Thin Films (FTO/BaTiO₃/AgNPs) for Enhanced Piezo-Photocatalytic Degradation of Methylene Blue and Ciprofloxacin in Wastewater

Daniel Masekela, Nomso C. Hintsho-Mbita, Bulelwa Ntsendwana, and Nonhlangabezo Mabuba*

ABSTRACT: In this study, we investigate the ability of barium titanate/silver nanoparticles (BaTiO₃/AgNPs) composites deposited on a fluorine-doped tin oxide (FTO) glass using tape-casting method to produce piezoelectric thin film (FTO/BaTiO₃/AgNPs) for piezocatalytic, photocatalytic, and piezo-photocatalytic degradation of methylene blue (MB) and ciprofloxacin (CIP) in wastewater. The prepared piezoelectric materials (BaTiO₃ and BaTiO₃/AgNPs) were characterized using XRD, SEM, TEM, EDS, UV-DRS, TGA, PL, BET, EIS, and chronocoulometry. The UV-DRS showed the surface plasmon resonance (SPR) of Ag nanoparticles on the surface of BaTiO₃ at a wavelength of 505 nm. The TEM images revealed the average Ag nanoparticle size deposited on the surface of BaTiO₃ to be in the range of 10–15 nm. The chronocoulometry showed that the photoreduction of silver nanoparticles (AgNPs) onto BaTiO₃ (BTO) resulted in a piezo-electrochemical current enhancement from 0.24 to 0.38 mA. The composites (FTO/BaTiO₃/AgNPs) achieved a higher degradation of MB and CIP when the photocatalysis and piezocatalysis processes were merged. Under both ultrasonic vibration and UV light exposure, FTO/BTO/AgNPs degraded about 72 and 98% of CIP and MB from wastewater, respectively. These piezoelectric thin films were shown to be efficient and reusable even after five cycles, suggesting that they are highly stable. Furthermore, the reactive oxygen species studies demonstrated that hydroxyl radicals (·OH) were the most effective species during degradation of MB, with minor superoxide radicals (·O₂⁻) and holes (h⁺). From this study, we were able to show that these materials can be used as multifunctional materials as they were able to degrade both the dye and pharmaceutical pollutants. Moreover, they were more efficient through the piezo-photocatalytic process.

1. INTRODUCTION

The release of organic contaminants from industries into wastewater contributes to water pollution.¹ Some of these organic contaminants include organic dyes such as methylene blue (MB), methyl orange (MO), and Rhodamine B, to mention a few. These organic dyes are used as coloring agents from various industries such as textile, paper printing, cosmetics, and pharmaceuticals and thus are mostly common in industrial waste water.²−⁴ Therefore, the consumption of wastewater containing these organic dyes can cause some detrimental effects to living organisms including human beings and aquatic living species. These dyes are extremely toxic, non-biodegradable, and carcinogenic.⁵ Of major concern, methylene blue is one of the most widely used dyes in the textile industry for a variety of applications. The production of these dyes from textile industries has been estimated to be roughly 10,000 tons per year, with about 100 tons being released into industrial wastewater.⁶−⁸ According to international standards, the allowed permissible chemical oxygen demand (COD), biological oxygen demand (BOD), and concentration color are <50 mg/L, <30 mg/L, and 1 mg/L, respectively.²,⁶,⁹,¹⁰ The consumption of water containing low concentrations of MB (even below 1 ppm) can result in extreme sweating, acute renal failure, liver damage, skin irritation, confusion, and dyspnea.¹¹−¹⁴ With the rapid growth of industries, there is an expected release of more and more tons of MB dye in the environment. Therefore, it is necessary to treat industrial wastewater contaminated with these dyes before they are released into the environment. Other organic contaminants, which are highly hazardous, include pharmaceutical pollutants such as ciprofloxacin, tetracycline, sulfamethoxazole, and penicillin.¹⁵,¹⁶ These antibiotics are known to treat bacterial infections.¹⁷ Ciprofloxacin (CIP) is the most widely prescribed antibiotic for the treatment of skin infections, sexually transmitted diseases, and cancer.¹⁷,¹⁸ In hospitals, a daily water use of 260–940 L containing CIP up to 101 g/L per bed is typical. The amount of CIP pollution detected in surface water and subsurface water was under the concentration range of <1 μg/L, according to the figures provided by health communities.¹⁷ However, high CIP concentrations of 150 and 50 μg/L, which are extremely harmful to human health is found in hospitals and drug manufactures, respectively.¹⁷,¹⁹ As
a result, it is critical for clinical wastewater to be treated before reaching community facilities for consumption or utilization. Several methods have been employed to remove organic pollutants; these include adsorption, chlorination, reverse osmosis, and membrane filtration. Unfortunately, most have been shown to be ineffective in completely removing organic pollutants from industrial wastewater. For instance, the adsorption method, which involves transfer of adsorbate (organic pollutants) onto adsorbent materials such as activated carbons, requires additional disposal of the adsorbate from the adsorbent after treatment, thus generating secondary pollution. Therefore, this makes this technique not suitable for elimination of organic waste pollutants. Another popular disinfection or removal technique is chlorination, which involves chemical reactions between organic pollutants and chlorine to produce some harmful toxic byproducts such as trihalomethanes (THMs) and haloacetic acid (Haa). On the other hand, electrochemical advanced processes (EAOPs), photocatalysis, and piezocatalysis have been reported to be the most suitable methods for the degradation of recalcitrant organics since they do not generate any secondary pollution. These methods use generated reactive oxygen species such as hydroxyl, superoxide, and hydrogen peroxy radicals to break down organic pollutants into less harmful byproducts such as water (H₂O) and carbon dioxide (CO₂). However, EAOPs require an external electric supply; thus, high energy consumption is used. Mostly, non-renewable energy sources such as fossil fuels are utilized as a source of electric power. The electric power derived from burning these fossil fuels tends to be associated with the emission of greenhouse gases such as CO₂, CH₄, and N₂O, which are harmful to the atmosphere. To sustain the EOAPs, renewable sources are required as a source of electric power. Electric power derived from renewable sources offers production of clean energy.

Piezoelectric materials are known to be energy harvesters and have been used in a wide range of applications, commonly as sensors or actuators. These materials are commonly known for their ability to produce electricity called piezoelectricity under mechanical vibration. Some researchers have shown that these materials can drive electrochemical reactions when immersed in water under ultrasonic vibration or any form of mechanical vibration. Recently, piezomaterials (PZM) have been employed to power electrocatalytic reactors. A lot of research nowadays is based on using PZM as self-powered electrocatalytic reactors for various applications including bacterial disinfection, sensing, and wastewater treatment. In wastewater treatment, a majority of piezocatalysts such as BiFeO₃, BaTiO₃, ZnO, MoS₂, WS₂, ZnSnO, BiOCl, PbTiO₃, PbZr₀.₅Ti₀.₅O₃, NaNbO₃, and Bi₂Ti₃O₁₂ are used as self-powered electrocatalytic reactors for the degradation of organic pollutants. In most cases, these piezocatalysts were applied in powdered form. Even though powered piezocatalysts offer full contact with the solution, they are not easily recovered from solution and thus they suffer from poor reusability. In order to enhance the reusability of piezocatalysts, many studies tend to deposit these bulky materials on soft substrate materials to produce piezo-thin films. Most of the piezocatalysts are considered as poor electrocatalysts and generally have a wide band gap. Several studies have shown that combining these materials with excellent electroactive materials such as noble metals (Au, Pt, Ag, and Pd) can enhance their electrochemical performance and also reduce their band gap. Another advantage of doping these piezocatalysts with noble metals in photocatalysis is to hinder or reduce rapid recombination of photogenerated electron–holes and further enhance photocatalytic performance. Amongst those noble metals, platinum group metals, including platinum (Pt) especially, have been reported to be the most effective catalysts to promote an electrochemical redox reaction; however, their practical application is limited due their high cost. Silver nanoparticles (AgNPs) are a non-platinum group metal (PGM) and thus are less expensive compared to other metals. Recently, several researchers have been deviating from the use of PGMs to AgNPs as an alternative cheap electrocatalyst. There are several studies that have been conducted were various semiconductors were doped with Ag nanoparticles including ZnO, TiO₂, Bi₂WO₆, BiVO₄, ZnTiO₃, MoS₂, and BaTiO₃ for photocatalytic degradation of organic pollutants. To our best knowledge, the performance of BTO/AgNPs as a piezo-thin film has not been yet reported for piezo-photocatalytic degradation of MB and CIP from wastewater.

