Supplementary Information for

## Enhanced Trimethoxypyrimidine Degradation by Piezophotocatalysis of BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> using Mechanical Vibration and Visible Light Simultaneously

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## Materials

All the reagents were of analytical grade and were used without further purification: trimethoxypyrimidine (TMP, Sigma, 99%), silver nitrate (AgNO<sub>3</sub>, Sigma, 99.8%), di-sodium hydrogen phosphate dihydrate (Na<sub>2</sub>HPO<sub>4</sub>, VWR Chemicals, 99%), barium hydroxide octahydrate (Ba(OH)<sub>2</sub> 8H<sub>2</sub>O, Aladdin, 98%), titanium (IV) butoxide (Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, Aladdin, 97%), nitro blue tetrazolium chloride (NBT, Thermo Fisher Scientific), terephthalic acid (TA, Sigma, 98%) and methanol (CH<sub>3</sub>OH, Merck, 99.9%). Ultrapure water (18.2 M $\Omega$  cm) obtained from a Cascada water purification system (Pall Corporation, Port Washington, NY, USA) was used to prepare all the solutions.

## **Experimental setup and procedure**

Photographs of the piezophotocatalysis reactor setup employed to perform the piezophotocatalytic degradation are shown in Fig. S1. An ultrasonic cleaner (40 kHz, 100 W, Mojie, China) was used to provide mechanical vibration for the piezocatalytic process. A compact fluorescent lamp (5.4 W/m<sup>2</sup> and peak emissive wavelength of 543 nm, Philips, China) was used to provide visible light for the photocatalytic process. A beaker, acting as a reactor, was placed in the ultrasonic cleaner, and the distance from the lamp to the surface of the reaction solution was 150 mm. The reaction was started by turning on the ultrasonic cleaner for providing ultrasonic wave and the lamp for providing visible light simultaneously. To avoid temperature increases induced by sonication and light irradiation over a long period of time, ice bags were put in the ultrasonic cleaner to keep the temperature around 25 °C, with temperature fluctuations less than 5 °C. Piezocatalytic experiments were conducted using a similar procedure without visible light, and photocatalytic experiments were conducted in a magnetic stirring apparatus (800 rpm) by a similar procedure without ultrasonic wave. As reported in the literature, in order to study the transformation reactions and the transformation kinetics, higher TMP concentrations than natural levels (in normal ng/L or  $\mu g/L$  levels), was often used in lab-scale studies, so the initial concentration of TMP in this study was 10 mg/L and the catalysts dosage was 0.8 g/L. The samples were taken at different time intervals, and filtered with 0.22 µm PTFE syringe filters.



Fig. S1 Photographs of piezophotocatalysis reactor setup: (a) Top view; (b) Front

view 3 Fig. S2 shows the optimization of the mass ratios for the hybrid  $BaTiO_3/Ag_3PO_4$ at 1:3, 1:1 and 3:1. From this figure, it can be seen that the adsorption efficiencies have no differences. The piezocatalytic efficiency is decreased with decreasing amounts of  $BaTiO_3$ , showing that  $BaTiO_3$  is a type of piezocatalyst. The photocatalytic efficiency is increased with increasing amounts of  $Ag_3PO_4$ , because  $Ag_3PO_4$  is a type of photocatalyst. For the piezophotocatalysis, the ratio of 1:3 for  $BaTiO_3/Ag_3PO_4$  shows the best efficiency of 85%. More importantly, no matter which ratio, their degradation efficiency for piezophotocatalysis is always higher than that of piezocatalysis, as well as higher than that of photocatalysis. This phenomenon is quite different from that of the pure  $BaTiO_3$  or pure  $Ag_3PO_4$ , as described in the main text, which attracts interests in studying hybrid materials.



