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Synergistic piezophototronic and plasmonic effects in Pt-Pd/BiVO$_4$ composites for enhanced tetracycline degradation

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Abstract

Piezo-photocatalysis has emerged as a promising strategy for environmental remediation, particularly in addressing persistent organic pollutants such as antibiotics. However, its practical implementation faces two critical challenges: (1) rapid recombination of photogenerated electron-hole pairs and (2) insufficient active sites for surface redox reactions. To overcome these limitations, we developed an innovative piezo-photocatalytic system composed of ultrathin $BiVO_4$ nanosheets decorated with bimetallic Pt-Pd alloy nanoparticles (Pt-Pd/$BiVO_4$) for efficient tetracycline (TC) degradation. As an efficient combination of photocatalysis and piezocatalysis, the built-in polarization field generated by the piezoelectric effect of $BiVO_4$ catalysts could serve as a powerful driving force for the separation and migration of photoexcited charges. Simultaneously, the Pt-Pd nanoparticles enhance catalytic performance through (i) localized surface plasmon resonance (LSPR)-induced hot electron generation and (ii) optimized charge transfer pathways due to their superior electrical conductivity. Under simultaneous ultrasonic vibration and visible light illumination, the PPB-0.5 composites achieves an outstanding TC degradation rate constant ($k = 0.071\ \text{min}^{-1}$), representing a 3.54-fold enhancement compared to pure $BiVO_4$. Furthermore, the degradation efficiency remains nearly 90% after four cycles, highlighting the system's stability. The result reveal that the synergistic coupling of photocatalysis, piezoelectric polarization and plasmonic excitation significantly promotes the generation of reactive oxygen species (ROS), particularly $\cdot OH$ and $\cdot O_2^-$ radicals, which play a dominant role in TC degradation. This work not only provides fundamental insights into piezo-photo-plasmonic coupling effects but also offers a viable design strategy for developing robust hybrid catalysts for wastewater treatment applications.

Keywords: Pt-Pd bimetallic nanoparticle; $BiVO_4$; Piezo-photocatalysis; Synergistic effect; Tetracycline degradation

1. Introduction

Over the past few decades, antibiotics have been widely utilized in human medicine and animal husbandry due to their broad-spectrum antimicrobial activity[1-2]. TC, one of the most commonly used antibiotic, is extensively present in various environment owing to its high water solubility and resistance to conventional degradation processes. Its pervasive occurrence poses considerable risks to ecosystem sustainability and human health, which is becoming increasingly urgent for effective governance strategies. Conventional treatment techniques often suffer from operational complexity and the potential for secondary environmental pollution, limiting their practical applicability[3-4]. In response to these challenges, piezo-photocatalysis has emerged as an innovative and integrated advanced oxidation process, demonstrating remarkable potential for the effective decomposition of TC [5-7]. This hybrid approach ingeniously couples photocatalytic with piezocatalytic processes, leveraging the piezophototronic effect to facilitate the spatial separation of photogenerated electron-hole pairs via a built-in polarization electric field. Such synergy not only suppresses charge carrier recombination but also enhances overall catalytic activity, creating a mutually reinforcing mechanism. For example, Gong et al. [8] developed an innovative $BaTiO_3$/TCN piezoelectric photocatalyst, achieving a 91.0% degradation rate within 60 minutes under visible light and ultrasonic vibration. Similarly, Wang et al. [9] constructed an α-Fe_2O_3/Bi_2WO_6 Z-scheme heterojunction, which exhibited an exceptional TC degradation efficiency of 82% within 20 minutes. The piezophototronic effect has been demonstrated to substantially improve the separation efficiency of photogenerated charge carriers through the strong driving force induced by the built-in polarization electric field [10-12]. This synergy creates a positive feedback loop: the electron-hole pairs from photocatalysis enhance the material's piezoelectric response[13-15]. Consequently, piezo-photocatalysis represents a pioneering and sustainable strategy for environmental antibiotic remediation.

