

电晕极化对钛酸钡粉体压电光催化性能的影响

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摘 要: 采用溶胶-胶法制备钛酸钡(BaTiO_3 , BT)粉体, 通过改变保温时间(2、5、12 h)获得了不同粒径尺寸的 BT 纳米颗粒。将 BT 纳米粉体在 6.56 kV 电压下分别进行 1 h 电晕极化, 探究极化前后晶格的畸变程度以及粉体的压电光催化性能。结果表明: 随保温时间延长, 颗粒粒径尺寸增大, 极化后晶体的晶格畸变程度增强, 四方度提高。同时, 极化使得 3 组粉体对染料的降解速率大幅提升, 动力学速率常数分别为极化前的 4.94、2.21、1.62 倍, 与晶格畸变程度呈现相同规律。其中, 保温 2 h 的粉体电晕极化后对有机染料罗丹明 B(RhB)的降解率在 180 min 内达到 96.81%, 具有最优的压电光催化性能, 这为电晕极化在粉体催化领域的应用提供了实验参考。

关键词: 钛酸钡; 压电光催化; 电晕极化; 罗丹明 B

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纺织、皮革、食品、印刷等行业含有机染料废水的排放加剧了环境污染与健康问题^[1-2]。与采用物理吸附、化学或者生物处理技术降解染料相比^[3-5], 半导体催化剂可将可再生能源太阳能转化为化学能, 为解决环境污染问题与能源危机提供了有效途径。然而, 光生电子和空穴的高复合率阻碍了光催化速率^[6], 新型催化剂及催化技术亟待开发^[7]。于是, BaTiO_3 、 LiNbO_3 、 KNaNbO_3 等铁电陶瓷作为一类新型催化剂引起了广泛关注^[8-10], 因为铁电体自发极化产生的内建电场可增强光生载流子分离的驱动力, 从而降低载流子复合率^[11]。而铁电体内建电场可通过施加外部电场进行极化得到增强^[12], 为提升电荷分离效率提供了新思路。

通常, 铁电陶瓷块材的极化需要电极以及绝缘液体^[13], 一般在硅油浴中极化后研磨至粉体作为催化剂使用, 但这种传统极化方式会带来附加的机械应力, 导致剩余极化减小^[14]。为简化并优化极化工艺, 用于薄膜和聚合物的电晕极化技术开始被用于粉体极化领域^[15], 它可以通过施加在尖端电极与放置样品的底电极之间的高场来使铁电畴结构改变。Rahul 等^[16]采用固相反应法合

成了 $0.5\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3-0.5\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ 铁电陶瓷, 发现极化后其在压电催化、光催化、压电光催化条件下速率常数分别为极化前的 1.4 倍、2.4 倍和 1.9 倍, 表明了电晕极化在催化领域应用的必要性与广泛性。Wen 等^[17]利用铁电体铌酸钾(TKN)粉体与反铁电体铌酸钠(ONN)粉体探究极化对晶体晶格参数产生的影响, 发现极化过程中 TKN 样品由四方相趋于立方相, 最后又趋于四方相, ONN 样品由正交相向四方相演化, 且极化后铌酸盐晶体光催化活性得到明显提高, 证明极化可以引起晶体晶格畸变, 也可以改变材料的铁电性及催化性能。Cheng 等^[12]将 BiFeO_3 纳米颗粒在不同电压下进行极化处理, 发现极化电压越高, 颗粒对甲基橙(MO)染料的降解率越高, 5.75 kV 电压极化后粉体的催化速率常数为 $0.006\ 84\ \text{min}^{-1}$, 是未经极化处理样品的 5.1 倍。电晕极化对不同铁电陶瓷粉体催化性能的促进作用被不断验证, 但相同极化条件下颗粒尺寸对极化的响应程度却鲜有研究提及。明确颗粒尺寸对极化的影响可使粉体极化更具目的性与可控性, 这有助于设计高催化性能的新材料或者新体系。

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利用溶胶–凝胶法在 800 °C 通过控制保温时间获得了不同尺寸的钛酸钡(BaTiO_3 , BT)纳米颗粒, 在 6.56 kV 电压下分别对粉体进行 1 h 电晕极化, 利用 X 射线衍射(XRD)以及扫描电子显微镜(SEM)观察粉体的物相结构以及微观形貌, 探究极化后不同尺寸颗粒的晶格畸变程度, 同时利用粉体对有机染料罗丹明 B (RhB)的降解速率来评估不同尺寸颗粒的催化性能。

1 实验

1.1 样品制备

以醋酸钡($\text{C}_4\text{H}_6\text{O}_4\text{Ba}$, 质量分数为 99%)、钛酸四丁酯($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, 质量分数 $\geq 98.5\%$)、为原料, 利用溶胶–凝胶法制备 BT 陶瓷粉体。按照化学计量比量取钛酸四丁酯加入适量乙醇及冰醋酸的混合液中搅拌 30 min 使其混合均匀, 另称取醋酸钡加入适量乙酸中搅拌 40 min 使其完全溶解, 将 2 份溶液混合搅拌至淡黄色透明状态, 静置 16 h, 放进干燥箱中烘干后用研钵研磨 30 min, 得到干凝胶。分别取适量干凝胶于马弗炉中, 依次在 800 °C 保温 2、5、12 h, 研磨后得到 BT 粉体(分别简称为 2、5、12 h)。搭建粉末极化装置^[12], 在 6.56 kV 电压下分别对不同粉体极化 1 h, 得到极化后的催化剂粉体。

1.2 样品表征

使用日本 Rigaku 公司生产的 SmartLab 型 X 射线衍射仪(XRD, K_α , $\lambda = 1.54182 \text{ \AA}$)分析陶瓷粉体的晶体结构。使用英国雷尼绍公司 InVia Reflex 型激光显微 Raman 光谱仪测量室温 Raman 光谱(激发波长 633 nm)。使用 Helios G4 UC 型场发射扫描电子显微镜仪器观察陶瓷颗粒的表面形貌。使用 Mapada UV-6300 型紫外可见分光光度计测量材料可见光波段的吸收谱。

