Piezo-Photocatalytic Degradation of Tetracycline by 3D BaTiO$_3$ Nanomaterials: The Effect of Crystal Structure and Catalyst Loadings

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Abstract: Piezoelectric photocatalysis improves catalytic activity by preventing photogenerated carrier recombination. Hence, three morphologies of BaTiO$_3$ (BTO) were successfully prepared for the piezoelectric photocatalytic degradation of tetracycline (TC, $C_{TC} = 40$ mg/L). The tetragonal-phase BaTiO$_3$ nanoparticles (BTO-NPs) showed the best performance in comparison with cubic-phase nanoflowers (BTO-Nf) and cubic-phase coral-like structures (BTO-Nc) under the same conditions ($C_{BTO} = 0.6$ g/L). When the loading of BTO-NPs was reduced to 0.2 g/L, the photocatalytic degradation efficiency was lowered from 64.2% to 50.1%. However, the 0.6 g/L BTO-NPs increased by only 12.8% after piezoelectricity induction. On the contrary, the BTO-NPs' degradation effect of 0.2 g/L with the piezoelectric effect was greatly improved from 50.1% to 78.0%, with an increase rate of 27.9%. As the quantity of catalyst was decreased, the increased inter-particle voids made the lattice more susceptible to deformation by external forces, producing a more pronounced piezoelectric effect. These findings indicate that crystal structure and catalyst loading are critical factors in increasing piezoelectric photocatalytic performance. This article emphasizes the application value of piezoelectric photocatalysis in degrading organic pollutants, and provides practical guidelines for optimizing its performance.

Keywords: BaTiO$_3$; morphology; piezoelectric photocatalysis; tetracycline

1. Introduction

Tetracycline (TC) is a type of broad-spectrum antibacterial with excellent inhibitory effects against Gram-negative and -positive bacteria; therefore, it is widely used in the medical and animal-husbandry industries. Because it is soluble in water, it tends to accumulate in surface water, groundwater, and soil [1–5]. Currently, TC is widely detected in a variety of environmental matrices, and ranges from ng/L to mg/L. Tetracycline was detected in three rivers in Hong Kong, with levels ranging from 30 to 497 ng/L [6]. Tetracycline was also found to be present in the marine environment when six sets of samples from the Bohai Sea’s coastal waters in China were tested [7]. Tetracycline is not only found in the aqueous environment, but also in mariculture organisms around the coastal area of the Yellow Sea [8]. Antibiotics were also commonly detected in poultry feces [9–11]. TC not only poses a significant risk to the nervous system of organisms through the food chain, but also disturbs the microbial community and ecological structure.
by affecting the composition and activity of microorganisms, which is hazardous to the aquatic environment [12].

Currently, several methods have been used to degrade TC in the aqueous phase [13–15]. Among these, photocatalytic technologies have received great attention due to their environmentally friendly nature, cost-effectiveness, and mild operating conditions, making them particularly conducive to practical applications [16–18]. However, the photogenerated carriers still suffer from the problem of easy compounding, leading to reduced photocatalytic performance. Normally, constructing heterojunctions is applied to facilitate the photogenerated carrier separation [19–22]. However, the complexity and high cost of the heterojunction material preparation strategy have limited the wide application of this method.

To overcome these constraints, piezoelectric materials with asymmetric centers are used. When an external force is applied to a piezoelectric material, it causes a measurable potential difference to be created within the material, which forms an electric field [23–25]. This electric field improves the photocatalytic activity by preventing the complexation of \( e^-\cdot h^+\) pairs, with simple and cost-effective properties [26–31]. \( \text{BaTiO}_3 \) (BTO) is a typical piezo-photocatalytic semiconductor with excellent piezoelectric, dielectric, and ferroelectric properties. Therefore, BTO-based materials are already being used in various areas of life [32]. The catalytic performance of piezoelectric materials in the degradation of pollutants is also affected by the photocatalyst crystal structure, morphology, and different auxiliary piezoelectric conditions [33]. However, in previous piezoelectric photocatalytic degradation experiments, a single ultrasonic frequency has usually been used for the degradation of pollutants (Table 1). In this experiment, three different frequencies of ultrasound were used to investigate the effect of ultrasound frequency on the performance of \( \text{BaTiO}_3 \) piezoelectric photocatalytic degradation of tetracycline.