Thus, in the current study, we report on a hydrothermally synthesized BTO as a lead-free piezoelectric material doped with photoreduced AgNPs. The novelty of this work can be observed from the modification of BTO using AgNPs, and the powder composites (BTO/AgNPs) were tape- pasted on a FTO glass substrate to form a reusable piezoelectric thin-film electrode. Furthermore, the novel piezoelectric thin-film electrode (FTO/BTO/AgNPs) was employed as a self-powered electrocatalytic reactor for piezoelectrocatalytic degradation of MB and CIP. It further assisted the piezoelectrocatalytic performance of piezo-thin films with visible-light irradiation. Therefore, this research project provides the future possible applications of piezo-thin films for wastewater treatment.

### 2. EXPERIMENTAL MATERIALS AND METHODS

#### 2.1. Reagents Used

The chemicals used in this work including barium chloride dihydrate (BaCl₂·2H₂O), titanium dioxide (TiO₂), sodium hydroxide pellets (NaOH), PVDF (polyvinylidene difluoride), NMP (N-methyl-2-pyrrolidone), tert-butyl alcohol (t-BuOH), hydrochloric acid (HCl), silver nitrate (AgNO₃), p-benzoquinone, and disodium salt of ethylenediaminetetraacetate (EDTA) were obtained from Sigma Aldrich (South Africa). To our best knowledge, the performance of BTO/AgNPs as a piezo-thin film has not been yet reported for piezo-photocatalytic degradation of MB and CIP from wastewater.

#### 2.2. Preparation of Piezoelectric Thin Films (FTO/BTO) and (FTO/BTO/AgNPs)

Barium titanate was synthesized according to a hydrothermal method. Here, an amount of 0.24 g (TiO₂) was dissolved in 10 mL of deionized water (DW), and the solution was purged by nitrogen gas and stirred for 10 min. Thereafter, 1.22 g of BaCl₂·2H₂O was added to the above solution and continued to stir for another 10 min. From the above mixed solution, a small amount of NaOH (0.20 g) was further added and the solution mixed was stirred for an additional 10 min. The solution mixture was transferred into a Teflon-autoclave and heated in an oven at 170 °C for 24 h to obtain BaTiO₃ (BTO) powder. The resultant BTO powder was washed with 50/50% of ethanol and deionized water, and the powder was further dried at 70 °C overnight.

To obtain BTO/AgNPs, silver nanoparticles were synthesized in the presence of BTO. A green method (photo-reduction) was used to deposit AgNPs on the surface of BTO. Typically, an amount of 0.25 g of the hydrothermally synthesized BTO was dispersed in 25 mL of 0.0100 M AgNO₃.
Thereafter, the solution was stirred for 10 min in the dark to form a homogeneous mixture. After 10 min, the homogeneous mixture was exposed to visible light (70 W) under constant stirring for 30 min to obtain a gray powdered product (BTO/AgNPs).

A method by Dr. Blade was used for the preparation of piezo-thin-film electrodes of FTO/BTO and FTO/BTO/AgNPs. Here, the resultant BTO (50 mg) was mixed with 90.0 μL of NMP and a small amount of PVDF (5 mg) as a binding agent and the solution mixture was deposited on the FTO glass substrate (2 cm × 2 cm) via tape-casting to obtain piezoelectric thin films (FTO/BTO) with a thickness of 93.66 μm. Thereafter, an oven was used to dry the thin film at 80 °C overnight. In order to obtain FTO/BTO/AgNPs thin films, the same procedure as above was followed, except that BTO was replaced with BTO/AgNPs. The schematic of the photo-reduction synthesis method and thin film fabrication is summarized in Scheme 1.

Scheme 1. Fabrication of Piezo-Thin Films

2.3. Material Characterization and Analysis. The identification of phases, crystallinity, and purity of the powdered materials were confirmed by X-ray diffraction (XRD, Ultima IV-Rigaku, Japan). The field emission-scanning electron microscopy (FE-SEM, Zeiss Crossbeam 540, United Kingdom) coupled with energy dispersive X-ray spectroscopy (EDS) was used for the determination of morphological structures, particle sizes, and elemental composition. The high-resolution images of the materials were obtained using transmission electron microscopy (TEM, JEM-2100, Japan). A UV–vis spectrophotometer (Agilent Technologies Cary 60 UV–vis, Malaysia) was used to study the optical properties of the synthesized materials and the degradation analysis of MB and CIP, while their total organic carbons were recorded using a TOC analyzer (Lotix-tekmar 15-1600-00, United States). The confirmation of functional groups was determined in a Fourier-transform infrared spectroscopy (FTIR, Bruker-Alpha, Germany). Ther- mal gravimetric analysis (TGA, Hitachi-STA7200RV, Japan) was used to investigate the thermal stability of the materials. To determine the rate of hole and electron recombination, a fluorescence spectrophotometer (LS 45, United Kingdom) was employed to measure the photoluminescence (PL) spectrum of the materials at 400 nm excitation. Brunauer–Emmett–Teller analysis (BET, Micromeritics TriStar II Plus, Germany) was employed to study the specific surface area of the prepared piezocatalyst. Electrochemical measurements including piezoelectrochemical response and electrochemical impedance spectroscopy (EIS) were performed using an Autolab Potentiostat (PGSTAT204, Netherlands). The prepared piezo-thin films acted as working electrodes, whereas Ag/AgCl (3.00 M KCl) and platinum wire were used as the reference electrode and contour electrode, respectively.

2.4. Piezocatalytic and Piezo-Photocatalytic Degradation Experiments. To study the piezocatalytic degradation of MB, the prepared piezoelectric thin films were immersed in 75.0 mL of solution containing 5 mg/L MB. The MB solution containing the thin films was stirred for 10 min to reach an adsorption–desorption equilibrium. Ultrasonic vibration (UP400St Ultrasonic processor probe, Hielscher (Germany), 24 kHz) was used to trigger the piezo-electrochemical reaction in the absence of light using the following setup (Figure S1). The temperature of the aqueous solution was maintained at 25 ± 1 °C with assistance of an ice water bath. For piezo-photocatalytic experiments, ultrasonic vibration and light were employed to trigger the piezo-photocatalytic reaction for the degradation of MB. The distance between the quartz beaker glass containing MB solution and light source (LD3001, 70 W) was 10 cm. The piezo-photocatalytic degradation of MB solution was monitored using UV–vis spectroscopy at a wavelength of 653 nm. After every 30 min interval, about 3 mL of the aliquot was taken from the MB solution for analysis. The effects of pH, ultrasonic power, and trapping agents on piezo-photocatalytic degradation were also investigated. The pH solution of MB was adjusted using 1.0 M NaOH and HCl from 2 to 10, and the ultrasonic power applied ranged from 10 to 30 W. In order to investigate the stability of the prepared piezo-thin-film composite, the piezo-thin film was dried at room temperature for 24 h after every piezo-photocatalytic degradation of MB for further re-usability. The chronoamperometry studies were conducted to investigate the piezoelectricity of the prepared thin films (FTO/BTO and FTO/ BTO/AgNPs). Sodium sulfate (Na2SO4, 0.10 M) was used as a supporting electrolyte solution at neutral pH (7.0). Electrochemical impedance spectroscopy was conducted in 5 mM solution of [Fe(CN)6]3−/4− containing 0.10 M KCl; the external bias voltage, amplitude, and frequency range applied were 0.23 V, 0.01 V, and 0.1–100 kHz, respectively.

