Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Synthesis of $Bi_4Ti_3O_{12}$ decussated nanoplates with enhanced piezocatalytic activity

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SI 1. Characterization of the $Na_2Ti_3O_7$ precursor

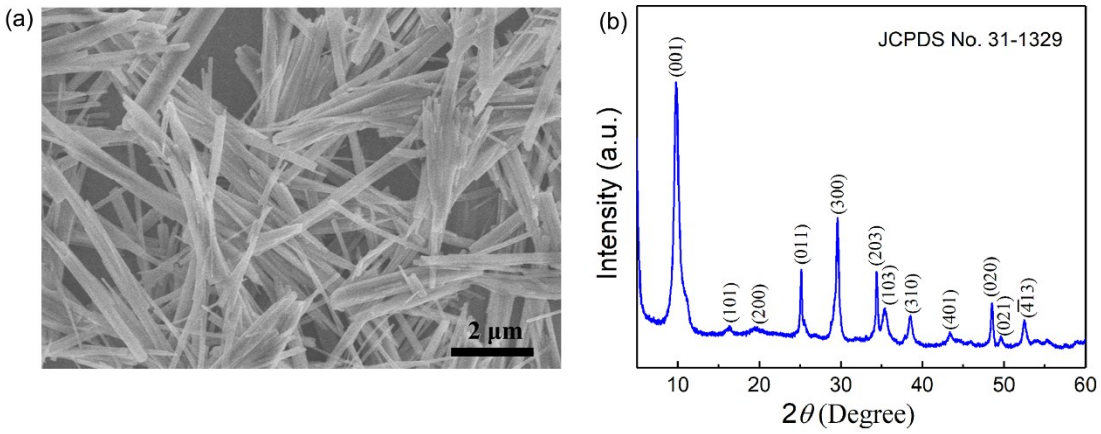

Figure S1. (a) SEM image and (b) XRD pattern of $Na_2Ti_3O_7$ nanowires.

SI 2. Synthetic parameters of the $Bi_4Ti_3O_{12}$ nanomaterials

Table S1. Synthetic parameters for preparing $Bi_4Ti_3O_{12}$ nanomaterials.

Sample name	Method and condition	NaOH ($mol \cdot L^{-1}$)	Starting materials	
			Ti source	Bi source
t-BiT-1M	template hydrothermal process, 200 °C for 48 h	1	0.15g $Na_2Ti_3O_7$	0.97g $Bi(NO_3)_3 \cdot 5H_2O$
t-BiT-3M	template hydrothermal process, 200 °C for 48 h	3	0.15g $Na_2Ti_3O_7$	0.97g $Bi(NO_3)_3 \cdot 5H_2O$
t-BiT-5M	template hydrothermal process, 200 °C for 48 h	5	0.15g $Na_2Ti_3O_7$	0.97g $Bi(NO_3)_3 \cdot 5H_2O$
o-BiT-1	one-pot hydrothermal process, 200 °C for 48 h	3	0.12g TiO_2	0.97g $Bi(NO_3)_3 \cdot 5H_2O$
o-BiT-2	one-pot hydrothermal process, 200 °C for 48 h	3	0.51g $Ti(OC_4H_9)_4$	0.97g $Bi(NO_3)_3 \cdot 5H_2O$
s-BiT	solid state reaction, 800 °C for 2 h	\	TiO_2	Bi_2O_3