Table 1. Overview of \( \text{BaTiO}_3 \) photocatalytic destruction of organic contaminants.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Morphology</th>
<th>Ultrasonic Frequency</th>
<th>Target Pollutants</th>
<th>Piezo-Photocatalytic Performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ce-BaTiO}_3 ) (0.1 g/L)</td>
<td>Sphere-like</td>
<td>80 kHz</td>
<td>Acid chrome blue K 10 mg/L; 100 mL</td>
<td>88.6% for 10 min Vis</td>
<td>[34]</td>
</tr>
<tr>
<td>( \text{BaTiO}_3@C ) (0.1 g/L)</td>
<td>Circular</td>
<td>40 kHz</td>
<td>Rhodamine B 10 mg/L; 100 mL</td>
<td>93% for 120 min UV</td>
<td>[35]</td>
</tr>
<tr>
<td>( \text{BaTiO}_3 ) (0.25 g/L)</td>
<td>Nanowires</td>
<td>40 kHz</td>
<td>Methyl orange 5 mg/L; 100 mL</td>
<td>98% for 100 min UV</td>
<td>[36]</td>
</tr>
<tr>
<td>( \text{BaTiO}_3/\text{g-C}_3\text{N}_4 ) (0.4 g/L)</td>
<td>Tubular</td>
<td>40 kHz</td>
<td>Tetracycline 10 mg/L; 50 mL</td>
<td>91% for 100 min Vis</td>
<td>[37]</td>
</tr>
<tr>
<td>( \text{Pt/BaTiO}_3 ) (0.25 g/L)</td>
<td>Cube-like</td>
<td>53 kHz</td>
<td>Methyl orange 10 mg/L; 80 mL</td>
<td>92.5% for 50 min UV</td>
<td>[38]</td>
</tr>
<tr>
<td>( \text{BaTiO}_3 ) (0.5 g/L)</td>
<td>Molar-like</td>
<td>24 kHz</td>
<td>Indigo carmine 10 mg/L; 100 mL</td>
<td>99.02% for 45 min UV</td>
<td>[39]</td>
</tr>
</tbody>
</table>

Ultraviolet light: UV; Visible light: Vis.

In this work, various morphologies, including granular, floral spherical, and coral-like, were prepared by simple solvent–thermal methods. Exploring the optimal conditions for TC degradation revealed that the dose and structure of the catalyst were the key factors affecting the effectiveness of piezoelectric photocatalysis, and the degradation mechanism was investigated. These findings provide a cost-effective method for removing TC from aqueous environments, and increase our understanding of the piezoelectric photocatalytic mechanism.
2. Materials and Methods

2.1. Chemicals and Reagents

All reagents, including tetracycline, tetrabutyl titanate, titanium dioxide (TiO$_2$), barium hydroxide monohydrate (Ba(OH)$_2$·H$_2$O), barium hydroxide octahydrate (Ba(OH)$_2$·8H$_2$O), sodium hydroxide (NaOH), anhydrous ethanol, ammonia, N,N-dimethylacetamide, and isopropanol, were of analytical reagent grade.

2.2. Preparation of BaTiO$_3$ Nanocrystals

Nanoparticulate BaTiO$_3$ (BTO-NPs): Firstly, 10 mmol of tetrabutyl titanate was added into a 50 mL polytetrafluoroethylene reactor, and 4 mL of anhydrous ethanol was added to make it dissolve under stirring. Next, 1.5 mL of ammonia was poured into the above solution and stirred for 20 min until completely dissolved to form a white gel. Finally, the Ba (OH)$_2$·H$_2$O white sol was mixed with the solution from the first step and stirred for 1 h. Then, the mixture was transferred into the stainless-steel reactor, and kept for 24 h at 200 °C. At the end of the reaction, the products were washed with acetic acid, H$_2$O, and ethanol, and dried at 60 °C.

