



# Investigating the synergistic effects in tourmaline/TiO<sub>2</sub>-based heterogeneous photocatalysis: Underlying mechanism insights

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## ABSTRACT

We proposed to combine a polarized mineral tourmaline and TiO<sub>2</sub> nanosemiconductor to form a hybrid photocatalyst, to simultaneously optimize the photocatalytic efficiency and macroscopic aggregation of nano-TiO<sub>2</sub>. Photoactivity assessment toward bisphenol A (BPA) degradation indicated the optimal T(20%)-TiO<sub>2</sub> catalyst exhibited higher performance than the bare TiO<sub>2</sub> or the mechanical mixtures. In view of the reactive species scavenging results and intermediate identification, a hydroxyl radical-initiated oxidation as the dominating BPA decomposition pathway was proposed. The results of photoluminescence spectra and photocurrent measurements along with electrochemical impedance spectra and Mott–Schottky analyses led us to a better understanding of the photocatalytic process involving the facilitated charge transfer and higher carrier density induced owing to tourmaline incorporation. The synergistic effects in tourmaline-involved photocatalysis would be attributed to the fact that the internal dipolar field, originating from tourmaline spontaneous polarization, resulted in spatially varied energy levels of the bands and changed band bending of TiO<sub>2</sub> semiconductor, which lowered the potential barrier for photoelectrons or holes to readily migrate to the surface and retarded electron–hole recombination. The concept of engineering internal field in heterogeneous photocatalysis using a polarized mineral of low cost will shed new light on applied photochemistry and development of nanotechnology enabled approaches for water treatment.

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## 1. Introduction

TiO<sub>2</sub>-based heterogeneous photocatalysis has gained far-reaching importance due to its strong photoreactivity, economic viability, non-toxicity and photostability [1], and has been widely used for pollution abatement. Generally, TiO<sub>2</sub> mediated photocatalysis is initiated by the absorption of photons with sufficient energy relative to the band gap ( $h\nu \geq E_g$ ), which results in charge separation with electrons promotion from the valence band (VB) to the conduction band (CB). The photogenerated electron–hole pairs can undergo recombination, get trapped in metastable states, or migrate to the surface and initiate redox reactions [2]. Because of the ineffective electron transfer and rapid recombination between

the charge carriers, however, the quantum efficiency is inherently low for most TiO<sub>2</sub> mediated photocatalysis. It is also noticeable that nanoscale size effects often come at the expense of the rapid recombination rate of the electron–hole pairs for restricted spatial proximity [3,4]. Yet, new directions are required to promote the quantum efficiency, which have inspired to extensive research efforts.

One strategy toward mitigating catalyst efficiency decrease from recombination is to utilize internal electric fields. In the presence of internal electric fields, the promoted motion of photogenerated charge carriers toward opposite directions and even the spatial separation of redox sites can be achieved [5], and band bending can be manipulated as well, for electron–hole pairs separating. Internal electric fields within photocatalysts can be associated with ferroelectric polarization [6,7], and electrochemical potential differences across phase boundaries which could be engineered in *p*–*n* junctions, polar surface terminations and

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polymorph junctions [8–11]. Recently, some reports focused on the polarizable semiconductors (e.g., ferroelectrics, such as LiNbO<sub>3</sub> [12], BiFeO<sub>3</sub> [13]) to improve photocatalytic activity. Moreover, the influence of ferroelectric polarization on photogenerated charge carriers and photochemical reactions can also extend to the supported non-ferroelectric coating [14–17]. This concept provides an innovative alternative for photocatalyst design with better performance. However, the reduction of TiO<sub>2</sub> or/and ferroelectric particle size will bring about new problems such as catalyst agglomeration and difficult recovery, which limit the practical application of TiO<sub>2</sub>, in spite of its large surface areas. Hence, in this work, to simultaneously optimize photocatalytic efficiency, nanoparticle aggregation and recovery, a method of immobilization of TiO<sub>2</sub> onto polarized tourmaline was proposed to approach the goal of mineral-induced spontaneous polarization assisted photocatalysis, which could indeed provide a promising alternative for cost-effective environmental application due to the environmentally benign nature, chemical inertia, low cost and ubiquity of tourmaline in the natural environment.

Tourmaline, distributed in different geologic environments, is categorized into a complex class of borosilicate with space group of R3m ( $C_{3v}^5$ ). The chemical compositions can be expressed by the general formula XY<sub>3</sub>Z<sub>6</sub>T<sub>6</sub>O<sub>18</sub>(BO<sub>3</sub>)<sub>3</sub>V<sub>3</sub>W. Its crystal structure contains hexagonal rings of corner-shared Si–O tetrahedra. The edge-sharing Y- and Z-octahedra bridging each tetrahedral ring are formed by Y cation (e.g., Li<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup>, or Cr<sup>3+</sup>) and Z cation (e.g., Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, Mg<sup>2+</sup>), respectively. The X-site is often occupied by Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, or vacancy. With dominant occupancy of Si, possible substitution by boron can also occur on the T-site. The V- and W-sites are occupied by OH<sup>-</sup>, O<sup>2-</sup>, and OH<sup>-</sup>, O<sup>2-</sup>, F<sup>-</sup>, respectively [18]. Tourmaline has fascinating properties analogous to ferroelectrics and exhibits a unique behavior with spontaneous and permanent poles, different from any other minerals in natural geologic environment. Internal dipolar field presents in the vicinity of the surface of micron-sized tourmaline with an intensity of 10<sup>6</sup>–10<sup>7</sup> V/m, which arises from the spontaneous polarization due to lack of symmetric center, mirror plane, or rotation axes oriented perpendicular to the *c* axis in the crystal [19]. In this sense, incorporation of TiO<sub>2</sub> to a polarizable mineral, tourmaline, can be envisioned to meet the challenges of both quantum efficiency and nanoparticles aggregation in TiO<sub>2</sub>-based photocatalysis. However, the limited assessments concerned to date [20–22] mainly concentrated on parameter optimization and kinetic analysis of the degradation process. Only Yeredla and Xu [19] attempted to explain the mechanism for the enhanced activity in photosplitting of water at the band bending level; nevertheless, the results obtained were highly speculative for deficiency in supportive data and characterization means available. As such, current researches are often subject to the poor interpretation for the synergistic effect as well as the ambiguous role of tourmaline, the relevant exploration with a deep investigation into the mechanism and experimental parameters is still insufficient.