SI 3. EDS analysis of the $Bi_4Ti_3O_{12}$ samples

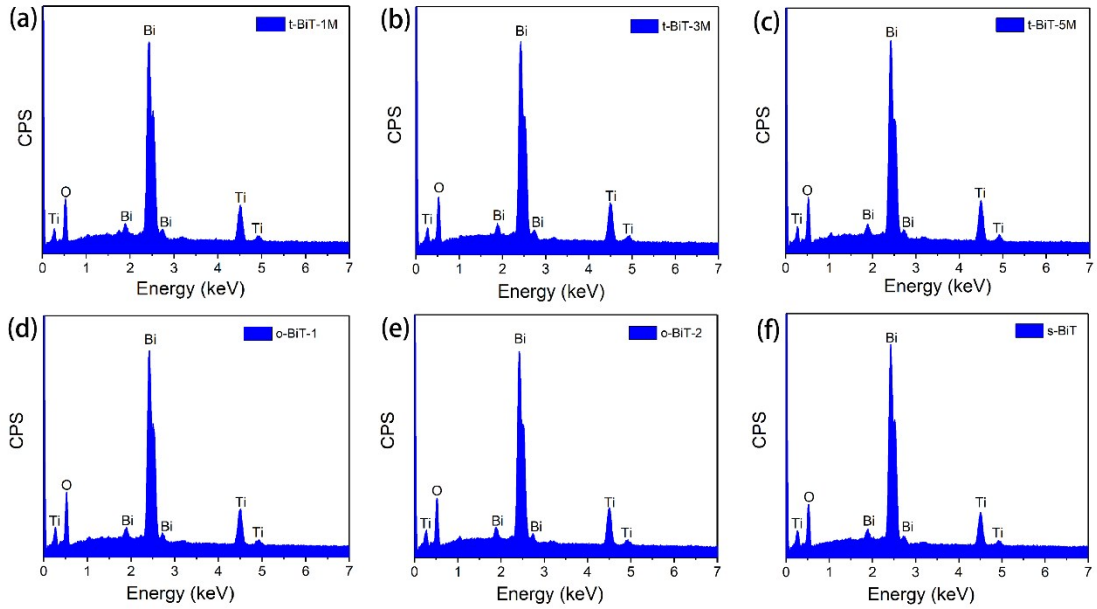

Figure S2. EDS patterns of (a) t-BiT-1M, (b) t-BiT-3M, (c) t-BiT-5M, (d) o-Bit-1, (e) o-BiT-2 and (f) s-BiT.

SI 4. Optical absorption spectra of dye solutions in the piezocatalytic degradation process