BaTiO$_3$ nanoflowers (BTO-Nf): These were prepared in a two-step process:

In the first step, 18.3 mL of N,N-dimethylacetamide and 58.3 mL of isopropanol were mixed thoroughly with continuous stirring for 1 min to form an organic solvent. Then, 2.5 mL of tetrabutyl titanate and the above organic solvent were mixed and stirred continuously for 8 min. Finally, the formed suspension was transferred to a 100 mL stainless-steel reactor and kept at 200 °C for 20 h. The product was centrifuged and washed with anhydrous ethanol, then dried at 60 °C.

In the second step, 70 mL of a solvent mixture of water and ethanol with the volume ratio of 1:4 (water:ethanol) was prepared. Then, 0.3915 g of the sample prepared in the first step, 14 mmol of NaOH, and 2 mmol of Ba (OH)$_2$·8H$_2$O were sequentially added to the solvent mixture, and stirred for 30 min. The obtained solution was transferred to the 100 mL stainless-steel reactor to complete the reaction at 160 °C within 12 h. The product was washed several times with 0.1 mol/L aqueous acetic acid and H$_2$O, dried at 60 °C, and then finely powdered to obtain BaTiO$_3$ nanoflowers.

Coral-like BaTiO$_3$ (BTO-Nc): In the first step, 0.5 g of anatase titanium dioxide powder was added into 50 mL NaOH solution 10 M, and stirred for 12 h to form a white suspension. The above suspension was transferred to a 100 mL autoclave and kept at 180 °C for 12 h. The resulting precipitate was gathered by centrifuging and then repeatedly washed with water to reach pH ≈ 7. It was then dried in an oven at 60 °C for 12 h. In the second step, 0.0025 mol of Ba(OH)$_2$·8H$_2$O was added to 50 mL of H$_2$O and stirred to make it completely dissolve. Then, 0.2416 g of the material prepared in the first step was added and stirring was continued for 30 min. The suspension was transferred into the 100 mL stainless-steel reactor, and heated at 180 °C for 9 h. The precipitate was then rinsed with 0.1 mol/L formic acid and anhydrous ethanol until the pH of solution reached up to 7. It was then dried at 60 °C. The product obtained was coral-like BaTiO$_3$.

2.3. Characterization of the Samples

The crystal structure of the samples was analyzed by X-ray diffractometer (XRD), instrument model D/Max-2200 PC from Rigaku Co., Tokyo, Japan. and a DXRxi model laser micro-Raman imaging spectrometer (THEM, Los Angeles, CA, USA). The morphology of the samples and their elemental composition were characterized by scanning electron microscopy (SEM, Zeiss Sigma 300, Gesher, Germany). The specific surface area of the samples was analyzed using an ASAP-2020 specific surface area analyzer from Micromeritics (Shanghai, China) (BET). Analysis of the elements, chemical states, and valence bands of the samples was carried out by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA). The UV–Vis absorption spectra of the catalysts were measured by Shimadzu UV 2600 spectroscopy (Kyoto, Japan) using barium sulfate as the reference.
material. This instrument was also used to determine the absorbance of TC. Photoluminescence (PL) spectra were recorded using an Edinburgh, UK FS5 fluorimeter (Edinburgh, UK). The electrochemical analyzer of Shanghai Chenhua Instrument Co (Shanghai, China) was used to explore the electrochemical properties. A Bruker E500 Instrument (Billerica, MA, USA) was used for electron spin resonance (ESR) measurements.

2.4. Piezo-Photocatalytic Activity Tests

Photocatalytic, piezocatalytic, and piezo-photocatalytic activities of as-prepared samples were evaluated for decomposing TC under different conditions. The light source was a 300 W xenon UV lamp (CEL-HXF300, Ceaulight, Beijing, China). BaTiO$_3$ powders with different morphologies and qualities were added to 50 mL of TC solution (40.0 mg·L$^{-1}$), and a small stirrer with a rotational speed of 500 rpm/min was sealed and placed in a water bath ultrasonic generator with controllable frequency (KQ2200B, Hao Mei, Kunshan, China; power: 100 W). The water temperature was maintained at 20–25 $^\circ$C using a circulating water stream, and ultrasonication was performed at 45, 80, and 100 kHz. Before the catalytic reaction, the adsorption equilibrium was attained after 30 min of nonstop stirring in the dark. Within 10 min of the reaction, 3 mL of the aliquot suspension was removed and filtered through a 0.45 $\mu$m filter membrane, and then the TC absorbance was determined by the UV–Vis spectrophotometer. Three replications were performed for each set of experiments.