Significant efforts have been devoted to designing piezo-photocatalytic heterostructures for enhanced catalytic performance. For example, Fu et al. [16] synthesized $BaTiO_3$/TiO_2 core-shell nanofibers, which demonstrated excellent piezo-photocatalytic activity in organic pollutant degradation. Wu et al. [17] developed an S-scheme V-$BiOIO_3$/FTCN heterojunction system that achieved remarkable tetracycline (TC) removal efficiency through synergistic piezo-photocatalysis. Additionally, the BiOBr/$BaTiO_3$ heterojunction showed dramatically enhanced activity under simultaneous ultrasonication and light, with a rate constant of 20.839×10^{-2} min^{-1}, far exceeding piezo- or photocatalysis alone [18]. Despite these advances, conventional heterostructures often suffer from complicated fabrication, interfacial instability, and severe charge recombination at junction interfaces, which considerably limit their practical applicability [7,19-20]. To overcome these limitations, researchers have focused on developing single-component materials that intrinsically combine both piezoelectric and photocatalytic properties. Such materials must simultaneously satisfy two critical requirements: a high piezoelectric voltage coefficient and an appropriate bandgap structure for visible-light absorption. Recent studies have identified several promising semiconductor candidates, including ZnO, CdS, $BiVO_4$, and $BaTiO_3$, which demonstrate effective degradation of hazardous pollutants under combined light irradiation and mechanical stimulation [5,19-23]. Among these, monoclinic $BiVO_4$, with its suitable bandgap (2.4 eV), has emerged as one of the most promising materials in the field of piezo-photocatalysis due to its excellent visible light response, abundant surface oxygen vacancies, and superior electronic conductivity [6, 22, 24]. Furthermore, the polycrystalline phase structure and surface activity of $BiVO_4$ make it highly suitable for coupling with other materials, thereby further enhancing the separation efficiency of electron-hole pairs and improving catalytic performance [25-26].

Recently, noble metal nanoparticles (NPs) featuring the localized surface plasmon resonance (LSPR) effect have garnered substantial attention as high-performance catalytic materials[27-29]. The Fermi levels in noble metals can facilitate electron transfer and extend the lifespan of charge carriers, thereby further enhancing catalytic activity [30-31]. Bimetallic alloys, in particular, often demonstrate superior catalytic activity and stability compared to their monometallic analogues due to synergistic electronic effects [32-34]. For example, Jessi et al. [35] designed Pd/Au core - shell nanorodes that were 50 times more active than monometallic counterparts. Guan et al. [36] reported that a bimetallic Pt-Au catalyst achieved 99% selectivity for haloanilines under mild conditions. As typical noble metals, Pd and Pt nanoparticles are extensively applied in plasmonic catalysis owing to their excellent chemical stability and reusability. Furthermore, Pt and Pd are exceptional co-catalysts for the oxygen reduction reaction, which is a pivotal step in the generation of superoxide radical anions. In the context of piezo-photocatalysis, noble metals would also effectively trap piezo-induced electrons, creating a synergistic ‘electron pool’ that maximizes the utilization of both photo and mechanical energy[37-41]. The combination of a piezo-photocatalytic semiconductor like $BiVO_4$ with bimetallic Pt-Pd NPs presents a compelling strategy to create a high-performance hybrid system. This architecture can leverage the LSPR effect to enhance light absorption and create efficient electron-sink sites, while the piezoelectric field from $BiVO_4$ further drives charge separation. Although considerable efforts have been dedicated to exploring the photocatalytic performance of $BiVO_4$ in environmental remediation, the application of Pt-Pd/$BiVO_4$ piezo-photocatalysis for antibiotic degradation remains largely unexplored. The catalytic mechanism in such a coupled system, where piezoelectricity, photoexcitation, and LSPR effects interact, is fundamentally distinct from conventional photocatalysis and requires dedicated investigation.