3. RESULTS AND DISCUSSION

3.1. Structural, Crystallinity, and Phase Identification Studies. To determine the phases found on the prepared composites and to confirm their formation, Figure 1 shows the X-ray diffraction patterns of TiO2, BTO, and BTO/AgNPs.
dihydrate (BaCl$_2$·2H$_2$O) is 113 °C. When barium chloride dihydrate (BaCl$_2$·2H$_2$O) reacted with titanium dioxide (TiO$_2$) through a hydrothermal reaction (conditions: 170 °C for 24 h), the contents were heated at temperatures above the melting point (>113 °C), and dissolution/melting of barium dihydrate in NaOH solution might have completed, thus resulting in BaTiO$_3$ precipitates. The splitting of the peaks at 2θ values between 45 and 45.2° confirmed the formation of the tetragonal BTO structure. The obtained results were in agreement with the reported literature. Moreover, it can be observed that there were no additional peaks for AgNPs on the composites; this could be due to the uniform dispersion of Ag NPs on the surface of tetragonal-BTO and the concentration of accumulated AgNPs on BTO being below the detection limit of powder X-ray diffraction (PXRD). To show and confirm the deposition of AgNPs on the surface of BTO, more characteristic techniques including SEM, TEM, and EDS were employed.

3.2. Morphological and Elemental Analysis Studies. The FE-SEM images of BTO and BTO/AgNPs are displayed in Figure 2a,b, respectively. The surface morphology of BTO microstructures appears to be very smooth, dense, and with some clear grain boundaries. Similar surface morphology was reported in various studies. There is no clear evidence of Ag nanoparticles being deposited on the surface morphology of BTO in Figure 2b. However, the presence of the Ag element in the EDS spectrum of the composite showed an evident successful deposition of AgNPs on the surface of BTO (Figure 2c). The cross-sectional image of the thin-film composite is shown in Figure 2d. It can be observed that the Dr. Blade method was a success for the fabrication of piezo-thin films based on an FTO glass substrate; the prepared BTO/AgNPs sample was successfully deposited on the FTO glass plate substrate via tape-casting. Furthermore, the thickness of the piezo-thin film was measured to be approximately 93.66 μm.

Figure 2e,f shows the TEM images of the pure BTO and silver-deposited BTO. The TEM images display large agglomerated grains of BTO (Figure S2). The small spherical nanoparticles, which are uniformly dispersed on the surface of the BTO, appears to be silver nanoparticles, which also confirms the successful deposition of Ag nanoparticles. The particle sizes of these spherical Ag nanoparticles on the surface of the BTO were measured by Image J (Figure S3), whereby the dominant average particle sizes were obtained between 10 and 15 nm. To further understand this formed composite, functional, thermal stability, and surface area studies were conducted.

3.3. Functional, Thermal Stability, and Surface Area Studies. To confirm the functional groups of the prepared materials, Figure 3a illustrates the FTIR spectrum of pure BTO and BTO deposited with AgNPs. The broad peak observed at approximately 557 cm$^{-1}$ can be attributed to the characteristic vibrations of the BTO, confirming the presence of metal bonded to oxygen. The characteristic peak exhibited at around 1401 cm$^{-1}$ can be ascribed to the stretching vibrations of a carbonate group (−CO$_3^{2-}$) from the small amount of BaCO$_3$. Several small absorption peaks were observed at lower frequencies (859–1085 cm$^{-1}$), which can be assigned to various residual groups or byproducts formed during the synthesis of BTO. The observed peak at 3145 cm$^{-1}$ represents the −OH group in all materials, which is due to the water molecules absorbed on the materials. Furthermore, it can be observed that there is no significant change in the FT-IR spectra of BTO/AgNPs relative to pure BTO, thus confirming that the deposition of AgNPs onto BTO did not tamper with the chemical structure of the pure BTO. The extent of the hydroxyl group was further slightly increased, whereas the metal-bonded oxygen peak became more sharpened after depositing silver nanoparticles on the surface of BTO. The extended surface hydroxyl groups might play an important role in the piezo-photocatalytic degradation process.

The TGA curves of BTO and BTO/AgNPs and their derivatives (DTG) are presented in Figure 3b,c. As shown in Figure 3b, the TGA curve of BTO shows two thermal decomposition steps, and its derivative (DTG curve) corresponds very well with it. The first and second thermal decomposition were around 310–450 °C and 730 °C, respectively. The first weight loss of 0.9% around 310–450 °C could be due to the thermal decay of dehydrated oxalate. The second thermal decomposition was due to the loss of a small amount of carbonate group. Upon the deposition of AgNPs onto BTO, a slight increment of thermal stability was observed occurring in the composite (BTO/AgNPs).

BET analysis was used to determine the specific surface area of the pure BTO and modified BTO deposited with AgNPs. The pore size distribution was measured from nitrogen (N$_2$) adsorption–desorption isotherms (Figure 3d). The hysteresis loops arises at around the relative pressure ($P/P_o$) range of 0.7–0.9 for both BTO and BTO/AgNPs. The hysteresis loops were classified as type IV, confirming the mesoporous structure of BTO and BTO/AgNPs. The specific surface area, pore volume, and pore size obtained from N$_2$ adsorption isotherms were 3.9611 m$^2$/g, 0.156632 cm$^3$/g, and 26.1875 nm for pure BTO, respectively. It was further observed that deposition of silver nanoparticles (AgNPs) onto the surface of BTO slightly

Figure 2. (a, b) FE-SEM images of BTO and BTO/AgNPs, (c) EDS spectrum of the composite, (d) cross-sectional imaging of piezo-thin films, and (e, f) TEM images of BTO/AgNPs.
increased the specific surface area and pore size of the composite to 4.8410 m$^2$/g and 26.5056 nm, respectively. Since the composite (BTO/AgNPs) has a large surface area, it has more binding sites and large contact area with the target material, thus allowing it to absorb more organic substances. An increment in the surface area of the composite plays a critical role in the catalytic degradation process.

3.4. Piezo-Electrochemical and Optical Characterization of Materials. The chronoamperometry studies were conducted to investigate the piezoelectricity of the prepared thin films (FTO/BTO and FTO/BTO/AgNPs). As shown in Figure 4a, both piezo-thin films exhibited piezoelectricity under ultrasonic vibration. The highest piezo-electrochemical currents measured exhibited by BTO and BTO/AgNPs were 0.24 and 0.38 mA, respectively (Table 1). It is worth noting that the piezo-electrochemical current response for the composite (FTO/BTO/AgNPs) was more enhanced when AgNPs were deposited on the surface of BTO. These results suggested that the piezo-potential generated under the influence of ultrasonic vibration induced the electric field, which improved the separation of photogenerated electrons and further reduced the fast recombination of the charge carriers (holes and electrons). The piezocatalyst (BTO) under mechanical vibration in water can promote a redox reaction. The electrochemical reactions (eqs 1–3) are as follows:

\[ \text{BTO} + \text{mechanical vibration} \rightarrow \text{BTO (e}^-, \text{h}^+) \]  
\[ \text{h}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ + \text{e}^- \]  
\[ \text{e}^- + \text{O}_2 \rightarrow \cdot\text{O}_2^- \]  

It is noteworthy from the redox reactions (eqs 2 and 3) that the piezoelectric thin films will generate a current when the rate of water oxidation is faster than the oxygen reduction reaction since a greater excess of electrons are available at the working thin-film electrode (BTO) and transfers to the platinum wire (contour electrode). Thus, the output current is generated via an electrocatalytic reaction; therefore, it is termed piezo-electrochemical current response instead of normal piezo-current produced via normal mechanical vibration of BTO in the absence of water.

The Nyquist plots of the prepared piezoelectric thin films are presented in Figure 4b. This plot was used to determine the charge-transfer resistance ($R_{ct}$) of the piezo-film electrodes. It has been reported that materials with a high charge-transfer resistance exhibit a large semi-circular arc. From the obtained Nyquist plot, FTO/BTO/AgNPs had a low charge-transfer resistance of 397.6 Ω as compared to FTO/BTO (799.5 Ω); these results were in agreement with the generated piezo-electrochemical current, as shown in Figure 4a. This showed that the deposition of AgNPs onto BTO significantly improved the charge-electron transfer of the composite and reduced the recombination of photogenerated charged carriers.

UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was also employed to investigate the optical absorption properties.
of the fabricated piezo-thin films (Figure 4c). Upon deposition of AgNPs on the surface of BTO, the extrapolated absorption edges slightly shifted from 395 to 431 nm, which could be due to the strong electronic interaction between the BTO and AgNPs. The broad absorption peak at approximately 505 nm was ascribed to the surface plasmon resonance (SPR) of the accumulated AgNPs on the BTO surface. The extrapolated absorption edges of the materials were in the same wave-number range (395−431 nm), which is consistent with the photon band gap of the BTO (3.1 eV) reported in the literature.

The band gaps of the thin films were determined of the fabricated piezo-thin films (Figure 4c). Upon deposition of AgNPs on the surface of BTO, the extrapolated absorption edges slightly shifted from 395 to 431 nm, which could be due to the strong electronic interaction between the BTO and AgNPs. The broad absorption peak at approximately 505 nm was ascribed to the surface plasmon resonance (SPR) of the accumulated AgNPs on the BTO surface. The extrapolated absorption edges of the materials were in the same wave-number range (395−431 nm), which is consistent with the photon band gap of the BTO (3.1 eV) reported in the literature.

The band gaps of the thin films were determined

| materials     | piezo-electrochemical current (mA) | charger-transfer resistance (Ω) | photon energy (eV) |
|---------------|-----------------------------------|---------------------------------|-------------------|
| BTO           | 0.24                              | 799.5                           | 3.12              |
| BTO/AgNPs     | 0.38                              | 397.6                           | 2.90              |

“Dimensions of the thin-film electrode: length, 2 cm; width, 2 cm; and surface area (4 cm²).
from the extrapolated Tauc's plot (Figure 4d) derived from eq 4 below:

\[(\alpha h v) = A(h v - E_g)^n\]  

where \(\alpha\), \(h\), \(v\), \(A\), and \(E_g\) represent the absorption coefficient, Planck's constant, incident light frequency, constant, and photon band gap, respectively. The value of “\(n\)” is constant; it
can either be 1, 2, or 3 depending mostly on the optical transition characteristics of semiconductors.

The direct band gaps extrapolated from the Tauc’s plot were estimated to be 3.12 and 2.90 eV for BTO and BTO/AgNPs, respectively (Table 1). Therefore, these results showed that the deposited AgNPs were able to slightly reduce the band gap of the BTO, thus improving the photocatalytic activity of the composite (BTO/AgNPs).

Another technique that was used to determine the rate of electron and hole recombination is photoluminescence (PL) spectroscopy. The PL spectra of BTO and BTO/AgNPs were measured at 400 nm excitation. As shown in Figure 4e, generally, the higher the intensity of PL peaks, the higher the rate of electron and hole recombination. As shown in Figure 4e, several PL emission peaks were observed in the wavelength between 500 and 600 nm, and a broad peak at approximately 503 nm was observed in both the BTO and composite (BTO/AgNPs). The PL intensity peak of BTO deposited with AgNPs was smaller than that of BTO. These results further confirmed the improvement of charge carrier separation, which plays an important role in photocatalytic reactions.

In the photoelectrochemical performance of the semiconductors, flat band potential is an essential property. The Mott—Schottky (MS) plot was used to analyze the change in the flat band potential, carrier density, and improved charge separation in the heterojunction according to eq 5 below in darkness.\(^6\) The Mott—Schottky plot data was obtained at pH 7 and a bias frequency of 1000 Hz.

\[
\frac{1}{C^2} = \frac{2}{(\varepsilon\varepsilon_0 N_0) (E_{\text{app}} - E_{\text{FB}} - \frac{kT}{e})}
\]

(5)

where \(C\), \(\varepsilon\), \(\varepsilon_0\), \(N_0\), \(E_{\text{app}}\), \(E_{\text{FB}}\), \(k\), and \(T\) are the capacitance at the semiconductor/electrolyte interface (Fcm\(^{-2}\)), elementary charge (1.60 \times 10^{-19} \text{ C}) dielectric constant of semiconductors, permittivity of vacuum, donor density, applied potential (V), flat band potential, Boltzmann constant, and absolute temperature, respectively. The flat band potential was obtained by extrapolating a straight line to intercept the X-axis from the MS plot of 1/C\(^2\) versus \(E_{\text{app}}\). Positive slopes were obtained from the MS plot, suggesting that all samples were n-type semiconductors. The measured flat band potential of BTO/AgNPs was 0.50 V (vs Ag/AgCl) in the aqueous solution of 3.5. The Mott—Schottky plots obtained from the MS plot, suggesting that all samples were n-type semiconductors.

3.5. Piezophotocatalytic Degradation of Methylene Blue (MB). The fabricated piezo-thin film (FTO/BTO/AgNPs) was investigated for the removal of methylene blue (MB) from aqueous solution via the piezo-photocatalytic degradation process. The concentration decay was monitored using a UV–vis spectrophotometer. The reduction of the absorption peak at 663 nm from the UV–vis spectra was evident enough that there is a decrease in MB concentration due to the degradation process as more time elapsed (Figure 5a). To further understand these materials, key parameters were investigated.

3.5.1. Effect of pH. Since the pH of the solution is the most pivotal parameter that tends to control the degradation process, in this experiment, we investigated the performance of the BTO/AgNPs piezo-thin film for the removal of MB at different pH values (acidic media (pH 2), neutral solution (pH 7) and alkaline medium solution (pH 10)). It was noticed that the piezocatalytic degradation was pH-dependent since the piezocatalytic degradation of MB was found to be increasing with an increase in pH solution (Figure 5b). The highest piezocatalytic degradation percentage of MB was obtained to be 90% at alkaline media (pH). This highest piezocatalytic degradation was due to the electrostatic interaction between cationic MB and the hydroxylated surface of the BTO/AgNPs piezo-thin-film composite.\(^78\) As seen from zeta potentials in Figure S4, the isoelectric point (IEP) for BTO/AgNPs was obtained at a pH value of 3.5. Above this isoelectric point (pH > 3.5), the surface charge of the BTO/AgNPs composite was negatively charged throughout. For further degradation experiments, the solution of MB was maintained at an optimum pH (10).

3.5.2. Effect of Ultrasonic Power. The piezoelectric potential (\(V_p\)) produced by piezoelectric materials depends on the types of mechanical vibrations applied such as wind, fluid flow, movement of people or vehicles, and rotating machines.\(^5,74\) These mechanical vibrations can be found anywhere in nature, unlike other energy-harvesting materials such as thermoelectric, photovoltaic, and pyroelectric effects, which depend on the nature of the environment.\(^75\) The existence of vibration anywhere is advantageous; another benefit of using vibration-based energy-harvesting approaches is that they do not depend on environmental conditions, which tend to change with time. The collection of these vibrations can be of great use for the production of electricity using piezoelectric materials. Ultrasonic vibration is one of the most applied mechanical vibrations to trigger the piezo-potential of several piezoelectric materials. In most previous studies, a high ultrasonic power (>110 W) was applied and was difficult to sustain due to high energy consumption.\(^76,77\) Therefore, in the present study, we employed a low ultrasonic power (10–30 W) for piezocatalytic degradation of MB. It is worth noting that the piezocatalytic degradation efficiency increased with an increase in ultrasonic power (Figure 5c), which could be due to the high pressure, causing more cavitation bubbles or ultrasonic water waves to actively pressurize the piezo-thin-film electrode in the MB aqueous solution.\(^78\)

3.5.3. Application of Different Materials (FTO, FTO/BTO, and FTO/BTO/AgNPs). Upon testing the piezocatalytic performance of the various materials, the FTO/BTO/AgNPs composite showed a better degradation (90%) as compared to the bare FTO and FTO/BTO. The piezocatalytic degradation percentages of MB using FTO and FTO/BTO were 21.1 and 81.2%, respectively (Figure 5d). Therefore, these results proved that deposition of AgNPs onto BTO further enhanced the piezocatalytic performance of the piezo-thin-film composite (FTO/BTO/AgNPs). Similar observations were reported by Xu et al.,\(^79\) where a powdered piezocatalyst doped with Ag nanoparticles enhanced piezoelectric efficiency. Table 2 shows
the comparative performance of various piezocatalysts doped with different dopants for the removal of organic pollutants. The results showed that powder piezocatalysts are more effective relative to piezo-thin films in terms of the rate of degradation; however, they suffer from poor re-usability.