3. Results

3.1. Morphology and Elemental Composition

Figure 1 illustrates the overall microscopic morphology and elemental distribution of different BTO samples. The BTO-NP sample presented a large number of square nanoparticles with a size of about 50 nm, a regular morphology, a smooth surface, and good dispersion (Figure 1a). The BTO-Nf sample was a three-dimensional spherical nanoflower consisting of two-dimensional nanosheets with thicknesses ranging from 5 to 10 nm and diameters ranging from 400 to 500 nm; meanwhile, there were some globular BaTiO$_3$ nanoparticles on the surfaces of the flowers and the whole surface could be slightly roughened (Figure 1b). A possible reason for this is that the stable BaTiO$_3$ nanoparticles could be readily synthesized before the reaction conditions shifted towards the formation of optimal BTO-Nf. The BTO-Nc was a coral-like BaTiO$_3$ sample with regular morphology and a smooth surface. It consisted of short rods of BaTiO$_3$ with diameters of 60–100 nm (for the long rods) and 45–60 nm (for the short rods) (Figure 1c). The energy dispersive spectrometer (EDS) elemental mapping analysis results are shown in Figure 1a–c, where Ba, Ti, and O elements are uniformly distributed in all BTO samples with any morphology, and the atomic ratio of Ba:Ti:O $\approx$ 1:1:3 is reasonable based on the structural stoichiometry. This provides logical preliminary evidence that nanoparticulate, spherical nanoflower, and coral-like BTO samples had been successfully prepared. The specific surface area of the three materials was to be determined, and their nitrogen adsorption desorption isotherms are shown in Figure 2. All three samples satisfied the criteria for type IV isotherms [40]. Among them, the specific surface area of BTO-Nf was the largest, which proved that it could adsorb more TC in the reaction, followed by the BTO-NPs, and then BTO-Nc, with the smallest surface area.

To acquire more precise data regarding the elemental composition and valence of the materials, the three BTO materials were further analyzed by XPS. The XPS data for the BTO samples are shown in Figure 3 and Table 2, and the peaks in Figure 3a indicate the main peaks of the Ba, Ti, and O elements. The Ba high-resolution XPS spectra in Figure 3b display two peaks around at 778 and 794 eV, which are recognized as being for Ba 3d$^{5/2}$ and Ba 3d$^{3/2}$, respectively. The green peaks 1 originated from surface Ba atoms, and the blue peaks 2 are attributed to internal Ba atoms, while both peaks 1 and 2 belong to the peaks of Ba$^{2+}$ [41,42]. The peaks of Ti 2p$_{3/2}$ and 2p$_{1/2}$ of all samples in Figure 3c are located near 458 and 464 eV, respectively, which proves the presence of Ti$^{4+}$ [42]. The O 1s high-resolution
spectra, as shown in Figure 3d, can be fitted into two peaks at binding energies of 529 and 530 eV, respectively, which are assigned to lattice oxygen ($O_{\text{lat}}$) and surface adsorbed oxygen ($O_{\text{ads}}$), respectively [43]. XPS further demonstrated the successful preparation of BTO materials.

![Figure 1. SEM and EDS mapping of BaTiO$_3$ samples with different morphologies. (a) BTO-NPs, (b) BTO-Nf, and (c) BTO-Nc.](image)

![Figure 2. Nitrogen adsorption–desorption isotherms of the prepared samples.](image)
near 458 and 464 eV, respectively, which proves the presence of Ti $^{4+}$ [42]. The O 1s high-resolution spectra, as shown in Figure 3d, can be fitted into two peaks at binding energies of 529 and 530 eV, respectively, which are assigned to lattice oxygen (O$_{lat}$) and surface adsorbed oxygen (O$_{ads}$), respectively [43]. XPS further demonstrated the successful preparation of BTO materials.