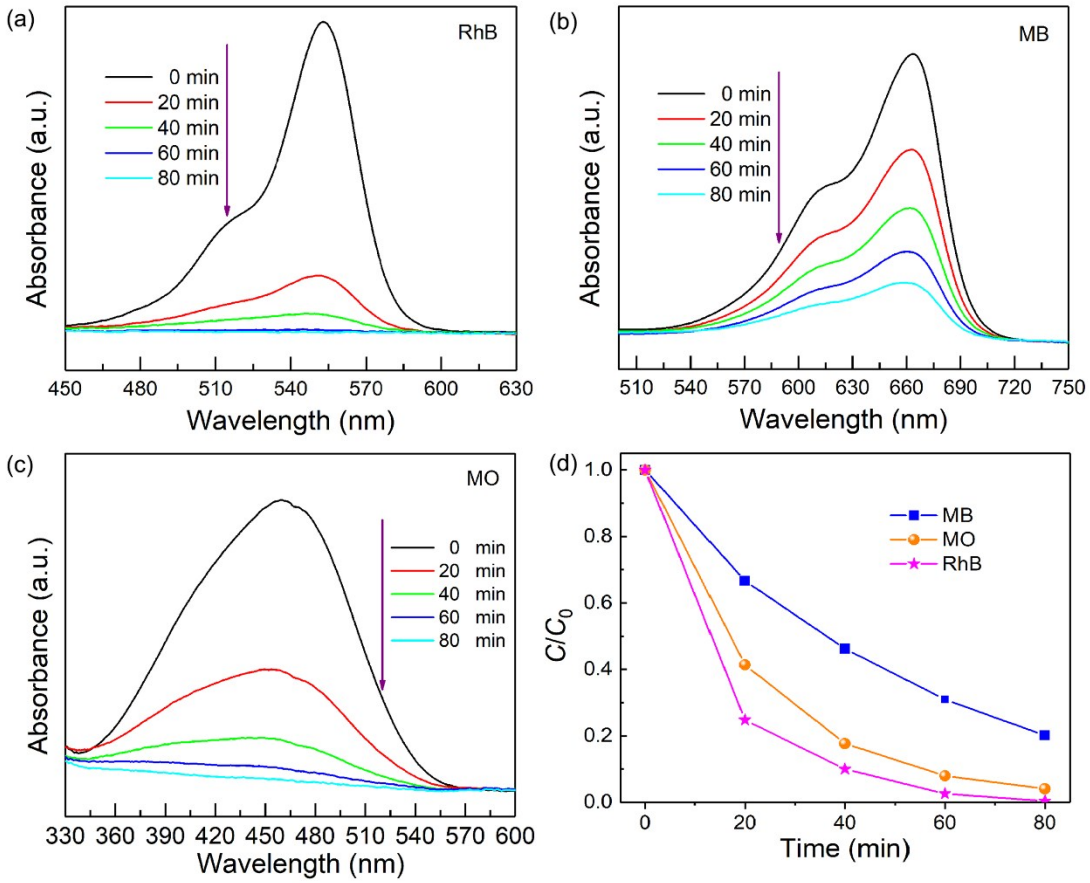

Figure S3. UV-vis absorption spectra of (a) RhB, (b) MB and (c) MO aqueous solutions at different time of degradation over t-BiT-3M piezocatalyst. (d) Variation of dye concentration as a function of time.

SI 5. Cycling stability of the t-BiT-3M piezocatalyst

To evaluate the cyclic stability of the piezocatalyst, the degradation experiment was repeated using recycled t-BiT-3M. As shown in **Figure S4**, a similar level of activity was maintained after four cycles of the degradation experiment, indicating a high cycling stability of the present piezocatalyst.