### Table 2. Comparative Performance of Various Doped Piezocatalysts for Removal of Organic Pollutants

| piezocatalyst         | organic pollutants | initial concentration | degradation time | rate constant | ref |
|-----------------------|--------------------|-----------------------|------------------|---------------|-----|
| Ag-BaTiO$_3$          | RhB                | 0.01 mM               | 75 min           | 0.0125 min$^{-1}$ | 79  |
| Pt/BaTiO$_3$          | TCZ                | 10 mg/L               | 60 min           | 0.0125 min$^{-1}$ | 80  |
| Au-BiVO$_4$           | 4-CP               | 0.1 mM                | 120 min          | 0.0125 min$^{-1}$ | 81  |
| Ag/ZnO                | MO                 | 5 mg/L                | 25 min           | 0.0125 min$^{-1}$ | 82  |
| Au/ZnO                | RhB                | 10 mg/L               | 20 min           | 0.0125 min$^{-1}$ | 83  |
| Fe@MoS$_2$            | TC                 | 100 mg/L              | 60 min           | 3.95 L mg$^{-1}$ s$^{-1}$ | 84  |
| Fe-ScTiO$_3$          | MB                 | 3.6 mg/L              | 210 min          | 0.00448 min$^{-1}$ | 85  |
| Co-Mo$_3$S$_4$        | MB                 | 30 mg/L               | 25 min           | 0.0150 min$^{-1}$ | 86  |
| Rh-ScTiO$_3$          | BPA                | 10 mg/L               | 60 min           | 0.16 min$^{-1}$ | 87  |
| Fe@3D-WS$_2$          | LEVO               | 25 mg/L               | 120 min          | 0.226 min$^{-1}$ | 88  |
| ZnO nanowire array    | MB                 | 10 mM                 | 180 min          | 0.008 min$^{-1}$ | 89  |
| Sn:ZnO                | RhB                | 2.5 mg/L              | 60 min           | 0.048 min$^{-1}$ | 90  |
| BaTiO$_3$/AgNPs       | MB                 | 5.0 mg/L              | 180 min          | 0.0150 min$^{-1}$ | this work |
| CIP                   | 5.0 mg/L           | 180 min               | 0.00764 min$^{-1}$ | 88  |

Table 2. Comparative Performance of Various Doped Piezocatalysts for Removal of Organic Pollutants

"NB: Rhodamine B (Rh B), tricyclazole (TCZ), 4-chlorophenol (4-CP), methyl orange (MO), tetracycline (TC), ciprofloxacin (CI), methylene blue (MB), bisphenol A (BPA), and levofloxacin (LEVO)."

### Scheme 2. (a, b) Piezo-Photocatalytic Degradation Mechanism for MB

where $C_0$, $C_t$, and $t$ respectively, represent the initial concentration, concentration at a certain time, and time interval.

The rate constants ($k$) obtained from the data plot were recorded to be 0.00079, 0.0031, 0.0150, and 0.02329 min$^{-1}$ for adsorption and photocatalytic, piezocatalytic, and piezo-photocatalytic degradation, respectively.

### 3.5.5. Re-usability Test

To ensure that we were able to fabricate an effective piezoelectric-thin-film electrode as a self-powered electrocatalytic nanoreactor assisted with visible light for wastewater treatment, it is crucial to produce piezo-thin films that are easily re-usable. Unlike the application of powder piezocatalysts or photocatalysts in wastewater treatment that suffers from poor recyclability, thin films offer easy re-usability and do not require any additional strong acid or base for the recovery process. The thin films such as the fabricated FTO/BTO/AgNPs can be rinsed with water and dried at room temperature for re-usability purposes. Figure 5g shows the re-usability and stability experiments conducted on the piezo-thin-film composite. The degradation efficiency of the thin-film composite decreased with an increase in the number of degradation cycles. It is worth noticing that after the third cycle, the degradation efficiency decreased slightly by 14% (from 98 to 84%) (Figure 5h). This might be due to the partial loss of the piezo-photocatalyst and blockage of active sites with time during the piezo-photocatalytic degradation process. Therefore, this showed that the fabricated thin film could be
effectively re-used up to three times, without losing much of its efficiency. As shown in Figure 5d, the SEM images confirm that the structural morphology and particle size of the thin film did not change after the third cycle of water treatment, so this further validates the stability of the piezoelectric thin film. It was further shown by the EDS spectrum (Figure S6) that there was no Ag nanoparticles leaching from the surface of the thin film after wastewater treatment.

### 3.6. Piezo-Photocatalytic Mechanism and Scavenger Studies

#### 3.6.1. Proposed Degradation Mechanism

The total decomposition of organic species such as organic dyes, for example, methylene blue (MB), during piezo-photocatalytic degradation occurs when the generated reactive oxygen species (ROS) such as hydroxyl and superoxide radicals react with organic species. Therefore, we further explored the possible mechanism for the synergic catalytic degradation of MB using fabricated piezo-thin films (FTO/BTO/AgNPs). The functioning mechanism is depicted in Scheme 2. Under the full-spectrum of light exposure, BaTiO$_3$ absorbs photons of higher energy to excite electrons from the valence band (VB) to conduction band (CB) and leave the holes behind in the valence band (VB)\(^{91,92}\). When AgNPs and BaTiO$_3$ are in contact, electrons and holes are redistributed in the interface between AgNPs and BaTiO$_3$ due to difference in Fermi energy levels. Furthermore, Ag nanoparticles on the surface of BTO may absorb visible light via localized surface plasmon resonance (LSPR), thus creating more excited electron and holes. The excited electrons generated by AgNPs have enough energy to move across natural Schottky barriers and be transferred into the conduction band of BaTiO$_3$ (Scheme 2)\(^{93}\). The BTO/AgNPs interface can promote interfacial charge transfer and reduce the rate of recombination of charge carriers. To get more insights into the charge separation of the BTO/AgNPs thin film, the mechanism of the transfer of photogenerated charge carriers (\(e^-\) and \(h^+\)) between the metal and semiconductor was inferred by calculating the respective band edge potentials of the metal–semiconductor utilizing eqs 7 and 8 below:

\[
E_{CB} = X - E'_s - 0.5E_g \tag{8}
\]
\[
E_{VB} = E'_s + E_{CB} \tag{9}
\]

where \(E_{CB}\), \(X\), \(E'_s\), and \(E_g\) represent the conduction band edge potential (band position), electronegativity of the semiconductor, energy of free electrons on the hydrogen scale (\(\approx 4.5\) eV), and energy band gap of the semiconductor, respectively. The absolute electronegativity (Ag-BaTiO$_3$ = 5.13) of the constitute atoms was adapted from Cui et al.’s work\(^4\), and the calculated band gap obtained from Figure 4d was 2.90 eV for metal–semiconductor (BTO/AgNPs). Therefore, the conduction band and valence band potentials were calculated to be \(-0.82\) eV (vs NHE) and \(+2.08\) eV (vs NHE). Furthermore, when BTO/AgNPs is exposed under ultrasonic vibration, BTO generates a piezoelectric field across CB and VB with positive piezo-potential and negative potential (\(V^+\) and \(V^-\), labeled by the red arrows in Scheme 2b), driving photogenerated electrons and holes on opposite sides (conduction and valence bands)\(^93,95,96\). Due to the piezo-electric effect, photogenerated charge carriers are further separated. The separated photo-induced electrons and holes (free electric charges) at the opposite surface sides of the thin film (BTO/AgNPs) to act as an anode and cathode, respectively, thus participate in redox reactions to form ROS such as hydroxyl and superoxide radicals. The reactions (eqs 9–12) show the formation of reactive oxygen species from free electric charges on the opposite sites of the piezoelectric thin film. As shown in eqs 10–13, the free positive charges (\(h^+\)) reacted with water to form hydroxyl radicals (\(\cdot OH\)), whereas the negative charges (\(e^-\)) reacted with free oxygen molecules to form superoxide radicals (\(\cdot O_2^-\)). These reactive oxygen species (\(\cdot O_2^-\) and \(\cdot OH\)) are regarded as strong oxidants and are responsible for the degradation of organic dyes (eqs 9–12).