以 10 mg/L 的 RhB 溶液降解情况评估 3 组 BT 粉体极化前后的光催化性能。称取 25 mg 罗丹明 B 粉末加水至 250 mL, 稀释 10 倍得到 10 mg/L 待降解染料水溶液。进行光催化反应前, 将 50 mg 催化剂在黑暗条件下投入 50 mL 罗丹明 B 水溶液中并磁力搅拌 30 min, 达到吸附–脱附平衡, 以此时溶液浓度为初始浓度。选用 300 W 氙灯作为光源模拟太阳光照射, 反应液面距离氙灯光源 7 cm, 利用超声波清洗机(35 kHz, 100 W)协助完成压电光催化反应, 每隔 30 min 从反应溶液里取约 5 mL 溶液并进行离心, 取离心后上层清液 3 mL 注入比色皿中, 通过紫外可见分光光度计测量吸收谱评估催化效果。

2 结果与讨论

2.1 物相分析

图 1 为 BT 陶瓷室温下的 XRD 谱以及 Raman 数据。由图 1a 可以看出, 陶瓷样品都呈现典型的钙钛矿结构^[18], 同时观察到不同样品 45°附近(200)衍射峰(图 1b)呈现不同程度劈裂现象, 这是四方相存在的特征^[19–20], 表明 3 组粉体中立方相与四方相共存^[21]。图 1c 展示了 2 h 粉体极化前后的 Raman 光谱, 立方相理论上不存在任何 Raman 活性模式, 图中显示在 261、305、520、717 cm^{-1} 处出现 Raman 峰, 分别对应 $[A_1(\text{TO})]$ 、 $[B_1, E(\text{TO}+\text{LO})]$ 、 $[A_1, E(\text{TO})]$ 和 $[A_1, E(\text{LO})]$ 振动模式^[22–23], 这也表明了四方相的存在, 且观察到极化并没有引起 Raman 振动模式的变化。

为进一步探究极化对粉体晶胞参数的影响, 利用 01-085-9533 立方相(C)和 01-085-9532 四方相(T)对 XRD 谱进行 Rietveld 全谱拟合。由图 1d~图 1f 可见测试值、拟合曲线、两者差值以及两相衍射峰位置, 拟合得到的结构参数及相比比例见表 1, 误差因子 R_{wp} 在 5.34%~6.75%之间, 均小于 10%, 测试值与拟合曲线比较吻合, 表明精修结构模型有效。由图 1g 可见, 在进行电晕极化前, 2、5、12 h 粉体四方相比比例分别为 60.5%、65.8%、72.7%, c_T/a_T 值分别为 1.00785、1.00800、1.00910, 随着保温时间延长, 粉体四方相比比例提升, c_T/a_T 值增大, 说明四方度变高^[24]。极化后, 3 种粉体四方相比比例分别为 71.6%、70.6%、75.2%, c_T/a_T 值分别为 1.00889、1.00844、1.00932, 与极化前相比, 四方相比比例提升, c_T/a_T 值增大, 表明 3 组粉体经过极化处理后四方性增强, 即极化进一步增加了晶格畸变程度。3 组粉体极化前后四方相比比例分别增加了 11.1%、4.8%、2.5%, 且随保温时间延长, $\Delta(c_T/a_T)$ 值也呈现逐渐减小的趋势。以上结果表明, 在相同极化条件下, 2 h 粉体 $\Delta(c_T/a_T)$ 值最高, 极化引起的晶格畸变程度最深。也有研究表明, 晶体结构中 c/a 值与铁电性成正比^[25], 铁电性变化的差异也预示着内建电场强度变化的高低, 进而对催化性能产生影响。

2.2 微观结构分析

颗粒尺寸也是影响催化性能的关键因素^[26], 因此需要通过结合粉体微观结构分析影响 BT 粉体催化活性的因素。图 2 为 3 组不同保温时间陶瓷颗粒的表面形貌以及相应陶瓷样品的粒径分布图。由图 2 可以看出: 保温 2 h 烧结陶瓷粉体颗粒尺寸主要分布在 50~80 nm 之间; 保温 5 h 烧结粉体粒径尺寸分布