Table 2. The XPS data of all BTO samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ba 3d (eV)</th>
<th>Ti 2p (eV)</th>
<th>O 1s (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3d$_{5/2}$</td>
<td>3d$_{3/2}$</td>
<td>2p$_{3/2}$</td>
</tr>
<tr>
<td>BTO-Nps</td>
<td>779.91</td>
<td>795.34</td>
<td>794.06</td>
</tr>
<tr>
<td>BTO-Nf</td>
<td>779.94</td>
<td>795.25</td>
<td>793.93</td>
</tr>
<tr>
<td>BTO-Nc</td>
<td>779.82</td>
<td>795.31</td>
<td>794.03</td>
</tr>
</tbody>
</table>

3.2. Crystal Structure

In order to determine the crystal structure of the catalysts, XRD patterns were examined for the three materials. The characteristic diffraction peaks of BaTiO$_3$ nanomaterials corresponded well to the standard BaTiO$_3$ diffraction files (Figure 4). Accordingly, BTO-Nf and BTO-Nc were matched to the BaTiO$_3$ cubic crystal structure (#31-0174, BaTiO$_3$, cubic) [44]. The peaks at 21.9, 31.4, 38.6, 44.9, 50.6, 55.8, 65.4, 74.4, and 78.5° were assigned to the BaTiO$_3$ crystals planes of (100), (110), (111), (200), (210), (211), (220), (300), (310), and (311) crystal faces, respectively [45]. The BTO-NPs’ diffraction peak split into two peaks at 45° with a large peak spacing, which corresponded to the BaTiO$_3$ (002) and (200) crystal planes (#05-0626, BaTiO$_3$, tetragonal). This denotes an asymmetric elongation along the c-axis, proving that this sample was more prone to indicate a spontaneous polarization and superior piezoelectric potential [44]. Although BTO-Nc and BTO-Nf did not have distin-
guishable characteristic peaks at $45^\circ$, their diffraction peaks were shifted to a higher angle, which means that the tetragonal phase BTO may have been present in the material, but at a lower dose [44]. The occurrence of tetragonal distortion is much clearer in the Raman spectra (Figure 5). According to the Raman active phonon, the symmetry of the tetragonal phase crystals was $3A_1 + B_1 + 4E$. The presence of the $[E, B_1(\text{TO} + \text{LO})]$ mode at $307 \text{ cm}^{-1}$ in the Raman spectra clearly demonstrates the formation of the tetragonal phase [46–48]. It also shows that small amounts of the tetragonal crystal phase existed in the BTO-Nc and BTO-Nf samples, which could be polarized to generate piezoelectric potentials.

Figure 4. XRD patterns of BTO samples with different morphologies.

**Figure 5.** Raman spectra of BTO samples with different morphologies.

### 3.3. Optical Properties

The photoelectric properties of the materials were investigated by UV–Vis absorption spectroscopy, photoluminescence spectroscopy, photocurrent, and electrical impedance. As shown in Figure 6a, all three materials were highly absorbent to UV light, and the BTO-NPs possessed the highest absorbance (200–400 nm) compared to the other morphologies. The bandgap energy of the semiconductors was calculated based on the equation $\alpha h\nu = A(h\nu-E_g)^n/2$, where $n = 1$ for direct bandgaps and $n = 4$ for indirect bandgaps [48]. Accordingly, the band gaps of the BTO-NPs, BTO-Nf, and BTO-Nc were 3.03, 3.08, and 3.23 eV, respectively (Figure 6b). Minor changes in the bandgap were caused by the different morphologies and sizes of the as-prepared samples [49]. The relatively small bandgap
of the BTO-NPs demonstrates that they had a higher tendency towards harvesting the visible-light photons which explains their improved photoactivity [50].

Figure 6. (a) UV–Vis absorption spectrum and (b) bandgap evaluation curves of BTO samples.