Fig. S2 Mass ratios optimization of  $BaTiO_3/Ag_3PO_4$  under different systems, TMP initial concentration: 10 mg/L; catalyst dosage: 0.8 g/L; mechanical vibration from ultrasonic wave: 40 kHz, 100 W; visible light: 5.4 W/m<sup>2</sup> and peak emissive wavelength of 543 nm

In order to confirm the promoting role of the piezoelectric potential, a type of non-piezoelectric material TiO<sub>2</sub> (P25) is used to replace piezoelectric material BaTiO<sub>3</sub> in the ultrasonic and visible light system. The hybrid material TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> (at 1:3 mass ratio) was prepared using the same co-precipitation technique as for BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>. 0.69 g of TiO<sub>2</sub> was dispersed in 50 mL of deionized water and sonicated for 10 min. 2.55 g of AgNO<sub>3</sub> was then added and stirred in the dark for 30 min. After that, Na<sub>2</sub>HPO<sub>4</sub>•2H<sub>2</sub>O (0.89 g, 50 mL) aqueous solution was added dropwise to the above mixture. After stirring for 1 h in the dark, the precipitate of TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> was obtained. The precipitate was washed with deionized water and dried at 60 °C for 12 h.

From Fig.S3, the synthesized hybrid material  $TiO_2/Ag_3PO_4$  has a strong adsorption capacity that is up to about 40% at 30 min for TMP, and the adsorption equilibrium is accelerated with the participation of ultrasonic vibration. 78% of TMP can be removed within 30 min under the visible light due to the photocatalysis of  $Ag_3PO_4$ , because  $TiO_2$  can only absorb the UV light. Under the combination of visible light and ultrasonic vibration, the removal efficiency of TMP is not much changed except for the accelerating adsorption, which is totally different from  $BaTiO_3/Ag_3PO_4$ . This result could provide an indirect evidence for the enhanced TMP degradation of the piezophotocatalysis of  $BaTiO_3/Ag_3PO_4$ .



Fig. S3 Degradation efficiency of TMP as a function of reaction time using

 $TiO_2/Ag_3PO_4$  (1:3) in different catalytic processes, S refers to ultrasonic vibration; L refers to visible light irradiation; S/L refers to both ultrasonic and visible light; A refers to adsorption; TMP initial concentration: 10 mg/L; catalyst dosage: 0.8 g/L; mechanical vibration from ultrasonic wave: 40 kHz, 100 W; visible light: 5.4 W/m<sup>2</sup> and peak emissive wavelength of 543 nm

The comparisons of TMP degradation efficiency in other experimental processes are shown in Fig.S4. TMP is degraded in the photocatalytic process of BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> for 30 min, and then the remaining TMP solution is further degraded in the piezocatalytic process of BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> for 30 min. The piezophotocatalytic efficiency (85%) is higher than the sum (76%) of the successive photocatalytic and piezocatalytic processes. In addition, TMP is degraded by the piezophotocatalysis of the physical mixed BaTiO<sub>3</sub> and Ag<sub>3</sub>PO<sub>4</sub>, showing that its efficiency (61%) is also much lower than the piezophotocatalysis of the hybrid BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> (85%). These results illustrate that the concurrence of ultrasonic/light and the utilization of hybrid BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> are necessary conditions for enhanced TMP degradation.



Fig. S4 Comparison of TMP degradation efficiency in different catalytic processes; TMP initial concentration: 10 mg/L; catalyst dosage: 0.8 g/L; mechanical vibration from ultrasonic wave: 40 kHz, 100 W; visible light: 5.4 W/m<sup>2</sup> and peak emissive wavelength of 543 nm

The piezocatalysis of pure BaTiO<sub>3</sub> for TMP degradation are studied through the scavenger tests and reactive species detection in Fig. S5. For the piezocatalytic process of BaTiO<sub>3</sub>, the degradation efficiency of TMP is decreased the most after adding TBA for scavenging hydroxyl radicals, illustrating that hydroxyl radicals are the key reactive species in the piezocatalytic process. The generations of electron-hole pairs are demonstrated through the on-off current response in Fig. S5 (b). The superoxide radicals and hydroxyl radicals are detected by the decreasing intensity of the UV-Vis absorption spectrum and the increasing intensity of the fluorescence spectral with reaction time, respectively, as shown in Fig. S5 (c, d).