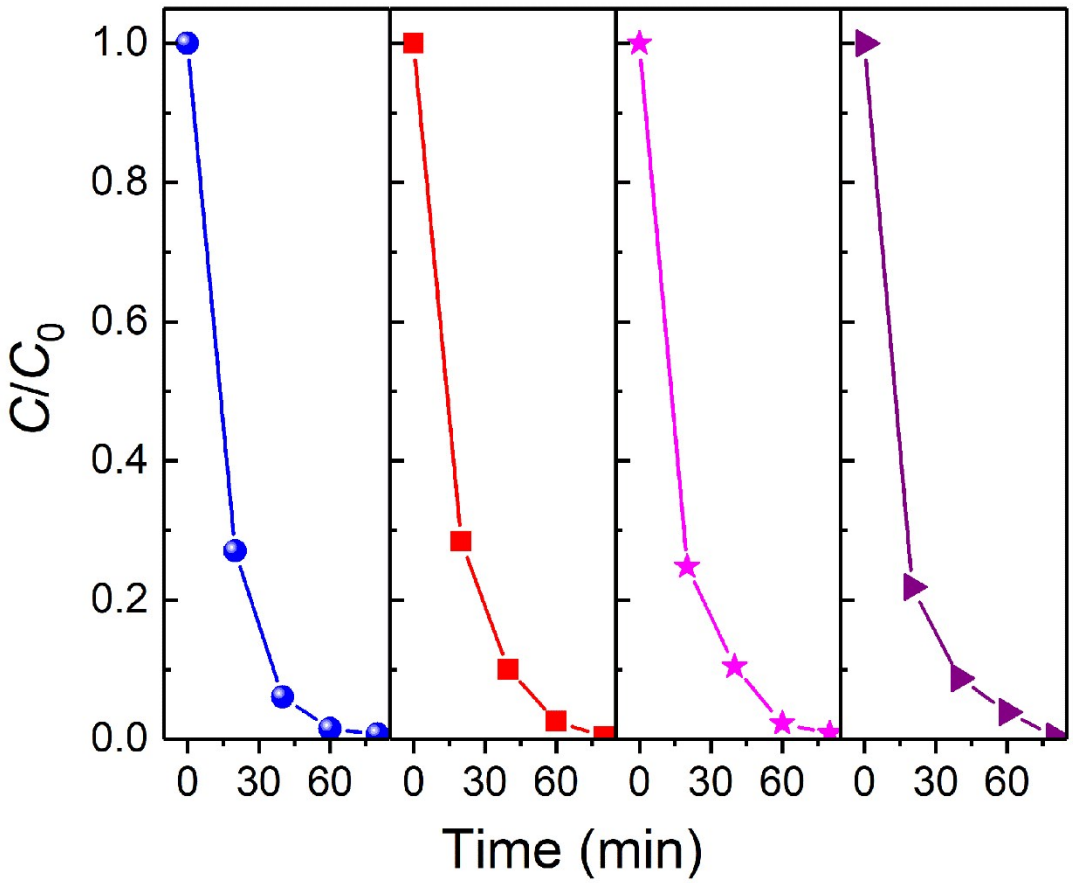

Figure S4. Plots of the relative intensity of the maximum absorption at 460 nm as a function of reaction time in four recycling processes.

SI 6. Evaluation of specific surface area

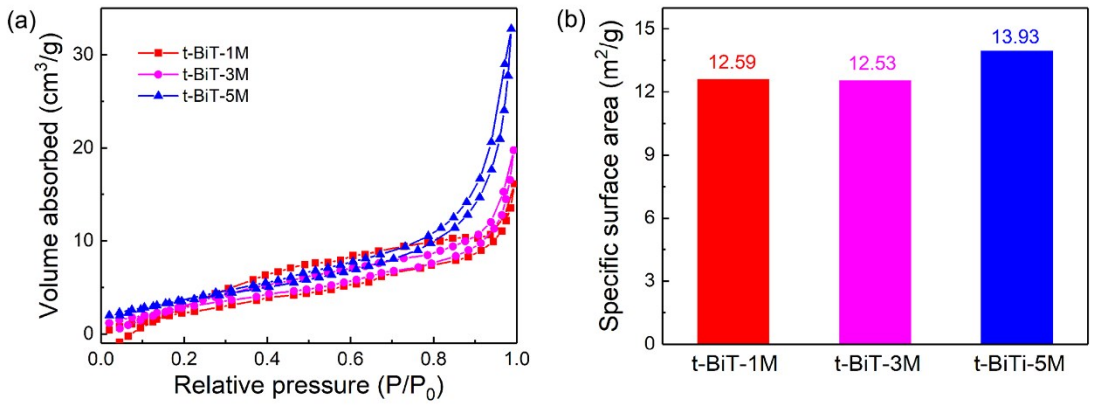

Figure S5. N_2 adsorption and desorption isotherms and specific surface area of $Bi_4Ti_3O_{12}$.

SI 7. Material parameters used in Comsol Multiphysics simulation

Because barium titanate is not defined in the data base of Comsol Multiphysics software package, the material parameters required by simulation were collected or calculated from literature. The theoretical density (ρ) of $Bi_4Ti_3O_{12}$ is 8039 kg m^{-3} according to the standard JCPDS Card No. 73-2181. The relative permittivity (ε_r) of the anisotropic crystal (monoclinic) is expressed as a diagonal tensor:[1]

$$\varepsilon_r = \begin{bmatrix} 120 & 0 & 0 \\ 0 & 205 & 0 \\ 0 & 0 & 140 \end{bmatrix} \qquad (1)$$

The piezoelectric constants (d) of crystals are also closely related to the crystal symmetry. The d-matrix, or namely coupling matrix (eES), can be expressed as

$$eES = d_{ij} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{bmatrix} \qquad (2)$$

corresponding to the monoclinic symmetry.[2] Based on a calculation using the known temperature dependence of the spontaneous polarization, lattice strain and dielectric permittivity, Neto and Cross worked out with an equivalent piezoelectric constant: [2]

$$eES = \begin{bmatrix} 44 & 18 & -48 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0.8 & 0 & {}_m d_{26} \\ -75 & -76 & 269 & 0 & 12 & 0 \end{bmatrix} \mathrm{pC \cdot N^{-1}}. \qquad (3)$$