\[
\text{ROS (}\cdot \text{OH/}\cdot \text{O}_2^-\text{)} + \text{MB} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \tag{14}
\]

#### 3.6.2. Scavenger Studies

In order to investigate which reactive oxygen species were more effective for catalytic degradation of MB, scavenger studies were conducted via the addition of trapping agents such as p-benzoquinone (\(p\)-BZQ), \(t\)-butanol (\(t\)-BuOH), and ethylenediaminetetraacetate salt.
(EDTA) to inhibit the generation of superoxide, hydroxyl radicals, and holes, respectively (Figure 6a). Upon the addition of 5 mM $t$-BuOH, the catalytic degradation efficiency decreased from 98 to 32%, whereas in the case of $p$-BZQ and EDTA, it decreased to 52 and 76%, respectively (Figure 6b). Therefore, this trapping experiment showed that hydroxyl radicals were the major ROS responsible for breaking down MB into less harmful products ($\text{CO}_2$ and $\text{H}_2\text{O}$), whereas superoxide and holes played a minor role in the catalytic degradation process.

### 3.7. Piezo-Photocatalytic Degradation of Ciprofloxacin (CIP)

#### 3.7.1. Effect of pH
The prepared piezo-thin-film composite (FTO/BTO/Ag) was further investigated for the removal of a pharmaceutical pollutant (5 mg/L ciprofloxacin) from wastewater. In this experiment, an optimum ultrasonic power of 30 W obtained from the previous piezocatalytic degradation of methylene blue (MB) was applied for all catalytic processes. However, the piezocatalytic degradation of CIP antibiotic drug by FTO/BTO/Ag was studied at different pH solutions since different organic pollutants behave differently at certain pH. Figure 7a shows the piezocatalytic degradation of CIP from wastewater at different pH range of 3–10. The maximum piezocatalytic efficiency of 68% was observed under ultrasonic vibration at pH 3. There are several contradicting studies on the removal of CIP at different pH values. However, some studies have reported the highest removal of CIP at the lowest pH (<4), which was consistent with our study.

#### 3.7.2. Application of Different Materials (FTO, FTO/BTO, and FTO/BTO/AgNPs)

The piezocatalytic degradation percentage of CIP using different piezoelectric thin films is shown in Figure 7b. As seen in the figure, BTO modified with AgNPs showed a significant piezocatalytic degradation as compared to the pristine BTO and FTO substrate. These results also confirm that the deposition of AgNPs on the surface of BTO greatly enhanced the piezocatalytic activity of the composite (FTO/BTO/AgNPs). The piezocatalytic degradation percentages of CIP were reported to be 18, 52, and 68% within 180 min when FTO, FTO/BTO, and FTO/BTO/AgNPs were applied as piezo-thin films, respectively.

#### 3.7.3. Comparison of Photocatalysis, Piezocatalysis, and Piezo-Photocatalysis

The removal of CIP from wastewater by the piezo-thin-film composite through adsorption and when photocatalysis is coupled with piezocatalysis is presented in Figure 7c. Without ultrasonic vibration and light exposure (via the adsorption process), the piezo-thin-film composite showed a low removal efficiency of CIP (only 6% of CIP was removed from wastewater). When the experiment was performed under ultrasonic vibration and light irradiation, it can be seen that these two processes were more effective when combined as compared to when singly applied. Under light irradiation alone, FTO/BTO/AgNPs degraded about 26% of CIP from
wastewater within 180 min. The coupled process (piezo-photocatalysis) showed a higher catalytic performance since the removal efficiency of CIP increased from 26% (photocatalysis) to 76% under both ultrasonic vibration and light irradiation (piezo-photocatalysis). Figure 7d shows the rate of each catalytic process: the photocatalysis reaction process was very slow as compared to piezocatalysis and piezo-photocatalysis. The rate constants were determined from the pseudo-first-order plot (ln C0/Ct vs time (t)). The apparent rate constant (k) could represent the activity of each process. It is clearly observed that the reaction rate constant (k) of the coupled process (piezo-photocatalysis) was greater than the individual processes; the rate constants were calculated to be 0.00033, 0.00175, 0.00615, and 0.00764 min\(^{-1}\) under adsorption, UV light exposure, ultrasonic vibration, and combined exposure (UV light and ultrasonic vibration), respectively. According to these obtained reaction rate constants, the piezo-photocatalytic process was four times faster than the photocatalysis process. This indicates that photocatalysis combined with piezocatalysis as AOPs for wastewater treatment could be applicable in the near future. Furthermore, the amount of mineralization of MB and CIP was determined by TOC (total organic carbon) analysis. Under optimal conditions, the TOC % values for CIP and MB were recorded to be 62 and 84%, respectively (Figure S7).

4. CONCLUSIONS

In summary, the piezo-thin film was successfully fabricated and investigated for piezo-photocatalytic degradation of MB and CIP. The deposition of Ag nanoparticles onto the BTO surface reduced the rate of electron and hole recombination and enhanced the piezo-electrochemical current of the piezo-thin-film composite (FTO/BTO/AgNPs). Piezophotocatalytic degradation percentages were recorded to be 98 and 72% for MB and CIP within 180 min, respectively. Scavenger studies showed that hydroxyl radicals (\(\cdot\)OH) were the major reactive oxygen species responsible for the piezo-photocatalytic degradation of MB followed by superoxide and holes. The fabricated piezo-thin films were shown to be more effective, stable, and re-usable. Thus, this study proves that the prepared piezo-thin film is more applicable for catalytic wastewater treatment of organic waste pollutants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01699.

The supporting information is attached as, (Figure S1) Piezo-photocatalytic degradation setup; (Figure S2) TEM images for pure BTO; (Figure S3) particle distribution of Ag nanoparticles on the surface of BTO; (Figure S4) zeta potential (surface charge) for BTO/AgNPs; (Figure S5) pseudo-second-order kinetics for catalytic degradation of MB; (Figure S6) SEM images of thin films; (Figure S7) total organic carbons (TOC) for methylene blue and ciprofloxacin; and (Table S1) synergic effect of photocatalysis and piezocatalysis (PDF).

AUTHOR INFORMATION

Corresponding Author

Nonhlangabezo Mabuba — Department of Chemical Sciences (formerly known as Applied Chemistry), University of Johannesburg, Johannesburg 2028, South Africa;

orcid.org/0000-0003-0209-7451;

Email: masekeladaniel@gmail.com

Authors

Daniel Masekela — Department of Chemical Sciences (formerly known as Applied Chemistry), University of Johannesburg, Johannesburg 2028, South Africa

Nomso C. Hintsho-Mbita — Department of Chemistry, University of Limpopo, Polokwane 0727, South Africa

Bulelw Ntsendwana — Energy, Water, Environmental and Food Sustainable Technologies (EWEF-SusTech), Johannesburg 1709, South Africa

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c01699

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by GES 4.0 (Global Excellence Structure 4.0), the Centre for Nanomaterials Science Research (CNSR) University of Johannesburg, National Research Foundation of South Africa (NRF) University of South Africa (NRF), University of Limpopo, South Africa, and the Faculty of Science University of Johannesburg (UJ), South Africa, for financial support.

REFERENCES

(1) Ye, S.; Chen, Y.; Yao, X.; Zhang, J. Simultaneous Removal of Organic Pollutants and Heavy Metals in Wastewater by Photoelectrocatalysis: A Review. *Chemosphere* 2021, 273, No. 128503.

(2) Katheresan, V.; Kansedo, J.; Lau, S. Y. Efficiency of Various Recent Wastewater Dye Removal Methods: A Review. *J. Environ. Chem. Eng.* 2018, 6, 4676–4697.