主要在 80~140 nm; 而保温 12 h 烧结粉体粒径集中在 120~150 nm 之间; 随着保温时间延长, BT 陶瓷颗粒

尺寸逐渐增大。与其它 2 种粉体相比, 保温 12 h 烧结的 BT 陶瓷颗粒尺寸趋于均匀, 且无明显团聚。

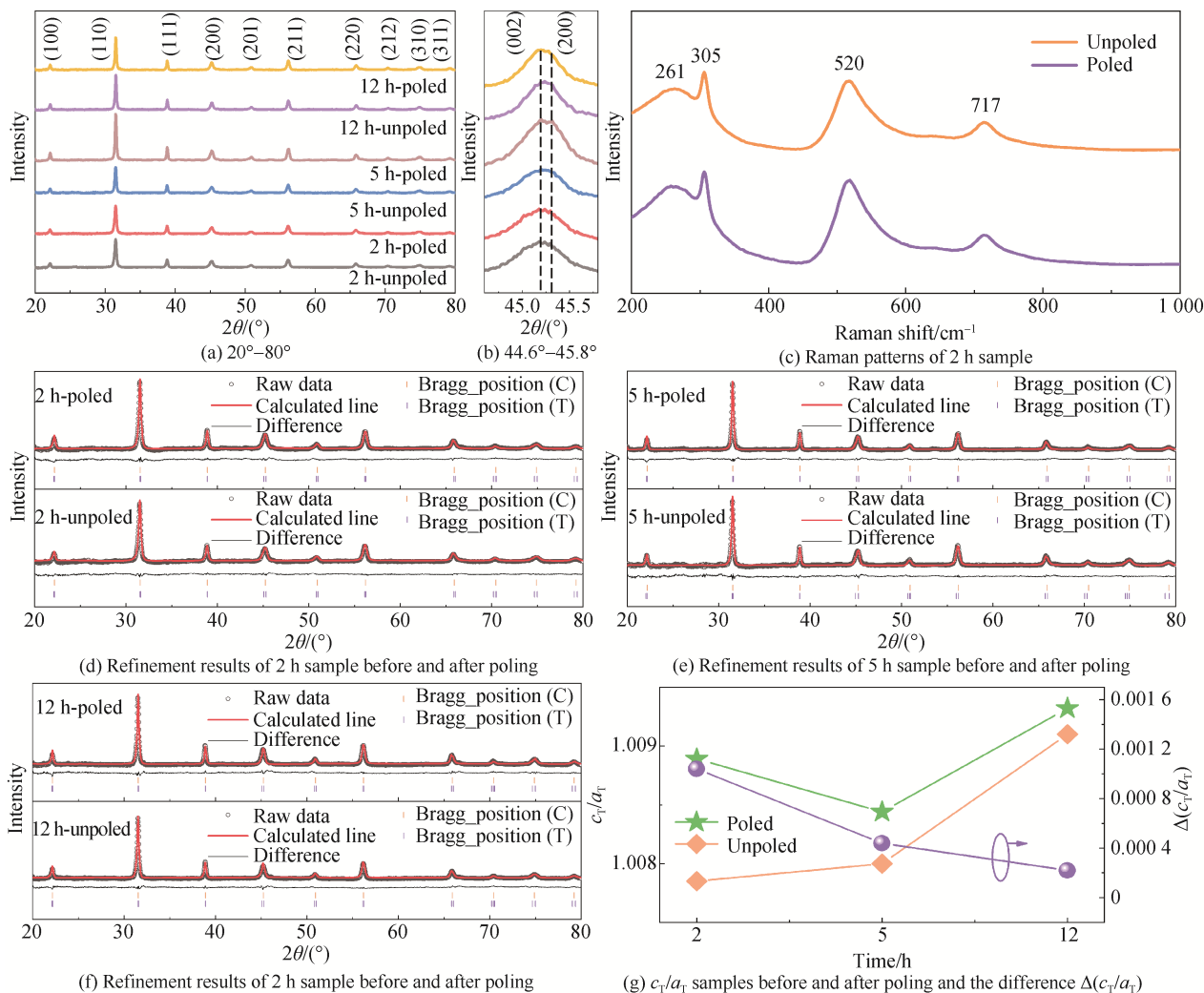


图 1 BT 陶瓷室温下的 XRD 谱以及 Raman 数据

Fig. 1 XRD and Raman patterns of BT ceramics at room temperature

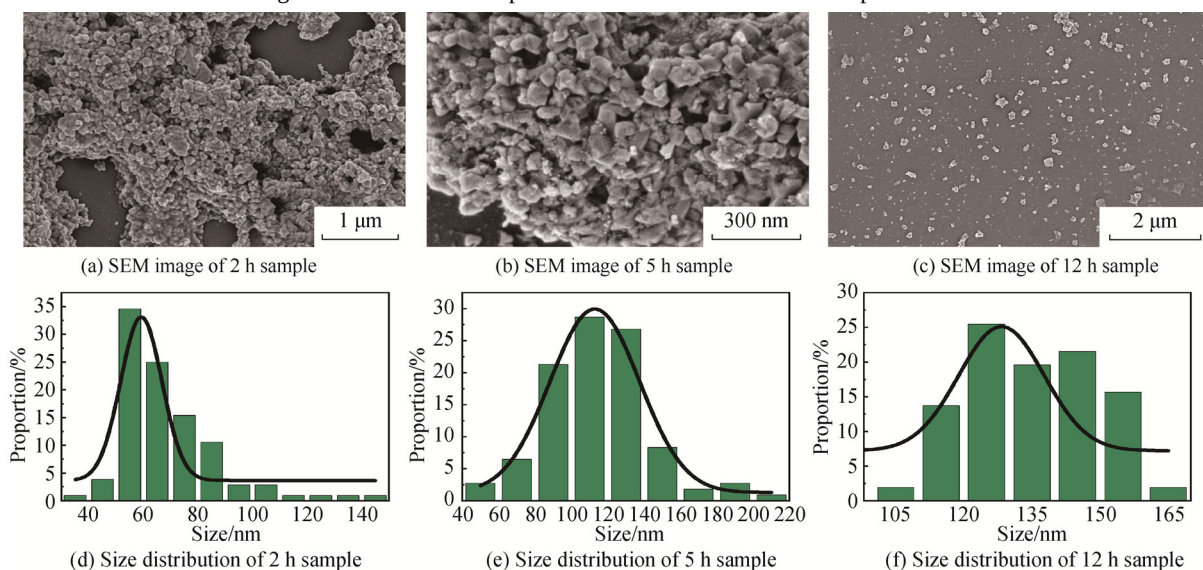


图 2 不同保温时间样品的 SEM 照片以及粒径分布图

Fig. 2 SEM images and size distribution of samples with different holding time

表 1 不同 BT 粉体极化前后 Rietveld 精修参数

Table 1 Parameters from Rietveld refinement for BT powders before and after poling

Sample	Phase composition/%	$a=b/\text{\AA}$	$c/\text{\AA}$	c_T/a_T	$R_{wp}/\%$
2 h-unpoled	C:39.5	C:4.011 81	C:4.011 81	1.007 85	6.33
	T:60.5	T:3.999 11	T:4.030 51		
2 h-poled	C:28.4	C:4.010 43	C:4.010 43	1.008 89	6.20
	T:71.6	T:3.998 87	T:4.034 41		
5 h-unpoled	C:34.2	C:4.012 83	C:4.012 83	1.008 00	5.66
	T:65.8	T:3.999 09	T:4.031 09		
5 h-poled	C:29.4	C:4.011 33	C:4.011 33	1.008 44	6.75
	T:70.6	T:3.996 70	T:4.030 44		
12 h-unpoled	C:27.3	C:4.011 81	C:4.011 81	1.009 10	5.34
	T:72.7	T:3.998 64	T:4.035 02		
12 h-poled	C:24.8	C:4.011 59	C:4.011 59	1.009 32	6.34
	T:75.2	T:3.991 11	T:4.028 31		

C and T represent cubic phase and tetragonal phase, respectively; a , b and c are lattice constants; c_T/a_T represents c/a value in tetragonal phase; R_{wp} is R-weighted pattern during refinement process.

2.3 催化性能分析

通过对罗丹明 B(RhB)染料的降解情况来评估各陶瓷粉体的催化性能,粉体对应的紫外-可见吸收谱如图 3 所示。由图 3 可以看出,不同催化条件下

RhB 染料溶液的紫外-可见吸收峰峰值都随反应时间增加而逐渐降低,表明 BT 粉体在极化前压光协同催化(U+L),极化后光催化(L)、压电催化(U)、压电光催化(U+L)条件下对 RhB 都有催化降解效果。