The calculated d_{11} (44 pC·N^{-1}) is close to the measured value (39 pC·N^{-1}) of a single domain single crystal of $Bi_4Ti_3O_{12}$, while the calculated d_{33} value (d_{33} = 269 pC·N^{-1}) deviates too much from the real measurement (d'_{33} = 9 pC·N^{-1}).[2] The big error in d_{33} calculation might be caused by an overestimation of the out-of-plane component of the spontaneous polarization (P_3). According to the functions used for calculation (see Equation 14 to 24 in Ref. [2]), all the d_{3j} and d_{i3} (i, j = 1, 2 and 3) constants are proportional to the P_3 value. It is reasonable to reduce the d_{3j} and d_{i3} constants with a uniform proportion

$$d'_{ij} = \delta d_{ij} \qquad (4)$$

The proportional coefficient δ can be estimated by

$$\delta = \frac{d'_{33}}{d_{33}} = \frac{9}{269} = 0.0334 \qquad (5)$$

which consequently leads to

$$eES = \begin{bmatrix} 44 & 18 & -1.6 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0.8 & 0 & {}_m d_{26} \\ -2.5 & -2.5 & 9 & 0 & 0.4 & 0 \end{bmatrix} \mathrm{pC \cdot N^{-1}} \qquad (6)$$

The d constants described in Equation 6 have been used for simulation in this work.

In principle, the compliance matrix (*sE*) of monoclinic crystals contain 13 independent components

$$sE = s_{ij} = \begin{bmatrix} s_{11} & s_{12} & s_{13} & 0 & s_{15} & 0 \\ s_{12} & s_{22} & s_{23} & 0 & s_{25} & 0 \\ s_{13} & s_{23} & s_{33} & 0 & s_{35} & 0 \\ 0 & 0 & 0 & s_{44} & 0 & s_{46} \\ s_{15} & s_{25} & s_{35} & 0 & s_{55} & 0 \\ 0 & 0 & 0 & s_{46} & 0 & s_{66} \end{bmatrix}. \qquad (7)$$

Because the crystal structure symmetry of bismuth titanate is close to tetragonal, the *s*-matrix can be approximately described by six independent constants as follows,

$$sE = \begin{bmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ s_{12} & s_{11} & s_{13} & 0 & 0 & 0 \\ s_{13} & s_{13} & s_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66} \end{bmatrix}. \qquad (8)$$

The primary *s* constants of $Bi_4Ti_3O_{12}$ have been proposed by Kitanaka et al. [3] as s_{11} = 7.9 Pa^{-1}, s_{33} = 13 Pa^{-1} and s_{66} = 17 Pa^{-1}. The other *s*-constants can be deduced from the primary *s*-constants, Young's modulus (*E*), Poisson's ratio (μ) and shear modulus (*G*) by

$$s_{12} = \mu_{12} s_{11} \qquad (9)$$

$$s_{13} = \mu_{13} s_{11} \qquad (10)$$

$$s_{44} = \frac{1}{G_{13}} = \frac{2(1+\mu_{13})}{E_1} = s_{11} \cdot 2(1+\mu_{13}). \qquad (11)$$

The Poisson's ratio of tetragonal perovskites $BaTiO_3$ and $PbTiO_3$ were determined based on the predefined *s*-constant in Comsol Multiphysics as $\mu_{12} = -0.29$ and $\mu_{13} = -0.33$. The calculation finally results in

$$sE = \begin{bmatrix} 7.9 & -2.3 & -2.6 & 0 & 0 & 0 \\ -2.3 & 7.9 & -2.6 & 0 & 0 & 0 \\ -2.6 & -2.6 & 13 & 0 & 0 & 0 \\ 0 & 0 & 0 & 10.6 & 0 & 0 \\ 0 & 0 & 0 & 0 & 10.6 & 0 \\ 0 & 0 & 0 & 0 & 0 & 17 \end{bmatrix} \mathrm{Pa}^{-1} \qquad (12)$$

