated PS

超声相较来说是一种高频的机械力，是实验室中常用于压电激活PS的方式．它常常用于液体和材料的微观混合，并可施加引起空化气泡破裂的周期性力产生超声空化效应．这导致非均相催化剂与水界面处的压力可高达10^8 Pa，为电子激发提供了充足的能量[12]．例如，朱明山团队[70]利用含有不同氧空位(OVs)浓度的ZnO压电材料研究缺陷含量对水净化中PMS压电活化的影响．结果表明，具有中等OVs浓度的ZnO压电材料在超声作用下表现出较高的PMS利用率以及更快的ORZ污染物降解速率, 而过量的OVs反而会抑制材料的压电催化性能.

高频的超声应力在PS的压电活化过程中展现出优异的激活效果，然而环境中的大多数机械力属于低频机械力．近期，赵纯课题组[34]利用搅拌这一低频机械力, 通过碳纳米管(CNTs)与$BaTiO_3$的复合, 在磁力搅拌的作用下，CNTs/$BaTiO_3$可活化PMS降解卡马西平(CBZ). 其研究发现复合催化剂会增强压电响应和促进高效的压电电荷分离, 进而提高活性物质的产率. 除此之外，朱明山课题组最近的研究表明水流也可以作为机械力, 驱动压电材料产生压电电荷激活PS, 用于污染物去除[9,31]．研究发现，通过设计螺旋管道模拟管道排水, 以表面修饰Fe单原子的MoS_2为压电催化剂, 通过螺旋管道, 利用水流的重力和向心力作用, 引发压电效应产生表面电荷, 并利用其表面的Fe单原子活性位点，构筑成高效率压电/PS-AOPs体系, 实现水的快速净化. 这一发现为不依赖任何外部能量输入，仅利用自然界中的弱机械力来引发压电催化反应提供可能，并增强了其与可持续发展的兼容性. 因此, 未来应考虑利用环境中自然存在的弱机械力来引发压电催化反应.

1.4 应用场景

目前，压电/PS-AOPs的应用场景主要包括污染物降解和废水资源化利用(图5)．如前所述，压电材料在受到外部机械力时会产生压电效应, 该过程可以诱导局部电荷的产生从而激活PS, 产生活性物种用于降解有机污染物．例如，敖燕辉团队[29]利用钴掺杂的ZnO纳米片压电激活PS用于污染物左氧氟沙星(LVX)降解．结果表明钴掺杂后ZnO结构发生扭曲，其压电性能得到增强; 压电外场加速了表面电荷的转移, 显著提高了PS的活化和污染物的降解效率．此外，最近的研究表明压电效应产生的压电势可以激发长程有序的驱动力，从而促进光生电子-空穴对在材料表面和体相中的有效分离[11,71]. 此外, 银仁莉课题组[35]合成了α-$SnWO_4$/ZnO异质结催化剂, 该催化剂在压电光催化活化PMS过程中可以实现CBZ的高效去除．这一开创性的发现为利用压电光催化激活PS来降解污染物提供了一种扩展方法.

除此之外, 近期研究人员发现, 压电/PS-AOPs在降解有机污染物同时实现废水的资源化利用并转化为化

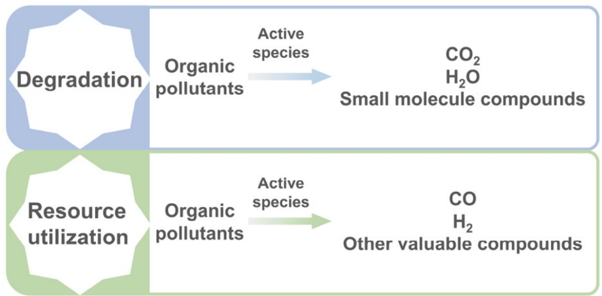

图 5 (网络版彩色)压电/PS-AOPs的应用场景
Figure 5 (Color online) Application scenarios of piezoelectric/PS-AOPs

工原料方面，显示出令人振奋的前景[55,72]. 例如，邢明阳课题组[72]通过建立MoS_2/Fe^0/PMS三元系统，并耦合压电催化和高级氧化过程，实现了各种废水中的有机污染物的高效去除和H_2的大量生成. 压电材料与PMS的结合在热力学上有利于MoS_2压电催化析氢，并解决了由于含有吸电子基团的有机污染物引起的电子损耗，从而抑制H_2产生所带来的挑战[72]，为燃料生产和同步实际废水的深度处理提供方法支撑. 此外，他们还合成了Co_3S_4/MoS_2催化剂[55]，利用Co_3S_4/MoS_2/PMS系统在实际复杂废水处理中实现了CO的选择性生成，凸显了其实际应用潜力. Co_3S_4的引入有效促进了压电电荷的分离、转移和利用，并显示出将碳酸盐高选择性转化成CO的能力. 这些突破性的发现标志着压电/AOPs在实现高效环境修复和可持续发展的战略方面取得了重大进展.

2 压电/PS-AOPs展望: 从机遇到挑战

压电催化已成为一种极具前景的PS活化方法，在环境修复和废水资源利用方面展现出巨大潜力. 由于压电/PS-AOPs能有效将水环境中的难降解有机污染物分解为CO_2和H_2O，或者转化为低毒性的小分子，因此压电催化有望作为AOPs工艺的处理单元之一，成为未来水污染控制工艺的重要组成部分.