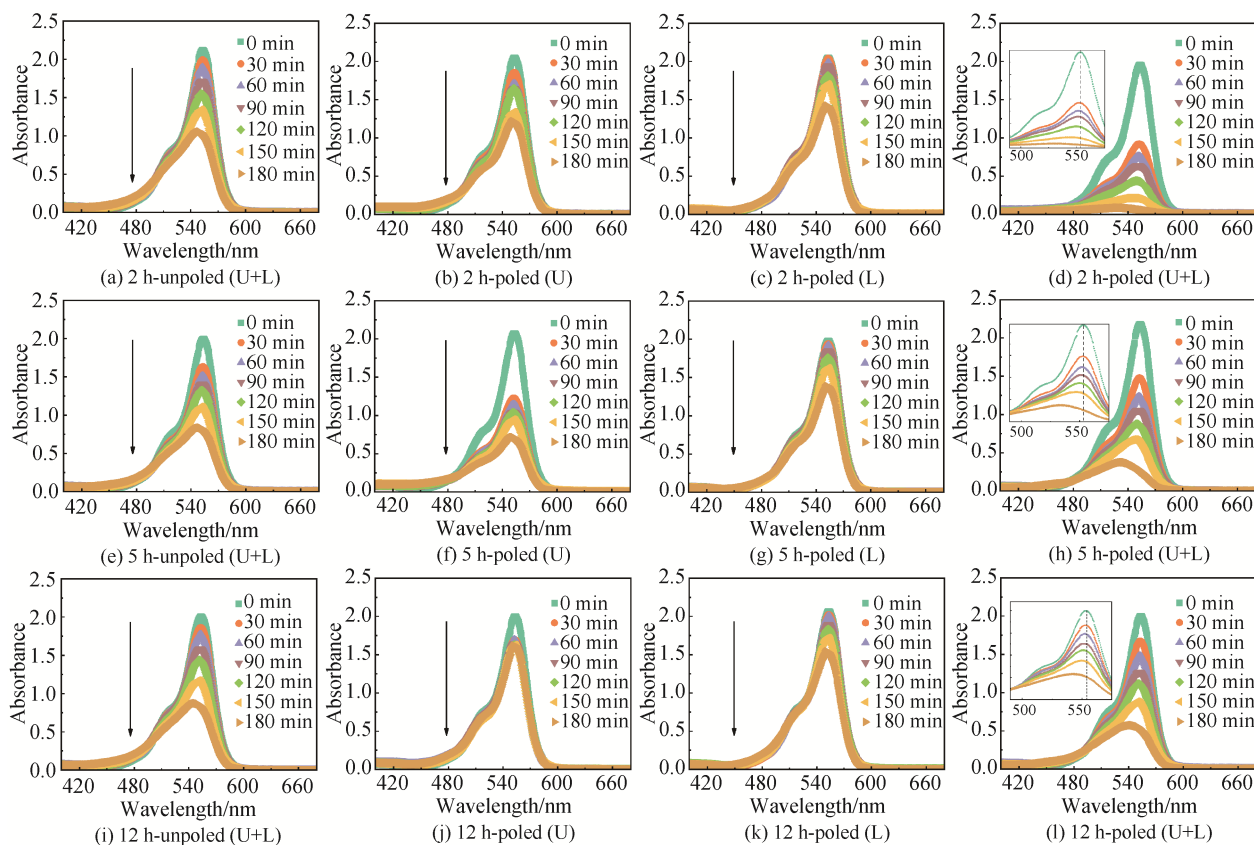


图 3 样品在不同条件下的紫外-可见光吸收谱

Fig. 3 UV-Vis spectra of samples under different conditions

对于 RhB 染料,其催化降解过程一般要经过 N-脱乙基化,产生 N, N-二乙基-N'-乙基罗丹明(DER)、N-乙基-N'-乙基罗丹明(EER)等中间体,然后发色团裂解,环打开,苯环被完全破坏, RhB 被

降解为 H_2O 与 CO_2 。其中, N-脱乙基中间体的逐步形成会导致特征吸收带的偏移以及较慢的催化速率^[27]。在图 3a~图 3c、图 3e~图 3g、图 3i~图 3k 中并没有观察到峰值偏移现象,这是因为催化速率较慢,

特征吸收带偏移不明显。由图 3d、图 3h 和图 3l 可以看出, RhB 的特征吸收带(约 553 nm)在 150 min 内降幅很大, 仅在 180 min 时明显向短波长偏移, 如图 3d、图 3h 和图 3l 插图所示, 2、5、12 h 3 组粉体特征吸收带分别移至 531、534、543 nm, 这表明与 N-脱乙基作用相比, 芳香环的裂解在 BT 催化 RhB 过程中占主导作用, 降解速率较快。

为探究不同催化条件下催化性能的差异, 利用 C/C_0 值来衡量 0~180 min 条件下不同时刻的催化效果, 其中: C_0 与 C 分别为 0 时刻与采样时刻对应的最高吸收峰峰值。图 4a 和图 4c 分别为 2、5、12 h 粉体在极化前 U+L、极化后 L、U、U+L 4 种条件下的 C/C_0 值。由图 4a 和图 4c 可以看出, 3 组样品极化

后压光协同催化效果最佳, 2 h 粉体极化后在压光协同催化 180 min 时 C/C_0 值为 0.03, 几乎全部降解。同时, 观察图 4a 中 2 h 粉体极化后仅超声条件下的降解曲线, 发现在 60~120 min 内催化效果不明显, C/C_0 值由 0.84 仅降至 0.80。同样, 观察 5 h 粉体与 12 h 粉体极化后仅超声下的降解曲线, 发现 5 h 粉体样品在 30~150 min 内 C/C_0 值仅由 0.59 降至 0.45, 12 h 粉体在 30~180 min 内 C/C_0 值仅由 0.85 降至 0.81, 都出现催化“瓶颈期”。在超声条件下, 不可避免会发生空气泡的产生与坍塌, 引起局部撞击, 颗粒表面产生压力脉冲, 以及由于超声作用, 颗粒旋转碰撞通过表面摩擦产生自由电荷^[26], 这也是仅在超声条件下出现“瓶颈期”以及降解速率不均匀的原因。