SI 8. Mass spectra of the degradation byproducts of RhB

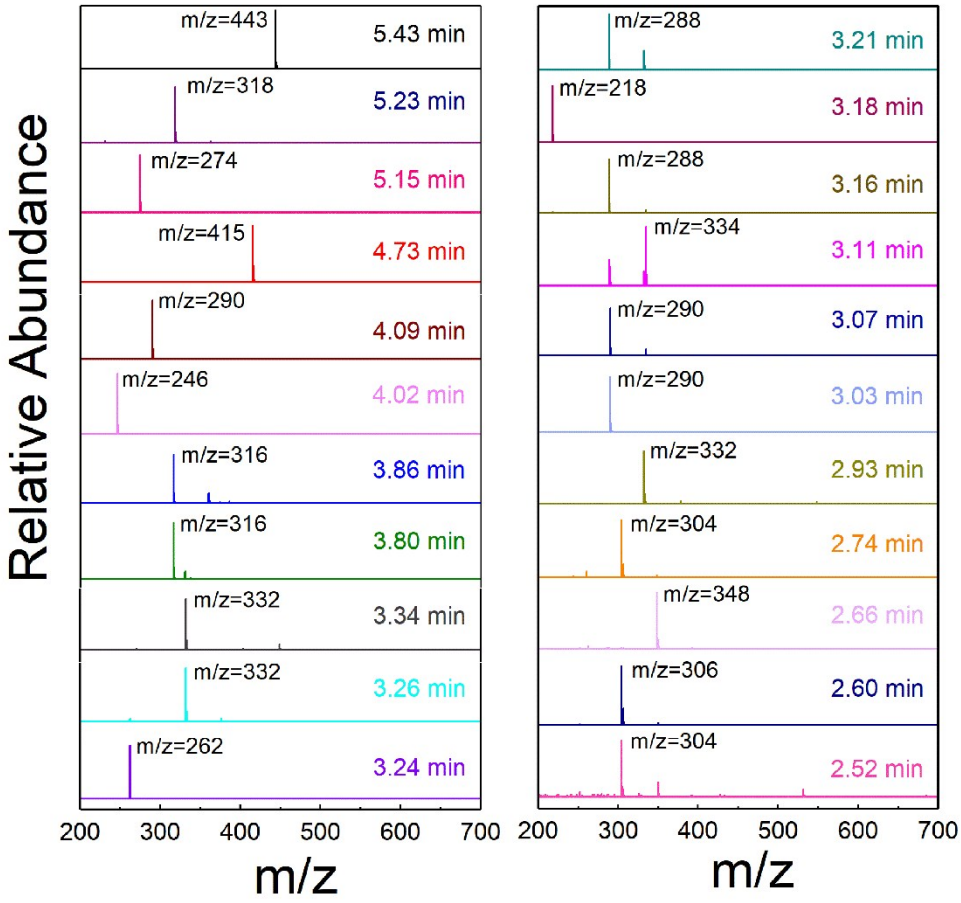

Figure S6. Mass spectra of the degradation byproducts of RhB.

References:

[1] A. Fouskova, L.E. Cross, Dielectric properties of bismuth titanate, J. Appl. Phys. 41 (1970) 2834-2838.

[2] L.E.C. A. Sa Neto, Electro-mechanical behaviour of single domain single crystals of bismuth titanate ($Bi_4Ti_3O_{12}$), J. Mater. Sci. 17 (1982) 1409-1412.

[3] Y. Kitanaka, Y. Noguchi, M. Miyayama, Y. Kagawa, Elastic and piezoelectric properties of high-quality ferroelectric $Bi_4Ti_3O_{12}$ single crystals, Jpn. J. Appl. Phys. 51 (2012) 09LD08.