Herein, we report the preparation, characterization, and catalytic activity of Pt-Pd/$BiVO_4$ piezo-photocatalyst for the degradation of antibiotics under visible light and/or ultrasound. The decoration of $BiVO_4$ nanosheets with bimetallic Pt-Pd NPs modifies its band structure and electronic distribution, thereby enhancing the stability and durability of the heterostructure. Moreover, the synergistic effect among the bimetallic alloy, localized surface plasmon resonance (LSPR), and piezo- photocatalysis effectively suppresses the recombination of charge carriers and accelerates the kinetic process of the catalytic reaction. The impacts of the Pt-Pd loading content, microtopography, and surface chemical composition of the heterostructures on the piezo-photocatalytic degradation of antibiotics are analyzed in detail. The mechanism underlying the enhanced piezo-photocatalytic activity is elaborated through active species trapping and electron spin resonance (ESR) tests. This study offers a novel approach for the design and synthesis of semiconductor composites by introducing bimetallic NPs into piezo-photocatalysts, holding great potential for applications in energy conversion and environmental remediation.

2. Experimental section

2.1 Materials

All chemicals employed in this study were of analytical grade and obtained from certified suppliers. The following reagents were procured from Sigma-Aldrich: bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, ≥98%), ammonium metavanadate (NH_4VO_3, ≥99%), nitric acid (HNO_3, 68–70%), aqueous ammonia ($NH_3 \cdot H_2O$, 28–30%), palladium chloride ($PdCl_2$, ≥99.9%), platinic chloride ($PtCl_4$, ≥99.9%), sodium borohydride ($NaBH_4$, ≥98%), and polyvinyl alcohol (PVA, Mw ~31,000–50,000). Tetracycline hydrochloride (TC, ≥95%), 1,4-benzoquinone (BQ, ≥98%), tert-butyl alcohol (t-BuOH, ≥99.5%), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, ≥99%), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, ≥97%), and dimethyl sulfoxide (DMSO, ≥99.9%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All solutions were prepared using ultrapure water (18.2 MΩ·cm at 25°C) obtained from a Millipore Milli-Q water purification system to ensure experimental consistency and minimize interference from impurities.

2.2. Preparation of catalysts

2.2.1 Preparation of $BiVO_4$

The monoclinic $BiVO_4$ was synthesized using a facile hydrothermal method, as described in previous literature [42-43]. In a typical synthesis, 7.2 mmol of NH_4VO_3 and 7.2 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ were initially dispersed in 80 mL of 2 mol L^{-1} HNO_3 solution under continuous stirring. Following this, an aqueous ammonia solution was gradually added to the mixture until a pH of 2.0 was achieved. The resulting yellow suspension was then transferred into a Teflon-lined autoclave and subjected to hydrothermal treatment at 180 °C for 24 hours. After the reaction, the yellow product was collected via centrifugation, thoroughly washed with deionized water multiple times, and dried at 80 °C overnight for subsequent use.

2.2.2 Preparation of Pt-Pd/$BiVO_4$ heterojunction

In this procedure, Pt-Pd noble alloy nanoparticles (NPs) were deposited onto the surface of $BiVO_4$ via a reduction method. Aqueous solutions of the metal precursors, $PdCl_2$ (0.01 M) and $PtCl_4$ (0.01 M), were dispersed into a $BiVO_4$/PVA suspension under vigorous stirring. A freshly prepared $NaBH_4$ solution (with a molar ratio of $NaBH_4$ to total metal ions of 5:1) was promptly added to the mixture. The reaction was allowed to proceed under continuous stirring for 24 hours in an ice bath. Subsequently, the product was collected and washed multiple times with deionized water and ethanol. The as-synthesized samples were then dried in a vacuum oven for further characterization and use. For comparative analysis, Pt-Pd/$BiVO_4$ heterojunctions with varying loading percentages of Pt and Pd were prepared and labeled as PPB-0.1, PPB-0.3, PPB-0.5, and PPB-0.7, respectively. Additionally, Pt/$BiVO_4$ and Pd/$BiVO_4$ samples were synthesized following the same procedure for reference. Actual Pt and Pd loadings in the $BiVO_4$ nanosheets, as measured by ICP-OES, are summarized in **Table 1**.