Fig. S5 (a) Piezocatalysis of BaTiO<sub>3</sub> for TMP degradation in the presence of different scavengers: AO (ammonium oxalate) $\rightarrow$ h<sup>+</sup>; TBA (ter-butyl alcohol) $\rightarrow$ •OH, p-BQ (p-benzoquinone) $\rightarrow$ •O<sub>2</sub><sup>-</sup>; K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  $\rightarrow$ e<sup>-</sup>; TMP initial concentration: 10 mg/L (0.0345 mmol/L); scavenger concentration: 1 mmol/L; catalyst dosage: 0.8 g/L; mechanical vibration from ultrasonic wave: 40 kHz, 100 W; (b) Piezo-current density of electrode with BaTiO<sub>3</sub>, showing the generation of electron-hole; (c) UV–Vis absorption spectra of nitro blue tetrazolium (NBT, 0.02 mmol/L) oxidized by •O<sub>2</sub><sup>-</sup>; (d) Fluorescence spectral of terephthalic acid (TA, 0.5 mmol/L) and •OH

Fig. S6 shows the photocatalysis of pure  $Ag_3PO_4$  for TMP degradation. The poorest performance of TMP degradation is found after using the supplementation of AO to capture holes in Fig. S6 (a), suggesting holes play the major roles in the photocatalytic process. The electron-hole pairs and hydroxyl radicals can be detected by the on-off current responses and the weak increasing signals of fluorescence spectral, respectively, as shown in Fig. S6 (b, d). However, the superoxide radicals are not found from the unchanged UV-Vis absorption spectrums of Fig. S6 (c).



Fig. S6 (a) Photocatalysis of Ag<sub>3</sub>PO<sub>4</sub> for TMP degradation in the presence of different scavengers: AO (ammonium oxalate) $\rightarrow$ h<sup>+</sup>; TBA(ter-butyl alcohol) $\rightarrow$ •OH; p-BQ (pbenzoquinone) $\rightarrow$ •O<sub>2</sub><sup>-</sup>; K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  $\rightarrow$ e<sup>-</sup>; TMP initial concentration: 10 mg/L (0.0345 mmol/L); scavenger concentration: 1 mmol/L; catalyst dosage: 0.8 g/L; visible light: 5.4 W/m<sup>2</sup> and peak emissive wavelength of 543 nm; (b) Photo-current density of electrode with Ag<sub>3</sub>PO<sub>4</sub>, showing the generation of electron-hole; (c) UV–Vis absorption spectra of nitro blue tetrazolium (NBT, 0.02 mmol/L) oxidized by •O<sub>2</sub><sup>-</sup>; (d) Fluorescence spectral of terephthalic acid (TA, 0.5 mmol/L) and •OH

To learn about the potential applicability of the BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> hybrids for practical use, the reusability was also evaluated in terms of cycling degradation experiments by centrifuging and collecting (10000 rpm, 5 min) the catalyst suspension. It can be seen from Fig. S7 (a) that the TMP removal efficiency of the second cycling run (74%) is much lower than the first run (97%) in 60 min. However, the removal ability decreases very slowly in the subsequent third (70%) and fourth cycling runs (64%). This result can be explained by the XRD patterns and color changes of the catalysts in Fig. S7 (b, c). Ag has no diffraction peaks before reaction and the color of the hybrid material BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> is yellow, but the signal peak of Ag can be observed in the diffraction patterns after the first cycling run and the hybrid catalyst becomes black. Evidently, a few thin Ag atoms appear on the surfaces of the samples due to the photo-corrosion of Ag<sub>3</sub>PO<sub>4</sub> under visible light irradiation, which causes the removal efficiency to decrease dramatically in the second run. The selfgenerated Ag can trap photo-electrons to protect Ag<sub>3</sub>PO<sub>4</sub> from corroding continuously in the following run and a relative balance appears between  $Ag^0$  and  $Ag_3PO_4$ . Its feature helps to maintain the relatively stable capability of BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> in the third and fourth cycles. Herein, the catalysts' stability depends on two roles during the recycling process: a negative role from the decreasing amount of Ag<sub>3</sub>PO<sub>4</sub> and a positive role from generated  $Ag^0$ , so finding a way to reduce the photo-corrosion of Ag<sub>3</sub>PO<sub>4</sub> so as to improve the stability will be of interest in future research.



Fig. S7 Cycling performance of BaTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> piezophotocatalysis for TMP degradation. TMP initial concentration: 10 mg/L; catalyst dosage: 0.8 g/L; mechanical vibration from ultrasonic wave: 40 kHz, 100 W; visible light: 5.4 W/m<sup>2</sup> and peak emissive wavelength of 543 nm