压电/PS-AOPs的独特之处在于其能够利用自然界中存在的微弱机械力，包括风、潮汐、水流、声音和大气力，使其与传统的能源和资源密集型PS活化方法有所区别，从而有望成为AOPs领域的变革性力量. 然而，目前压电PS-AOPs仍处于早期发展阶段，许多潜在的反应机制和激活模式仍然不完善. 为了推动压电/PS-AOPs的发展, 未来需要在以下几个方面付出努力.

(1) 开发更高效的压电材料用于PS活化. 将研究范围扩展到除了$BaTiO_3$、MoS_2和ZnO之外的材料，并延伸到其他具有固有不对称性结构的二维(2D)材料. 探索这些具有固有不对称性结构的新材料在PS压电激活中的应用具有广阔的前景，有望发现能够改善压电响应和催化活性的新型催化剂.

(2) 优化压电/PS-AOPs的外力. 目前的压电催化反应主要依赖超声波作为外力. 然而，压电催化反应的激活机制涉及多种效应的耦合，包括压电效应、超声空化作用、挠曲电效应、接触电催化效应和能带理论机制. 因此，阐明各种效应之间的不同作用及其影响变得具有挑战性. 利用搅拌、水流等外力来活化PS的方法也面临同样的挑战. 因此，探索有效施加压电外力的创新方法至关重要，因为它有望揭示压电催化错综复杂的反应机理.

(3) 压电/PS-AOPs中活性物种的调控. PS-AOPs涉及多种活性物种的生成，包括自由基($HO^•$、$SO_4^{•-}$和$O_2^{•-}$)和非自由基($^1O_2$和e^-). 自由基物种展现出相对稳定的反应活性，缺乏明显的选择性; 而非自由基物质则能提供可控的反应强度和一定的反应选择性. 材料的分子设计有望精确控制活性物种的生成. 这为未来指导反应路径以获得所需的活性产物，从而提高压电催化活化PS的选择性和效率，以应对实际水体中复杂的有机污染物提供了希望.

(4) 对压电/PS-AOPs机理的探索. 目前压电催化反应还是一个比较新兴的领域，其激活机制涉及多种效应的耦合，而PS-AOPs又涉及多种活性物种的生成. 因此，在压电活化PS产生各种活性物种用于催化反应的过程中，阐明各种效应之间的不同作用及其影响变得具有挑战性，从而阻碍了对压电催化的内在机制的全面理解. 对压电/PS-AOPs机理的探索仍是将来研究的重点方向.

(5) 扩展压电/PS-AOPs的实际应用. 由于传统的活化方法存在高能耗和多种污染物的共存的问题，实际水体中有机污染物的降解仍然面临挑战. 水流自驱动力的成功应用为污水处理提供了巨大的潜力，预示着该技术在未来城市管道排水中具有广阔的应用前景.

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Summary for “压电效应在过硫酸盐高级氧化技术中的应用与展望”

The prospect of piezoelectric effect in persulfate-based advanced oxidation processes

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Compared to traditional Fenton technology, persulfate-based advanced oxidation processes (PS-AOPs) represent an emerging method for eliminating organic pollutants in water. However, the existing PS activation methods, such as ultraviolet (UV), microwave, heat, and transition metal activation, require large energy consumption or continuous chemical reagent input, limiting the practical application of PS-AOPs. Piezoelectric activation of PS involves using the piezoelectric effect of materials to initiate PS and generate a variety of active species. The piezoelectric effect refers to the phenomenon that non-centrosymmetric crystal materials display polarization when subjected to a mechanical stress or pressure. This interaction enables the effective conversion of environmental mechanical energy, such as wind, tides, water flow, sound, and atmospheric forces, into electrical energy. It has been reported that the local charges generated by the piezoelectric effect of the material assist in breaking O–O bond in PS, thereby facilitating PS activation.

In this review, we primarily discuss the application of the piezoelectric effect of materials in PS-AOPs, elucidating the significant potential of piezoelectric/PS-AOPs and emphasizing their broad prospects as integral components of AOPs. Firstly, we summarize the basic principle of piezoelectric/PS-AOPs. Specifically, when piezoelectric material is excited by an external force, it generates a local charge, leading to the breaking of O–O bond in PS through an electron transfer reaction. This process results in the formation of various active substances (such as $HO^{\bullet}$, $SO_4^{\bullet-}$) for pollutant removal. Next, we introduce common piezoelectric materials and their modification methods. $BaTiO_3$ stands out as the most extensively studied piezoelectric catalyst, while other materials like ZnO, MoS_2, and $BiVO_4$, have emerged as viable competitors for piezoelectric activation of PS. Modified technologies such as morphology control, noble metal loading, single atom anchoring, element doping, defect engineering, and hybrid construction can optimize the structure and properties of the catalyst, thereby enhancing its piezoelectric response and catalytic activity during PS activation. In addition, we also explore the mechanical force sources and potential application scenarios of piezoelectric/PS-AOPs. Currently, the external forces have been used into piezoelectric catalytic activation of PS including ultrasonic, stirring and water flow. The application scenarios of piezoelectric/PS-AOPs mainly involve pollutant degradation and wastewater resource utilization. Lastly, we discuss the prospects of piezoelectric/PS-AOPs, including their potential application in urban pipeline drainage systems in the future.

In summary, piezo-catalysis has emerged as a promising method for PS activation, holding great potential for environmental remediation and wastewater resource utilization. Unlike traditional energy-intensive PS activation methods, this technology harnesses weak mechanical forces existing in nature, making it a transformative force in the field of AOPs. Through this review, we aim to offer valuable suggestions for the more efficient application of piezoelectric/PS-AOPs in wastewater treatment and environmental remediation, thereby promoting the advancement of this emerging field.

persulfate, piezoelectric effect, piezoelectric activation, water treatment, organic pollutants

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