2.3 Catalyst characterization

The morphology and structure of as-prepared samples were obtained by transmission electron microscopy (TEM; JEM-2100F, JEOL Ltd). The crystal structure was characterized by X-ray diffraction patterns (XRD, D2 PHASER, Bruker) with Cu Kα as radiation (30 kV, $\lambda = 1.542$ Å) in a range of 10–70° (2θ). Fourier transform infrared (FTIR) spectra was recorded in a Bruker infrared spectrometer (VERTEX 80V, Germany). The chemical states and elemental compositions of the as-synthesized samples were observed by X-ray photoelectron spectroscopy (XPS, ESCA LAB MK-II) with monochromatized Al Kα radiation, using an ion source energy for charge compensation.

Ultraviolet-visible diffuse reflectance spectra (UV–vis DRS were performed by a Hitachi S-3100 spectrophotometer. An N_2 adsorption-desorption analyzer (BEL BELSORP) was employed to measure the specific surface area, pore size, and pore volume of the catalysts. The active species in the degradation process were detected by trapping experiments. Radical scavengers, including benzoquinone (BQ), *t*-butanol (*t*-BuOH), and disodium ethylenediaminetetraacetate (EDTA-2Na), were introduced into the catalytic system to capture superoxide radicals ($\cdot O^{2-}$), hydroxyl radicals ($\cdot OH$), and holes (h^+), respectively. The electron spin resonance (ESR) measurements were detected by using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as spin-trapping agent on a Bruker EMX PLUS spectrometer.

2.4 Photoelectrochemical and piezophotoelectrochemical activity

The photoelectrochemical (PEC) measurements were conducted using an Ivium electrochemical workstation equipped with a standard three-electrode system. A platinum wire served as the counter electrode, an Ag/AgCl electrode as the reference electrode, and 0.2 M aqueous Na_2SO_4 solution as the electrolyte. To evaluate the piezophotoelectrochemical activity, the three-electrode cell assembly was placed in an ultrasonic transducer with a power of ~100 W and a frequency of ~40 kHz. A 300 W xenon lamp was utilized as the light source for the PEC measurements. Both photocurrent response and electrochemical impedance spectroscopy (EIS) analyses were performed using the electrochemical workstation with the three-electrode configuration.

2.5 Piezo-photocatalytic TC measurement

The piezo-photocatalytic performance of the PPB catalysts was evaluated through the degradation of tetracycline (TC). In a typical experiment, 10 mg of the catalyst was dispersed into 100 mL of an aqueous TC solution (20 mg/L). Before initiating the reaction, the suspension was stirred in the dark for 30 minutes to achieve adsorption-desorption equilibrium between the catalyst and the TC solution. The degradation experiment was conducted under light irradiation (using a 300 W Xe lamp with a 350 nm bandpass filter, 100 mW/cm^2) and/or ultrasonic treatment (100 W, 40 kHz). At specified time intervals, 5.0 mL of the reaction solution was collected, centrifuged, and analyzed using a UV spectrophotometer to monitor the degradation progress. Additionally, electron spin resonance (ESR) measurements were performed to detect reactive species. These measurements utilized 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin-trapping agent and were carried out on a Bruker EMX PLUS spectrometer.

For quantitative evaluation, the degradation rate and kinetics were applied to describe the degradation effect, the following Eq. (1) and (2)

$$\text{Degradation efficiency} = (C_0\text{-}C_t/C_0) \times 100\% \qquad (1)$$

$$kt = -\ln(C_t/C_0) \qquad (2)$$

where C_0 and Ct are the initial and residual concentration of TC; k is the rate constant, and t is the reaction time.