Carrier separation was studied using photoluminescence spectroscopy, photocurrent, and electrical impedance (Figure 7). The BTO-NPs had the lowest PL intensity among the three materials, and possessed the highest electron-hole separation ability (Figure 7a). The BTO-NPs also had the highest current density (Figure 7b), a result in agreement with the photoluminescence analysis observations. The electrochemical impedance spectra of BTO samples are shown in Figure 7c, where the radius of curvature for BTO-NPs is the smallest, indicating that BTO-NPs had the highest charge separation efficiency. In summary, BTO-NPs exhibited an excellent electron-hole pair separation and transfer ability compared to the others, and their lower recombination rate made them more favorable for the degradation of TC pollutants.

Figure 7. (a) PL spectra, (b) transient photocurrent response patterns, and (c) electrochemical impedance spectra of BTO samples.

3.4. Piezo-Photocatalytic Performance

The catalytic performance of the BTO samples for degrading the TC solution under experimental conditions including light, ultrasound, and light with different ultrasound frequencies was explored (Figure 8a–c). BTO-NPs had the best piezo-photocatalytic degradation performance. The dark adsorption efficiencies were 7.9%, 19.4%, and 4.1%, for BTO-NPs, BTO-Nf, and BTO-Nc, respectively. The maximum adsorption capacity of BTO-Nf is due to it having a larger specific surface area than BTO-NPs and BTO-Nc. Under 45 kHz sonication only, BTO-NPs degraded 12.3% of the pollutant, which was higher than the figures obtained for BTO-Nf (4.8%) and BTO-Nc (9.9%), indicating that BTO-NPs performed a better piezoelectric degradation of TC. The TC degradation efficiencies of BTO-NPs, BTO-Nf, and BTO-Nc after 60 min of irradiation were only 64.2, 65.3, and 52.7%,
3.4. Piezo-Photocatalytic Performance

The catalytic performance of the BTO samples for degrading the TC solution under photocatalysis and piezoelectric photocatalysis, and it can be seen that the BTO-NPs’ piezoelectric photocatalytic effect was significantly enhanced. This was attributed to the fact that the BTO-NPs had an obvious tetragonal crystalline phase and Ti$^{4+}$ in BTO nanoparticles in the tetragonal crystalline phase was displaced along the c-crystal-axis direction to form an asymmetric crystal structure, which was more easily polarized after ultrasound assistance and promoted the separation of electron-hole pairs, thus enhancing the piezoelectric photocatalytic degradation of TC. BTO-Nf and BTO-Nc belong to the cubic crystalline phase. The cubic crystalline phase of the BTO material Ti$^{4+}$ is located in the body center of the crystalline cell, which is a centrosymmetric material; hence, there is no spontaneous polarization, and, therefore, a piezoelectric effect cannot be produced [52,53]. This evidently supports the statement that nanomaterial crystal structure is a key factor influencing the effectiveness of piezoelectric photocatalysis.

![Figure 8](image)

Figure 8. Piezoelectric photocatalytic degradation performance of BTO with different morphologies. (a) BTO-NPs, (b) BTO-Nf, (c) BTO-Nc, and (d) performance comparison chart.