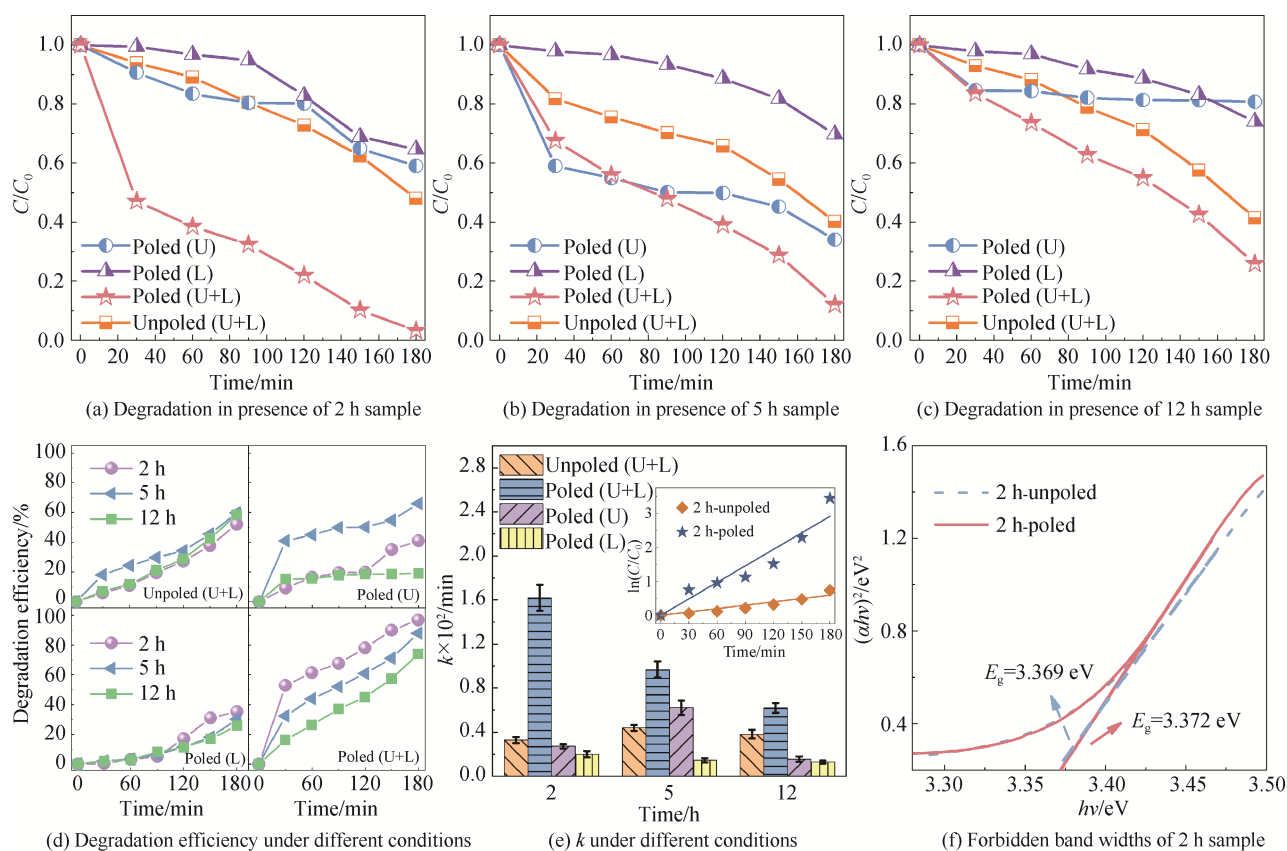


图 4 不同样品的降解率、速率常数以及带隙分析

Fig. 4 Degradation efficiency, rate constant and band gap analysis of different samples

在此基础上, 利用式(1)计算不同条件下染料的降解率^[28], 进一步探究极化对粉体催化性能的影响:

$$\text{Degradation efficiency} = \left(1 - \frac{C}{C_0}\right) \times 100\% \quad (1)$$

计算结果如图 4d 所示。极化前, 3 组粉体催化效率较低且相差较小。其中, 2 h 粉体与 12 h 粉体降解率曲线在 120 min 内基本重合, 但在 120~180

min 内, 12 h 粉体催化效率高于 2 h。一般情况下, 颗粒尺寸越小, 比表面积越大, 染料与粉体之间接触面积越大, 催化效率越高^[26], 但 2 h 粉体 c_T/a_T 值低于 12 h 粉体, 四方度较低, 四方相对催化有促进作用^[29], 同时随保温时间增加, 氧空位浓度提升^[30], 氧空位对压电光催化有促进作用^[31-33]。所以, 2 h 粉体与 12 h 粉体的催化效率差异可能与粒径、四方相以及氧空位浓度贡献程度大小有关。

电晕极化 1 h 后, 3 组粉体 c_T/a_T 值(表 1)分别为 1.008 89、1.008 44、1.009 32, 差别较小, 此时颗粒尺寸对催化性能影响程度较大。超声条件下, 3 组粉体对染料的降解率 180 min 时分别为 41.01%、65.94%、19.21%, 颗粒尺寸越大, “瓶颈期”越长。2 h 粉体颗粒尺寸(约为 55 nm)虽小, 但由图 2a 可以看出, 颗粒与颗粒之间有黏连现象, 所以 120~150 min 催化效率的大幅提升可能得益于超声对颗粒的分散作用。而 5 h 粉体颗粒(约为 110 nm)虽然比 2 h 粉体粒径大, 但其分散性较好, 前 180 min 内对染料降解率较高。仅光照条件下, 180 min 染料的降解率分别为: 35.27%、30.26%、25.91%, 颗粒尺寸小的优势在 120 min 左右逐渐显现, 2 h 粉体对染料的降解率最高。观察压光协同催化曲线可知, 催化效率随时间变化都较为均匀, 2、5、12 h 粉体 180 min 时对 RhB 的降解率分别为 96.81%、87.98%、74.06%, 随颗粒尺寸增大, 降解率降低。

为更直观对比极化前后粉体对染料的降解速率, 利用 Langmuir–Hinshelwood 一阶动力学模型

[34–35] 计算速率常数, 该模型可由方程 $-\ln(C/C_0)=kt$ 描述, 其中: k 为动力学速率常数, 计算结果如图 4e 所示。粉体极化前在压光协同催化下速率常数 k 分别为 0.003 28、0.004 39、0.003 82 min^{-1} , 相差较小, 2 h 粉体极化后在压光协同催化条件下 k 值达到 0.016 20 min^{-1} , 是极化前 k 值的 4.94 倍, 5 h 粉体和 12 h 粉体极化后 k 值为 0.009 69 min^{-1} 和 0.006 20 min^{-1} , 分别为极化前的 2.21 倍和 1.62 倍, 远高于极化前降解速率, 表明极化极大增强了粉体的催化活性。