(3) Fernández, C.; Larrechi, M. S.; Callao, M. P. An Analytical Overview of Processes for Removing Organic Dyes from Wastewater Effluents. *TrAC, Trends Anal. Chem.* 2010, 29, 1202–1211.

(4) Abdi, J.; Vossoughi, M.; Mahmoodi, N. M.; Alemzadeh, I. Synthesis of Metal-Organic Framework Hybrid Nanocomposites Based on GO and CNT with High Adsorption Capacity for Dye Removal. *Chem. Eng. J.* 2017, 326, 1145–1158.

(5) Van Der Zee, F. P.; Villaverde, S. Combined Anaerobic-Aerobic Treatment of Azo Dyes—A Short Review of Bioreactor Studies. *Water Res.* 2005, 39, 1425–1440.

(6) Mojsov, K. D.; Andronikov, D.; Janevski, A.; Kuzelov, A.; Gaber, S. The application of enzymes for the removal of dyes from textile effluents. *Adv. Technol.* 2016, 5, 81–86.

(7) De Gisi, S.; Lofrano, G.; Grassi, M.; Notarnicola, M. Characteristics and Adsorption Capacities of Low-Cost Sorbents for Wastewater Treatment: A Review. *Sustainable Mater. Technol.* 2016, 9, 10–40.

(8) Gupta, V. K.; Kumar, R.; Nayak, A.; Saleh, T. A.; Barakat, M. A. Adsorptive Removal of Dyes from Aqueous Solution onto Carbon Nanotubes: A Review. *Adv. Colloid Interface Sci.* 2013, 193-194, 24–34.

(9) Ballav, N.; Das, R.; Giri, S.; Mulwa, A. M.; Pillay, K.; Maity, A. L-Cysteine Doped Polypyrrole (PPy@L-Cyst): A Super Adsorbent for the Rapid Removal of Hg\(^{2+}\) and Efficient Catalytic Activity of the Spent Adsorbent for Reuse. *Chem. Eng. J.* 2018, 345, 621–630.
(10) Manavi, N.; Kazemi, A. S.; Bonakdarpour, B. The Development of Aerobic Granules from Conventional Activated Sludge under Anaerobic-Aerobic Cycles and Their Adaptation for Treatment of Dyeing Wastewater. *Chem. Eng. J.* 2017, 312, 375–384.

(11) Mohan, S. V.; Bhaskar, Y. V.; Karthikeyan, J. Biological Decolourisation of Simulated Azo Dye in Aqueous Phase by Algae Spirogyra Species. *Int. J. Environ. Pollut.* 2004, 21, 211–222.

(12) Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A. Adsorption of Methylene Blue on Low-Cost Adsorbents: A Review. *J. Hazard. Mater.* 2010, 177, 70–80.

(13) Rodriguez-Couto, S.; Osma, J. F.; Toca-Herrera, J. L. Removal of Synthetic Dyes by an Eco-Friendly Strategy. *Eng. Life Sci.* 2009, 9, 116–123.

(14) Salleh, M. A. M.; Mahmoud, D. K.; Karim, W. A. W. A.; Idris, A. Cationic and Anionic Dye Adsorption by Agricultural Solid Wastes: A Comprehensive Review. *Desalination* 2011, 280, 1–13.

(15) Anjali, R.; Shanthakumar, S. Insights on the Current Status of Occurrence and Removal of Antibiotics in Wastewater by Advanced Oxidation Processes. *J. Environ. Manage.* 2019, 246, 51–62.

(16) Gulkowska, A.; Leung, H. W.; So, M. K.; Taniyasu, S.; Yamashita, N.; Yeung, L. W. Y.; Richardson, B. J.; Li, A. P.; Giysi, J. P.; Lam, P. K. S. Removal of Antibiotics from Wastewater by Sewage Treatment Facilities in Hong Kong and Shenzhen, China. *Water Res.* 2008, 42, 395–403.

(17) Ahmadzadeh, S.; Asadipour, A.; Pouramdari, M.; Behnam, B.; Rahimi, H. R.; Dolatabadi, M. Removal of Ciprofloxacin from Hospital Wastewater Using Electrocoagulation Technique by Aluminium Electrode: Optimization and Modelling through Response Surface Methodology. *Process Saf. Environ. Prot.* 2017, 109, 538–547.

(18) Bojer, C.; Schöbel, J.; Martin, T.; Ertl, M.; Schmalz, H.; Breu, J. Clinical Wastewater Treatment: Photochemical Removal of an Anionic Antibiotic (Ciprofloxacin) by Mesostructured High Aspect Ratio ZnO Nanotubes. *Appl. Catal., B* 2017, 204, 561–565.

(19) El-Shafey, E. S. I.; Al-Lawati, H.; Al-Sumri, A. S. Ciprofloxacin Adsorption from Aqueous Solution onto Chemically Prepared Aluminium Electrode: Optimization and Modelling through Response Surface Methodology. *Process Saf. Environ. Prot.* 2017, 109, 538–547.

(20) Singh, N. B.; Nagpal, G.; Agrawal, S.; Rachna. Water Purification by Using Adsorbents: A Review. *Environ. Technol. Innovation* 2018, 11, 187–240.

(21) Gupta, V. K.; Suhas. Application of Low-Cost Adsorbents for Dye Removal - A Review. *J. Environ. Manage.* 2009, 90, 2313–2342.

(22) Pole, M.; Gamboa, B.; Bhalla, A.; Guo, R. Degradation of Piezoelectric Device as an Energy Harvester under Equivalent Traffic Stress Condition. *Ferroelectrics* 2019, 540, 112–123.

(23) Hong, K.-S.; Xu, H.; Konishi, H.; Li, X. Direct Water Splitting Through Vibrating Piezoelectric Microfibers in Water. *J. Phys. Chem. Lett.* 2010, 1, 997–1002.

(24) Zhang, Y.; Xie, M.; Adamaki, V.; Khanbaredh, H.; Bowen, C. R. Control of electro-chemical processes using energy harvesting materials and devices. *Chem. Soc. Rev.* 2017, 1, 7757–7786.

(25) Jia, S.; Su, Y.; Zhang, B.; Zhao, Z.; Li, S.; Zhang, Y.; Li, P.; Xu, M.; Ren, R. Few-Layer MoS2 Nanosheet-Coated KNaBO3 Nanowire Heterostructures: Piezo-Photocatalytic Effect Enhanced Hydrogen Production and Organic Pollutant Degradation. *Nanoscale* 2019, 11, 7690–7700.

(26) Biswas, A.; Saha, S.; Jana, N. R. ZnSnO3 Nanoparticle-Based Piezocatalysts for Ultrasound-Assisted Degradation of Organic Pollutants. *ACS Appl. Nano Mater.* 2019, 2, 1120–1128.

(27) Feng, Y.; Ling, L.; Wang, Y.; Xu, Z.; Cao, F.; Li, H.; Bian, Z. Engineering Spherical Lead Zirconate Titanate to Explore the Essence of Piezo-Catalysis. *Nano Energy* 2017, 40, 481–486.

(28) Singh, S.; Khare, N. Coupling of Piezoelectric, Semiconducting and Photoexcitation Properties in NaNdO3 Nanostructures for Controlling Electrical Transport: Realizing an Efficient Piezo-Photoanode and Piezo-Photocatalyst. *Nanotechnology* 2017, 38, 335–341.

(29) Mustaq, F.; Chen, X.; Hoop, M.; Torlakcik, H.; Pellicer, E.; Sort, J.; Gattionini, C.; Nelson, B. J.; Pané, S. Piezoelectrically Enhanced Photocatalysis with BiFeO3 Nanostructures for Efficient Water Remediation. *Science* 2018, 4, 236–246.

(30) Ma, J.; Ren, J.; Jia, Y.; Wu, Z.; Chen, L.; Haugen, N. O.; Huang, H.; Liu, Y. High Efficiency Bi-Harvesting Light/Vibration Energy Using Piezoelectric Zinc Oxide Nanorods for Dye Deposition. *Nano Energy* 2019, 62, 376–383.