In the present study, the synthesis, characterization and preliminary photoactivity evaluation of nanosized TiO<sub>2</sub> supported on tourmaline were performed with the aim to retard electron–hole recombination and to overcome nanoparticles aggregation. Bisphenol A (BPA) was chosen as a model pollutant for its ubiquity in aquatic environment and endocrine-disrupting properties associated with various adverse health effects. The tourmaline/TiO<sub>2</sub>-based heterogeneous photocatalysis was evaluated in terms of the extent of BPA degradation, and the impacts of coexisting substances. Furthermore, intermediate products of BPA degradation were identified, and for the first time, the mechanism of the tourmaline-involved photocatalysis was proposed with emphases on the charge-transfer process and the energy level

associated with band bending of TiO<sub>2</sub> based on the investigation of the photoluminescence spectra and photocurrent measurements along with the electrochemical impedance spectra and Mott–Schottky analyses.

## 2. Experimental

### 2.1. Reagents and materials

BPA was supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). *N,O*-Bis(trimethylsilyl) trifluoroacetamide with 1% of trimethylchlorosilane as the catalyst (BSTFA+TMCS, 99:1) was purchased from Regis Technologies, Inc. (Morton Grove, IL, USA). Methanol (J.T. Baker), acetonitrile and dichloromethane (Concord Technology Co., Ltd.), *t*-butanol (Guangfu Fine Chemical Research Institute), *n*-hexane (CNW Technologies GmbH) were all of high performance liquid chromatography (HPLC) grade and were used as received. All other chemicals were of analytical grade without any purification.

Tourmaline was provided by Lingshou Minerals Processing Co., Ltd., Hebei, China. Its chemical composition (wt.%) was as follows: SiO<sub>2</sub>, 37.44%; Al<sub>2</sub>O<sub>3</sub>, 29.79%; Fe<sub>2</sub>O<sub>3</sub>, 20.2%; CaO, 0.71%; Na<sub>2</sub>O, 2.18%; MgO, 0.55%; K<sub>2</sub>O, 0.14%; TiO<sub>2</sub>, 0.49%; B<sub>2</sub>O<sub>3</sub>, 0.78%, and others 7.72%.

### 2.2. Materials synthesis and characterization

Tourmaline/TiO<sub>2</sub> nanocomposites were prepared by a typical sol–gel method (Supplementary information). Generally, the catalysts were obtained through thermal treatment (80 °C for 12 h, 120 °C for 2 h) and then calcination (400 °C for 3 h) of the resulting hydrogel formed by the controlled hydrolysis of tetrabutyl titanate in ethanol/acetic acid/water solution with tourmaline. The yielded tourmaline-TiO<sub>2</sub> nanocomposites were defined as T(*x*%)–TiO<sub>2</sub>, where *x*% referred to the mass ratio of tourmaline/TiO<sub>2</sub>. The bare TiO<sub>2</sub> was also prepared by the same procedure above without the addition of tourmaline.

The morphologies of catalysts were examined using a LEO 1530VP field emission scanning electron microscopy (FE-SEM). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500 X-ray diffractometer operated at 40 kV and 100 mA. Cu–K $\alpha$  radiation ( $\lambda = 0.154$  nm) was employed for continuous scanning over a  $2\theta$  range of 3–80° with step intervals of 0.02°. Nitrogen adsorption–desorption isotherms were obtained at 77 K using an ASAP 2020/TRISTAR 3000 instrument (Micromeritics, USA). Photoluminescence (PL) spectra were recorded at room temperature on a FLS 920P Edinburgh Analytical Instrument apparatus. Photocurrent measurements were performed in a three-electrode electrochemical system (Princeton Applied Research Versa STAT 3), using a standard calomel reference electrode (SCE) and a platinum wire as a counter electrode, respectively. The chronoamperometric responses were collected in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with a 1.0 V (vs. SCE) potential bias, under simulated sunlight illumination from a 150 W xenon lamp. The cell potential was controlled using a Gamry Interface 1000 potentiostat for impedance measurements and Mott–Schottky plot analyses without light illumination. Electrochemical impedance spectra (EIS) were measured at the open-circuit voltage with oscillation amplitude of 10 mV over the frequency range from 0.2 to 10<sup>5</sup> Hz. The interface capacitance behavior under applied potential polarization (Mott–Schottky analysis) was conducted at 100 Hz with potential steps of 50 mV.

### 2.3. Photocatalytic activity evaluation

Photocatalytic tests were performed in a XPA-7 photochemical reactor (Xujiang Electromechanical Plant) which is displayed in Fig.

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