表 2 为各粉体极化前后的反应速率差值 Δk ($k_{\text{poled}} - k_{\text{unpoled}}$), 随着粉体颗粒粒径增大, 极化前后粉体 Δk 值减小, 与四方度变化规律一致。为了更好地评估 2 h 粉体极化后的催化性能, 将不同催化剂对有机染料的反应速率与降解率进行对比, 如表 3 所示, 此粉体在 180 min 内对染料的降解率达到 96.81%, 实现了较好的催化效果, 且反应速率高于其它无铅铁电陶瓷粉体^[11,16,26,36–40], 说明电晕极化是一种有效提升粉体催化性能的方法。

表 2 不同条件下 BT 粉体极化前后的反应速率常数
Table 2 Reaction rate constant of BT powders before and after poling under different conditions

Sample	U+L(unpoled)/min ⁻¹	U(poled)/min ⁻¹	L(poled)/min ⁻¹	U+L(poled)/min ⁻¹	$\Delta k/\text{min}^{-1}$
2 h	0.003 28	0.002 71	0.002 00	0.016 20	0.012 92
5 h	0.004 39	0.006 23	0.001 44	0.009 69	0.005 30
12 h	0.003 82	0.001 55	0.001 30	0.006 20	0.002 38

Δk represents difference in rate constant of piezo-photocatalysis before and after poling.

表 3 使用不同催化剂降解有机染料的速率常数以及降解率对比
Table 3 Rate constant and degradation efficiency of organic dyes using different catalysts

Catalyst used and amount	Degradation conditions	Dye and volume	Reaction time/min	Rate constant k/min^{-1}	Degradation efficiency/%	Reference
BaTiO ₃ 50 mg	L:300 W Xe U:35 kHz, 100 W	RhB 10 mg·L ⁻¹ , 50 mL	180	0.016 20	96.81	This work
BaTiO ₃ 100 mg	U:40 kHz, 80 W	MO 5 mg·L ⁻¹ , 100 mL	160	0.008 70	91.00	[36]
BaTiO ₃ 1 g/L	L+U	MO 4 mg·L ⁻¹ , Without	240	0.012 50	95.00	[26]
Ba _{0.5} Sr _{0.5} TiO ₃ 100 mg	L: Two UV U:40 kHz, 150 W	MB 5 mg·L ⁻¹ , 10 mL	180	0.008 02	81.00	[37]
BaZr _{0.02} Ti _{0.98} O ₃ 100 mg	L:70 W UV U:40 kHz	RhB 6 mg·L ⁻¹ , 10 mL	240	0.008 84	89.00	[38]
BaTiO ₃ 150 mg	L:100 mW·cm ⁻²	RhB 10 mg·L ⁻¹ , 50 mL	60	0.001 20	5.00	[11]
Ag–BaTiO ₃ 150 mg	L:100 mW·cm ⁻²	RhB 10 mg·L ⁻¹ , 50 mL	60	0.009 60	43.00	[11]
0.5BaZr _{0.2} Ti _{0.8} O ₃ –0.5Ba _{0.7} Sr _{0.3} TiO ₂ 100 mg	U: 40 kHz, 150 W	MB 5 mg·L ⁻¹ , 10 mL	180	0.006 98	79.00	[16]
Ba _{0.77} Sr _{0.23} TiO ₃ 100 mg	L:180 W UV	MO 5 mg·L ⁻¹ , 100 mL	120	0.006 90	90.00	[39]
BaBi ₄ Ti ₄ O ₅ 100 mg	U: UV	MB 5 mg·L ⁻¹ , 10 mL	120	0.007 50	62.00	[40]

此外, 利用 $(\alpha h\nu) = A(\alpha h\nu - E_g)^{1/2}$ 公式^[17](其中: α 为吸收系数; h 为 Planck 常数; ν 为入射光频率; A 为常数)探究极化对晶体禁带宽度的影响。图 4f 反映了 2 h 粉体极化前后禁带宽度变化, 观察到极化前 E_g 为 3.369 eV, 极化后 E_g 值略微变大, 为 3.372 eV。带隙偏移是由极化前后样品的内建电场差异引起的, 但目前对极化铁电体与非极化铁电体的带隙研究并不足以得出任何结论, 不同的工作报道了极化时带隙的不同行为^[10,41-43]。显然, 未极化与极化的颗粒 E_g 值位于紫外范围^[44], 因此, 粉体在

极化前后对 RhB 染料都表现出催化活性。

2.4 稳定性及机理分析

为验证 BT 粉体催化活性的稳定性, 将 2 h 粉体催化反应前后 XRD 进行对比。图 5 为样品催化稳定性及自由基淬灭实验。由图 5a 可见, 反应前后 BT 粉体都为钙钛矿结构, 没有观察到衍射峰消失或衍射峰相对强度突变现象, 表明粉体催化前后没有发生晶体结构变化^[25]。且从图 5(b)循环降解催化效率结果可以看出, 经过 4 次循环降解, 催化活性并没有显著下降, 表明粉体可保持较高的催化稳定性。

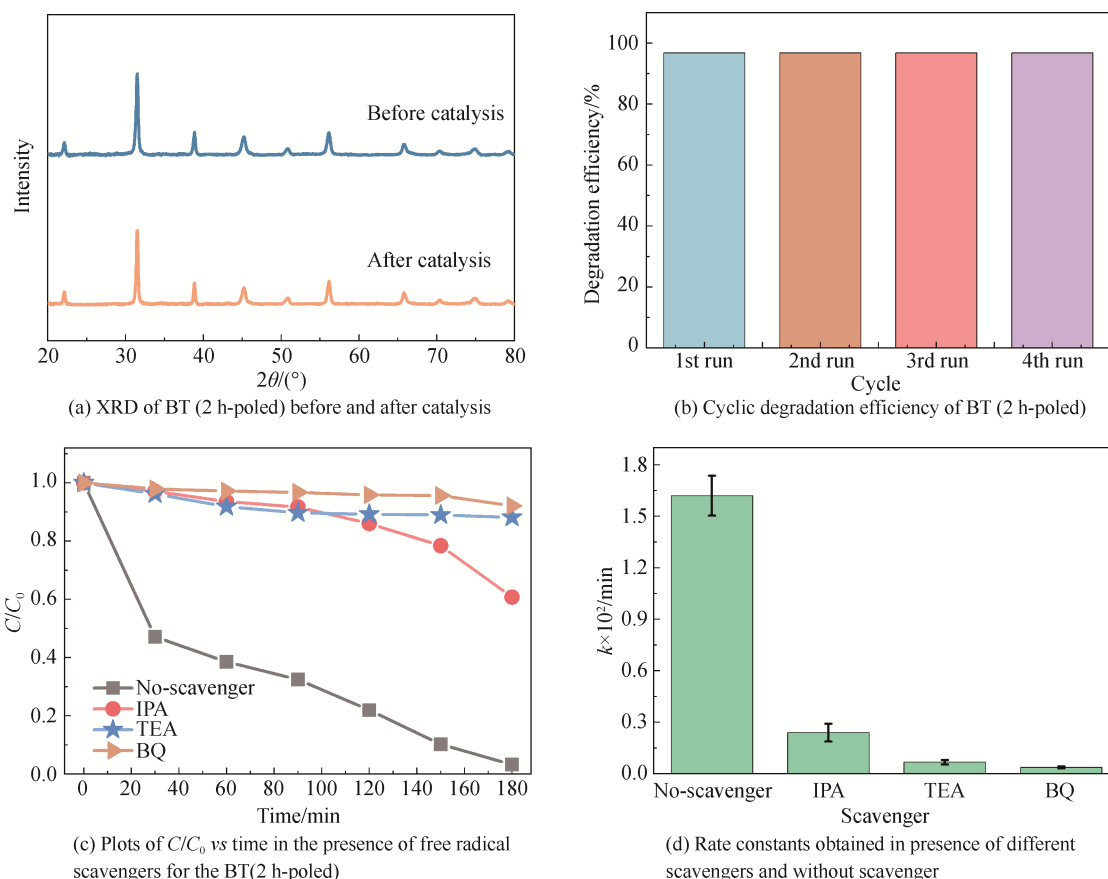
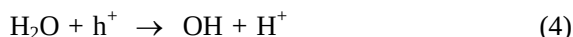
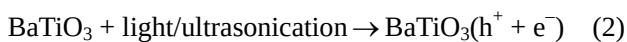