3. Results and discussion

3.1. Crystal stucture and composition

The Pt-Pd/$BiVO_4$ composite was synthesized via a combination of hydrothermal and chemical reduction methods, with varying concentrations of Pt-Pd. The crystallographic structures of the as-prepared catalysts were characterized using XRD analysis, as depicted in **Fig. 1**a. The diffraction peaks corresponding to $BiVO_4$ matched well with the monoclinic structure of $BiVO_4$ (JCPDS card No. 14-0688) [44-45]. As the weight ratio of Pt-Pd nanoparticles (NPs) increased, the characteristic peaks of $BiVO_4$ slightly weakened, indicating the successful formation of Pt-Pd/$BiVO_4$ composites. No diffraction peaks of Pd or Pt species were observed, which is consistent with the formation of a highly dispersed bimetallic structure. The absence of separate metallic peaks, combined with the HR-TEM evidence, further supports the formation of highly dispersed bimetallic entities rather than large, segregated crystalline phases(**Fig. S**1**)**.In the FT-IR spectra (**Fig. S**2), the two characteristic peaks at 758 and 852 cm^{-1} were attributed to the asymmetrical and symmetrical stretching vibrations of the VO_4^{3-} tetrahedron in $BiVO_4$ [45-46]. No distinct diffraction peaks associated with Pt or Pd species were observed, likely due to their low concentration and high dispersion on the $BiVO_4$ surface. Raman spectroscopy was further employed to analyze the structure of the as-prepared materials (**Fig. 1**b). The Raman spectra of pristine $BiVO_4$ exhibited peaks at 125, 210, 327, 366, 710, and 828 cm^{-1}, corresponding to the external mode (rotation/translation), symmetric/asymmetric bending modes, and asymmetric/symmetric V-O stretching modes, respectively. Notably, the higher intensity vibrational bands observed for PPB-0.5 were likely due to the surface-enhanced Raman scattering (SERS) effect induced by the Pt/Pd NPs, suggesting a strong interaction between Pt-Pd and $BiVO_4$. To further confirm the presence of Pt and Pd, the samples were analyzed using TEM and XPS techniques. These analyses provided additional evidence for the successful incorporation and dispersion of Pt-Pd NPs on the $BiVO_4$ surface.

The morphologies of the synthesized PPB-0.5 catalysts were characterized using TEM, as illustrated in **Fig. 2**. From **Fig. 2**a and 2b, it is evident that bimetallic Pt-Pd nanoparticles (NPs) with sizes ranging from 5 to 10 nm were uniformly dispersed on the surface of the $BiVO_4$ nanosheets. High-resolution TEM analysis revealed well-defined lattice fringes measuring 0.253 nm, which can be indexed to the (002) planes of crystalline $BiVO_4$. Lattice fringes with interplanar spacings of 0.226 nm and 0.224 nm were clearly observed in **Fig. S**1, which corresponded to the crystal plane of Pt and crystal plane of Pd, respectively. This uniform dispersion is critical for facilitating efficient charge transfer. Energy-dispersive X-ray (EDX) spectroscopy mapping images (**Fig. 2**c-h) further confirmed the homogeneous distribution of Pd, Pt, Bi, V, and O elements, providing strong evidence for the successful integration of Pt-Pd NPs with $BiVO_4$ in the composite. To assess the piezoelectric properties of the Pt-Pd/$BiVO_4$ catalysts, piezoelectric force microscopy (PFM) was employed. The topography, amplitude, and phase images of PPB-0.5 (**Fig. 3**a-c) revealed a distinct piezopotential and clear phase differences, indicating significant piezoelectric behavior. The corresponding amplitude loop exhibited a characteristic butterfly shape, with a maximum amplitude of approximately 600 pm under ±10 V ramp voltage loop (**Fig. 3**e). Additionally, a well-defined 180° phase angle inversion was observed (**Fig. 3**d), further confirming the presence of a local piezoelectric field in the PPB-0.5 catalyst. These results collectively demonstrate the enhanced piezoelectric properties of the PPB-0.5 composite.

The specific surface area and pore characteristic of Pt-Pd/$BiVO_4$ composites were estimated by N_2 sorption analysis (**Fig. 4**). As shown in **Table S**1, the SBET of the $BiVO_4$, Pd/$BiVO_4$, and PPB-0.5 is calculated as 4.4 m^2/g, 7.1 m^2/g, and 10.5 m^2/g (type IV), respectively. Compared to pure $BiVO_4$, the PPB-0.5 composite possesses a significantly higher specific surface area. We attribute this to the dual function of the metal precursors, which act as a growth moderator during $BiVO_4$ crystallization. This process inhibits excessive crystallite growth and agglomeration, resulting in a finer and more porous microstructure, thereby imparting a higher specific surface area **(Fig. 4**a). The pore size distribution curves (**Fig. 4**b) revealed that a wide range of macropores (2-40 nm), according to the IUPAC definition. The well-developed pore structures and higher specific surface areas are beneficial to enhancing the catalytic performance through facilitating reactant adsorption and charge conduction[47-48]. As a result, the introduction of bimetallic Pt-Pd NPs is expected to effectively degrade pollutants in the degradation process.