The dosage of materials can significantly affect the performance of wastewater treatment approaches. In order to find the optimum dosage, the BTO-NP sample was tested with different amounts of the catalyst and the results are shown in Figure 9a,b. When the catalyst dosage was reduced to 20 mg (0.4 g/L) and 10 mg (0.2 g/L), the photocatalytic degradation of BTO-NPs was 55.9% and 50.1%, respectively, and the piezoelectric photocatalytic degradation efficiency was 66.3% and 78.0%, respectively, implying an improvement of 10.4% and 27.9% for the aforementioned dosages. It was found that with the decrease in catalyst dosage, the photocatalytic degradation efficiency gradually decreased. This was...
because the number of active radicals produced decreased. However, the degradation effect of high-dose BTO-NPs, which had the best photocatalytic degradation effect, was not significantly improved after piezoelectricity induction, and was only 12.8%. In contrast, the degradation effect of low-dose BTO-NPs with poor photocatalytic effect after the piezoelectric effect was greatly improved, from 50.1% to 78.0%, an increase of 27.9%. This may have been due to the fact that the small amount of catalyst increased the inter-particle voids, making the catalyst more susceptible to deformation under pressure, resulting in a pronounced piezoelectric effect. Figure 9c compares the enhanced performance of piezoelectric photocatalytic degradation of different concentrations of BTO-NPs over photocatalytic degradation only. While there was no significant difference in the degree of performance enhancement between 0.6 g/L and 0.4 g/L of BTO-NPs, 0.2 g/L of BTO-NPs significantly improved the performance by 27.9%. Based on our findings, the best experimental conditions for the BTO-NP sample to degrade TC were the dosage of 0.2 g/L and an ultrasonic frequency of 45 kHz, demonstrating that the tetragonal phase BTO-NPs can exhibit better piezo-photocatalytic performance of TC degradation at lower dosages.

Figure 9. TC degradation curves with 0.4 g/L (a) and 0.2 g/L of the catalyst (b). Percentage increase in photocatalytic degradation of different amounts of BTO-NPs after ultrasonication (c). The results of cycling experiments of BTO-NPs with 0.2 g/L (d). XRD and SEM patterns before and after degradation (e).
In order to investigate the stability of the catalysts, recycling experiments were carried out, in which the used materials were washed with 10% acetic acid, ultrapure water, and ethanol, respectively, and then dried and reused (Figure 9d). The catalyst powder was repeatedly washed, gathered by centrifuging, and dried at the same temperature, after each run of the reaction. From the results, the degradation performance decreased smoothly from 78.0% to 71.3% after three cycles. After the fourth cycle, the degradation efficiency decreased meaningfully, from 71.3% to 61.4%, which might have been due to the inactivation of the surface reactive sites after multiple reactions. Comparison of XRD patterns and SEM before and after degradation revealed no significant changes in crystal structure or morphology (Figure 9e), showing that BTO-NPs can ensure stable operation within three cycles and have the potential to degrade pollutants in practical applications.

3.5. Mechanism Exploration

Determining the position of the valence and conduction bands is necessary for mechanistic investigations. The valence band position was obtained from XPS valence band spectroscopy as 2.15 eV (Figure 10a), and, by using the relationship between the conduction band and the valence band \( E_g = E_{VB} - E_{CB} \) \[54\], the position of the conduction band was calculated to be -0.88 eV. The redox potentials of \( e^- \) reacting with \( O_2 \) to produce \( \cdot O_2^- \), and \( h^+ \) reacting with \( H_2O \) to produce \( \cdot OH \) were satisfied \[29,55\]. The effect of active species on the degradation process was explored by trapping the corresponding active species with a quencher (Figure 10b). \( \cdot O_2^- \), \( \cdot OH \), \( ^1O_2 \), \( e^- \), and \( h^+ \) were captured with p-benzoquinone (PBQ), tert-butanol (TBA), furfuryl alcohol (FA), AgNO\(_3\), and KI, respectively \[56–58\]. The addition of PBQ, FA, and AgNO\(_3\) significantly decreased the piezoelectric photocatalytic degradation efficiency, suggesting that \( \cdot O_2^- \) and \( ^1O_2 \) are of great importance during the degradation of tetracycline. After adding TBA and KI to the reaction system, catalytic activity was reduced by 8.4% and 14.6%, respectively, indicating that part of \( h^+ \) can also react with \( H_2O \) in the medium to generate \( \cdot OH \) to participate in the degradation process. In order to determine the presence of the three active species \( \cdot O_2^- \), \( ^1O_2 \), and \( \cdot OH \), electron paramagnetic resonance (EPR) analysis was carried out with the aid of DMPO and TEMP, as shown in Figure 10c–e. All clearly show the characteristic peaks of the three active species, and the detection results were consistent with the quenching test results.