图 5 样品催化稳定性及自由基淬灭实验

Fig. 5 Catalytic stability and free radical scavenging experiment of sample

研究表明, BT 颗粒在光照下吸收能量发生电荷分离, 导带电子迁移到颗粒表面, 与吸附在 BT 表面的氧反应, 产生超氧自由基。同时, 价带产生的空穴可与 H_2O 反应产生羟基自由基。自由基进一步与 RhB 染料反应, 以实现降解^[45-46], 超声将会促进这一过程, 可用下列方程式描述^[26]:



这种压电纳米材料的催化活性目前可用能带理论或电荷屏蔽效应来解释^[47]。能带理论认为超声振动下产生的空气泡坍塌时, 会产生约 10^8 Pa 的高压, 作用在 BT 纳米颗粒上, 导致压电效应进而产生压电电势, 此时 BT 的导带和价带处于倾斜状态, 被激活的电子-空穴对以相反方向被吸收到催化剂表面参与氧化还原反应中^[43], 促进了样品内产生的电子-空穴对分离以及传输。电荷屏蔽效应认为压电电势产生表面结合电荷, 进而被颗粒外部产生的自由电荷补偿或屏蔽。可见, 2 个模型都表明压电势

在催化活性中起着至关重要的作用。由图 4 可以看出, 与光催化相比, 压光协同催化效率明显大幅提升, 表明将压电催化与光催化结合可对染料降解起促进作用。为评估不同种自由基在催化过程中的作用, 分别以异丙醇(IPA)、三乙醇胺(TEA)、苯醌(BQ)作为羟基自由基($\cdot\text{OH}$)、空穴(h^+)以及超氧阴离子自由基(O_2^-)的淬灭剂, 催化结果如图 5c~图 5d 所示。IPA、TEA 和 BQ 被引入后, 反应速率分别降低了 85%、96%、98%, 与未加淬灭剂的粉体催化效果相比, 添加淬灭剂后反应速率被显著抑制, 特别是添加 TEA 或 BQ 后, 染料基本无降解, 说明催化过程中主要是空穴和超氧阴离子自由基参与了氧化还原反应^[26]。

与极化前反应速率相比, 2、5、12 h 粉体极化后在压光协同催化下反应速率分别为极化前的 4.94、2.21 倍和 1.62 倍, 这主要源于电晕极化促进了陶瓷铁电畴的排列有序度。虽然未极化 BT 粉中存在自发极化现象, 但由于铁电畴的无序性, 极化强度有限。电晕极化使得极化方向趋于一致, 内建电场增强, 导致催化剂表面氧化和还原反应空间分离, 使得载流子寿命延长, 大大降低超声与光协同催化下产生的载流子的复合率, 催化速率得以有效提升^[37]。随保温时间延长, 粉体颗粒粒径尺寸变大, 极化前后 $\Delta(c_T/a_T)$ 值减小, 极化后粉体催化速率的提升值 Δk 也减小, 表明电晕极化也通过引起晶格畸变来影响催化速率。其中, 2 h 粉体极化后可达到 96.81% 的高降解率以及 $0.016\ 20\ \text{min}^{-1}$ 的速率常数, 这是因为相同极化电压与极化时间下, 不同粒径粉体的晶胞畸变程度不同, 2 h 粉体受极化影响程度最深, 表现出较高的四方性, 同时其较小的粒径尺寸使得催化剂粉体与 RhB 染料接触面积最大, 从而达到较理想的催化效果。

3 结论

采用溶胶-凝胶法在 800 °C 制备了保温时间分别为 2、5、12 h 的 BT 粉体, 并在 6.56 kV 电压下分别进行 1 h 极化, 通过极化前后粉体对有机染料 RhB 的降解效果来评估电晕极化对光催化性能的影响。

极化前 3 组粉体压光协同催化下染料降解速率常数 k 分别为 $0.003\ 28$ 、 $0.004\ 39$ 、 $0.003\ 82\ \text{min}^{-1}$, 催化速率较低, 极化后 k 值分别提升至 $0.016\ 20$ 、 $0.009\ 69\ \text{min}^{-1}$ 和 $0.006\ 20\ \text{min}^{-1}$, 为极化前的 4.94、2.21 倍和 1.62 倍, 说明电晕极化使得粉体催化降解速率大幅提升。这主要源于极化极大增强了铁电体