(31) Wu, J. M.; Chang, W. E.; Chang, Y. T.; Chang, C. K. Piezocatalytic Effect on the Enhancement of the Ultra-High Degradation Activity in the Dark by Single- and Few-Layers MoS2 Nanoflowers. *Adv. Mater.* 2016, 28, 3718–3725.

(32) Ismail, M.; Wu, Z.; Zhang, L.; Ma, J.; Jia, Y.; Hu, Y.; Wang, Y. High-Efficient Synergy of Photocatalysis and Photocatalysis in Bismuth Oxychloride Nanomaterial for Dye Deposition. *Chemosphere* 2019, 228, 212–218.

(33) Wu, J.; Qin, N.; Lin, E.; Yuan, B.; Kang, Z.; Bao, D. Synthesis of Bi10Ti12O40 Decussated Nanoplates with Enhanced Piezocatalytic Activity. *Nano Energy* 2019, 11, 21228–21316.

(34) Liu, E.; Qin, N.; Wu, J.; Yuan, B.; Kang, Z.; Bao, D. Bi10Ti12O40 Nanosheets and Caps Grown on TiO2 Nanorods as Thin-Film Catalysts for Piezocatalytic Applications. *ACS Appl. Mater. Interfaces* 2020, 12, 14005–14015.

(35) Lin, J.-H.; Tsao, Y.-H.; Wu, M.-H.; Chou, T.-M.; Lin, Z.-H.; Wu, J. M. Single- and Few-Layers MoS2 Nanocomposite as Piezocatalyst in Dark and Self-Powered Active Sensor. *Nano Energy* 2017, 31, 575–581.

(36) Dai, B.; Zhang, L.; Huang, H.; Lu, C.; Kou, J.; Xu, Z. Photocatalysis of Composite Film PDMS-PNN-PT@TiO2 Greatly Improved by Spatial Electric Field. *Appl. Surf. Sci.* 2017, 403, 9–14.

(37) Feng, J.; Sun, J.; Liu, X.; Zhu, J.; Tian, S.; Wu, R.; Xiong, Y. Coupling Effect of Piezomaterial and DSA Catalyst for Degradation of Metronidazole: Finding of Induction Electrocatalysis from Remnant Piezoelectric Filed. *J. Catal.* 2020, 381, 530–539.
(83) Ye, Y.; Wang, K.; Huang, X.; Lei, R.; Zhao, Y.; Liu, P.
Integration of Piezoelectric Effect into a Au/ZnO Photocatalyst for Efﬁcient Charge Separation. Catal. Sci. Technol. 2019, 9, 3771–3778.

(84) Meng, F.; Ma, W.; Wang, Y.; Zhu, Z.; Chen, Z.; Lu, G. A Tribo-Positive Fe@MoS2 piezocatalyst for the Durable Degradation of Tetracycline: Degradation Mechanism and Toxicity Assessment. Environ. Sci.: Nano 2020, 7, 1704–1718.

(85) Singh, K. P.; Singh, G.; Vaish, R. Utilizing the Localized Surface Piezoelectricity of Centrosymmetric Sr1-xFeTiO3 (x≤0.2) Ceramics for Piezocatalytic Dye Degradation. J. Eur. Ceram. Soc. 2021, 41, 326–334.

(86) Win, T. Y.; Wang, Q.; Jian, J.; Li, Y.; Wu, X. Preparation of Novel Ultrathin Co Doped MoS2 Nanosheets Piezocatalyst for Fast Simultaneous Decomposition of Cr(VI) and MB in Dark. Chem. Res. Chin. Univ. 2019, 35, 892–900.

(87) Zhou, Q.; Shi, Q.; Li, N.; Chen, D.; Xu, Q.; Li, H.; He, J.; Lu, J. Rh-Doped SrTiO3 inverse Opal with Piezoelectric Effect for Enhanced Visible-Light-Directed Photodegradation of Bisphenol A. Environ. Sci.: Nano 2020, 7, 2267–2277.

(88) Meng, F.; Ma, W.; Duan, C.; Liu, X.; Chen, Z.; Wang, M.; Gao, J.; Zhang, Z. High Efﬁcient Degradation of Levofloxacin by Edge-Selectively Fe@3D-W5S: Self-Renewing Behavior and Degradation Mechanism Study. Appl. Catal., B 2019, 252, 187–197.

(89) Zhang, Y.; Huang, X.; Yeom, J. A Floatable Piezo-Photocatalytic Platform Based on Semi-Embedded ZnO Nanowire Array for High-Performance Water Decontamination. Nano-Micro Lett. 2019, 11, 11–14.

(90) Laurenti, M.; Garino, N.; Garino, N.; Canavese, G.; Hernández, S.; Hernández, S.; Cauda, V. Piezo- And Photocatalytic Activity of Ferroelectric ZnO:Sb Thin Films for the Efﬁcient Degradation of Rhodamine-B Dye Pollutant. ACS Appl. Mater. Interfaces 2020, 12, 25798–25808.

(91) Li, S.; Cai, M.; Wang, C.; Liu, Y.; Li, N.; Zhang, P.; Li, X. Rationally Designed Ta3N5/BiOCl S-Scheme Heterojunction with Oxygen Vacancies for Elimination of Tetracycline Antibiotic and Cr(VI): Performance, Toxicity Evaluation and Mechanism Insight. J. Mater. Sci. Technol. 2022, 123, 177–190.

(92) Li, S.; Wang, C.; Cai, M.; Yang, F.; Liu, Y.; Chen, J.; Zhang, P.; Li, X.; Chen, X. Facile Fabrication of TaON/Bi2MoO6 Core–Shell S-Scheme Heterojunction Nanofibers for Boosting Visible-Light Catalytic Levofloxacin Degradation and Cr(VI) Reduction. Chem. Eng. J. 2022, 428, No. 131158.

(93) Kumar, D.; Sharma, S.; Khare, N. Piezo-Phototronic and Plasmonic Effect Coupled Ag-NanoBiO3 Nanocomposite for Enhanced Photocatalytic and Photoelectrochemical Water Splitting Activity. Renewable Energy 2021, 163, 1569–1579.

(94) Cui, Y.; Goldup, S. M.; Dunn, S. Photodegradation of Rhodamine B over Ag Modiﬁed Ferroelectric BaTiO3 under Simulated Solar Light: Pathways and Mechanism. RSC Adv. 2015, 5, 30372–30379.

(95) Li, S.; Zhao, Z.; Liu, M.; Liu, X.; Huang, W.; Sun, S.; Jiang, Y.; Liu, Y.; Zhang, J.; Zhang, Z. Remarkably Enhanced Photocatalytic Performance of Au/AgNbO3 Heterostructures by Coupling Piezoelectric with Plasmonic Effects. Nano Energy 2022, 95, No. 107031.

(96) Shi, J.; Xie, Z.; Tang, X.; Wang, Y.; Yuan, G.; Liu, J.-M. Enhanced Piezo-Photocatalytic Performance of Ag@Nb0.5Bi0.5TiO3 Composites. J. Alloys Compd. 2022, 911, No. 164885.

(97) Zhou, Y.; Fan, X.; Zhang, G.; Dong, W. Fabricating MoS2 Nanoflakes Photoanode with Unprecedented High Photocatalytic Performance and Multi-Pollutants Degradation Test for Water Treatment. Chem. Eng. J. 2019, 356, 1003–1013.

(98) Wu, D.; Huo, P.; Lu, Z.; Gao, X.; Liu, X.; Shi, W.; Yan, Y. Preparation of Heteropolyacid/TiO2 /Fly-Ash-Cenosphere Photocatalyst for the Degradation of Ciprofloxacin from Aqueous Solutions. Appl. Surf. Sci. 2012, 258, 7008–7015.

(99) Zhang, X. X.; Li, R.; Jia, M.; Wang, S.; Huang, Y.; Chen, C. Degradation of Ciprofloxacin in Aqueous Bismuth Oxybromide (BiOBr) Suspensions under Visible Light Irradiation: A Direct Hole Oxidation Pathway. Chem. Eng. J. 2015, 274, 290–297.