A plausible TC degradation mechanism over the BTO-NP piezoelectric photocatalyst was suggested based on the abovementioned findings (Equations (1)–(9) and Figure 11). The polarized electric field caused the oxidation and reduction reactions to occur in two different directions, inhibiting the combination of \( e^- \) and \( h^+ \), which demonstrated a synergistic effect of ultrasound and light resulting in an improved catalytic TC degradation under the mild conditions. Under light, \( e^- - h^+ \) pairs are generated in the conduction band and valence band of BTO-NPs (Equation (1)). When the ultrasound (US) source was turned on, BTO-NPs were deformed by the force, causing the conduction and valence bands to tilt, forming a piezoelectric potential on the surface through inducing a strong polarized electric field consisting of negatively charged regions (C\(^-\) domain) and positively charged regions (C\(^+\) domain) (Equation (2)) \[59\]. As a result, the \( e^- \) and \( h^+ \) were easily attracted to the positively and negatively charged regions, respectively (Equations (3) and (4)) \[60\]. The \( e^- \) and \( O_2 \) reacted to form \( \cdot O_2^- \), and \( \cdot O_2^- \) continued to be attacked by \( e^- \) generated by piezoelectricity and photocatalysis to generate \( ^1O_2 \) (Equations (5) and (6)). The \( h^+ \) and \( H_2O \) reacted to form \( \cdot OH \) and \( H^+ \) (Equation (7)) \[61\]. The generated radicals attacked the TC chemical structure to transform it into products (Equations (8) and (9)). This mechanism is equally applicable to other similar piezoelectric photocatalytic materials.

\[
\text{BTO} + \text{Light} \rightarrow h^+_{VB} + e^-_{CB} \quad (1)
\]

\[
\text{BTO} + \text{US} \rightarrow \text{C}^-\text{ domain} + \text{C}^+\text{ domain} \quad (2)
\]
e\(^-\)\(_{\text{CB}}\) → C\(^+\) domain \hspace{1cm} (3)

h\(^+\)\(_{\text{VB}}\) → C\(^-\) domain \hspace{1cm} (4)

e\(^-\) + O\(_2\) = \cdot O\(_2\)\(^-\) \hspace{1cm} (5)

e\(^-\) + \cdot O\(_2\)\(^-\) → \text{^1}O\(_2\) \hspace{1cm} (6)

h\(^+\) + H\(_2\)O = \cdot OH + H\(^+\) \hspace{1cm} (7)

\cdot OH + TC → products \hspace{1cm} (8)

\cdot O\(_2\)\(^-\) + \text{^1}O\(_2\) + TC → products \hspace{1cm} (9)

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Figure 10. VB–XPS spectra of BTO-NPs (a). The results of active species quenching tests (b), and the ESR signals for: \cdot O\(_2\)\(^-\) (c), \text{^1}O\(_2\) (d), and \cdot OH (e).
Figure 11. Piezo-photocatalytic degradation mechanism of TC antibiotic over BTO-NPs.

4. Conclusions

Three-dimensional BTO nanomaterials with controllable morphology were successfully prepared to degrade TC pollutants through a piezo-photocatalytic system. The degradation capability of tetragonal-phase BTO-NPs, cubic-phase BTO-Nf, and cubic-phase BTO-Nc was improved after piezoelectricity induction. The higher activity of BTO-NPs, as the best catalyst, was attributed to their tetragonal crystalline phase, which can be easily polarized compared to the other phases and promoted the efficient separation and migration of photogenerated charge carriers, leading to an improvement in the overall piezo-photocatalytic activity. The effect of catalyst dosage on the piezo-photocatalysis was investigated and the results indicated that by decreasing this parameter to 0.2 g/L at an ultrasonic frequency of 45 kHz, the degradation efficiency was enhanced to 78.0%, 27.9% higher than that of under light alone, supporting the effective coupling of piezoelectricity and photocatalysis. In conclusion, our findings demonstrate that, in addition to the crystalline phase, catalyst dosage is a key factor in controlling the efficiency of piezo-photocatalytic activity. This work provides a feasible strategy for achieving better removal efficacy of nanoparticulated systems through the coupling of piezoelectricity and photocatalysis, which, as a green technology, benefits from specific economic and environmental impacts.

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