内建电场, 光生电荷分离驱动力增大, 光生载流子复合率降低。同时观察到极化前后不同粒径晶格畸变程度与催化速率常数变化值呈现相同规律, 说明极化也通过影响晶体结构来影响染料降解速率。其中, 2 h 粉体极化后在 180 min 内可达到 96.81% 的降解率, 一方面, 其颗粒粒径(约为 55 nm)小于 5 h 粉体(约为 110 nm)与 12 h 粉体(约为 130 nm), 极化引起的晶格畸变程度最高, 四方度得到增强; 另一方面, 其较小的粒径尺寸使其与 RhB 染料充分接触, 从而实现较高的反应速率与降解率。由此可见, 极化对粒径小的颗粒作用效果更明显, 相同条件下颗粒尺寸越小, 晶格畸变程度越高, 同时具有较大的与有机染料接触面积, 这使粉体的电晕极化更具目的性与选择性, 为设计高降解率的催化剂粉体提供了实验参考。

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Effect of Corona Poling on Piezo-Photocatalytic Performance of Barium Titanate Powders

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Extended Abstract

Introduction Photocatalysis is an effective technology to solve environmental pollution. Ferroelectric ceramics, as a new type of catalyst, have been received widespread attention mainly attributed to the ability to reduce the recombination rate of photo-induced carriers and to improve catalytic performance by building a built-in electric field. In order to avoid the decrease of remanent polarization in ceramic bulks during the traditional poling technology and simplify the poling process, corona poling technology has been used for the poling of powders. Several researches indicated that corona poling could significantly improve the catalytic performance, while the relationship among the particle size, phase structure, and piezo-photocatalytic performance was still not so clear. Therefore, BaTiO₃ (BT) nanoparticles with different particle sizes were prepared via sol-gel method and then polarized these powders for 1 h under a voltage of 6.56 kV. The phase structures and the lattice distortion before and after poling were carefully explored. In addition, the effect of corona poling on the piezo-photocatalytic performance of BT powders was investigated, Rhodamine B (RhB) was utilized as the target pollutant.

Methods Barium acetate (C₄H₆O₄Ba) and tetrabutyl titanate (C₁₆H₃₆O₄Ti) were used as raw materials, both were dissolved in acetic acid and ethanol, respectively. Subsequently, these two solutions were mixed and then stirred for 3 h, after that, the solution was left to stand for 16 h, and then dried in an oven at 70 °C for 24 h. The mixtures were calcined at 800 °C for 2, 5 h and 12 h, respectively, in order to obtain BT powders with different particle sizes (the corresponding BT powders were respectively referred to as 2, 5 h and 12 h).

A SmartLab type X-ray diffractometer (XRD) was used to analyze the crystal structure of the obtained powders. The obtained powders were measured using an Invia Reflex model laser micro Raman spectrometer (Raman). In addition, the Helios G4 UC type scanning electron microscopy (SEM) was used to observe the surface morphology of the obtained powders. A Mapada UV-6300 UV-Vis spectrophotometer (UV-Vis) was used to characterize the transmittance of the obtained powders, thereby evaluating the degradation rate of powders. A home-made corona poling set-up at 6.56 kV for 1 h was used to polarize the BT powders. The unpoled/poled BT powders were mixed in RhB and stirred for 30 min to complete the dark adsorption. A Xe lamp (300 W) was used to simulate the sunlight irradiation, and an ultrasonic machine (30 kHz, 100 W) was used to assist in completing the piezo-photocatalytic test.

Results and discussion Particle sizes of the 2, 5 h and 12 h BT powders were 55, 110 nm, and 130 nm, respectively. XRD patterns showed that the cubic and tetragonal phases coexisted for all kinds of samples, and Raman spectroscopy confirmed the presence of tetragonal phases. The c/a values of tetragonal phase (c_T/a_T) in these BT powders, evaluated by Rietveld refinement analysis, were 1.007 85 (2 h-unpoled), 1.008 00 (5 h-unpoled), and 1.009 10 (12 h-unpoled), respectively, these were closely related to the particle size. The larger size corresponded to the higher c_T/a_T , illustrating that the ratio of the tetragonal phase would be increased in 12 h BT nanoparticles. After corona poling process, the lattice distortion further strengthened and the c_T/a_T values were 1.008 89 (2 h-poled), 1.008 44 (5 h-poled), and 1.009 32 (12 h-poled), respectively. The difference of c_T/a_T between unpoled and poled BT powders ($\Delta(c_T/a_T)$) was significantly decreased with the increase of particle size, demonstrating the higher poling effectiveness in nanoparticles with smaller size.

Moreover, effect of poling on the piezo-photocatalytic performance of samples was evaluated via observing the degradation of RhB. It was found that the piezocatalysis existed a "bottleneck period", being related to the pressure pulse generated by cavitation bubbles and the free charges generated by particles through surface friction. The reaction rate constants k for unpoled BT powders were 0.003 28 min⁻¹ (2 h-unpoled), 0.004 39 min⁻¹ (5 h-unpoled), and 0.003 82 min⁻¹ (12 h-unpoled), respectively. After poling, the k values were 0.016 20 min⁻¹ (2 h-poled), 0.009 69 min⁻¹ (5 h-poled), and 0.006 20 min⁻¹ (12 h-poled), 4.94, 2.21 and 1.62 times higher than before poling, respectively, mainly attributed to the enhancement of the built-in electric field caused by corona poling, which could increase the driving force for the separation of photo-induced carriers and prolong the lifetime of carriers. Among them, the 2 h-poled powder exhibited the highest rate constant and a degradation efficiency of 96.81%, as that particle size of 2 h-poled samples

was smaller than that of 5 h powders and 12 h powders, resulted in a high degree of lattice distortion and enhanced the tetragonality. Moreover, the small particle size of samples was considered to be favorable for the sufficient contact with RhB. Therefore, highest reaction rate constant and degradation efficiency were achieved for the 2 h-poled sample.

Conclusions BT powders with different particle sizes were prepared and poled by corona poling technology. Effect of the poling process on the degree of lattice distortion, phase structure, and piezo-photocatalytic performance for degrading RhB of BT powders was systematically investigated. Results indicated that the corona poling could deepen the crystal lattice distortion and increase the tetragonality of BT nanoparticles. In addition, poling process could enhance the built-in electric field, reduce the recombination rate of photo-induced carriers, and significantly improve catalytic performance. The rate constants k of the poled powders were 4.94 times (2 h-poled), 2.21 times (5 h-poled), and 1.62 times (12 h-poled) higher than those of unpoled BT powders. Among all samples without and with poling process, the 2 h-poled BT powder achieved the highest degradation efficiency of 96.81% within 180 min, indicated the optimal piezo-photocatalytic performance. This work could provide a simple and rational method to design ferroelectric materials for achieving the high catalytic performance.

Keywords barium titanate; piezo-photocatalysis; corona poling; Rhodamine B