The surface compositions and chemical states of the catalysts were analyzed using XPS. The full-scan survey spectra (**Fig. 5**a) of the as-prepared samples revealed distinct XPS signals corresponding to Bi, V, O, Pt, and Pd, consistent with the elemental mapping results (**Fig. 2**). As shown in **Fig. 5**b, the two spin-orbit splitting peaks at 163.9 eV and 169.2 eV were assigned to the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ states of Bi^{3+} species, respectively. In the V $2p_{3/2}$ XPS spectra (**Fig. 5**c), the two peaks at 521.2 eV and 516.4 eV were associated with the surface V species in the PPB-0.5 phase. The O 1s spectrum (**Fig. 5**d) exhibited two characteristic peak at 533.7 and 529.8 eV, corresponding to the oxygen species and hydroxyl groups in PPB-0.5. As illustrated in **Fig. 5**e, three distinct platinum species are identified based on their characteristic binding energies: Pt^{4+} (74.9 eV), Pt^{2+} (72.6 eV), and Pt^{0} (71.2 eV). For the Pd 3d spectrum (**Fig. 5**f), four peaks were observed at 341.5 eV, 339.5 eV, 336.2 eV, and 334.5 eV, which were attributed to Pd $3d_{3/2}(Pd^{2+})$, Pd $3d_{3/2}(Pd^{0})$, Pd $3d_{5/2}(Pd^{2+})$, and Pd $3d_{5/2}$ (Pd^{0}), respectively. Additionally, the presence of zero oxidation states for both metallic Pd and Pt NPs (**Fig. 5**e and **5**f) confirmed the successful deposition of Pd and Pt NPs on the surface of the photocatalysts. Generally, variations in electron density can lead to shifts in binding energies due to electron screening effects. The observed shift in binding energies toward higher values upon combining Pt and Pd NPs with $BiVO_4$ (**Fig. 5**) further corroborates the formation of the PPB-0.5 hybrid structure.

3.2. Optical and electronic characteristics

The UV-vis diffuse reflectance spectroscopy (DRS) (**Fig. 6**a) was employed to evaluate the light absorption properties of the samples. The absorption edge of pure $BiVO_4$ was observed at approximately 550 nm, corresponding to the band transition from the Bi 6s orbital to the V 3d conduction band. The Pt-Pd/$BiVO_4$ composite exhibited enhanced light absorption with a slight red shift in the visible light region, indicating improved visible light utilization. This enhancement can be attributed to the deposition of metallic Pt and Pd species on the crystal facets of $BiVO_4$, which induced a surface plasmon resonance (SPR) effect. The as-prepared $BiVO_4$ exhibits a bandgap energy of ~2.4 eV, determined from the extrapolated intercept on the abscissa.

To investigate the generation, transfer, and separation of charge carriers during the catalytic reaction, transient photocurrent measurements were conducted under simultaneous light irradiation and ultrasound. As shown in **Fig. 6**b, the PPB-0.5 sample demonstrated the highest photocurrent density among all samples, consistent with its superior piezo-photocatalytic performance. To further explore the influence of the piezoelectric field on photocatalysis, the photocurrent response of PPB-0.5 was measured with and without ultrasound (**Fig. 6**c). Notably, the photocurrent density significantly increased when ultrasound was applied, demonstrating that the piezoelectric field generated by vibrational energy effectively promoted the separation and migration of photogenerated charge carriers, thereby enhancing the photocurrent response.

Electrochemical impedance spectroscopy (EIS) measurements were conducted to further assess the charge transfer behavior of the as-prepared samples. As shown in **Fig. 6**d, the EIS Nyquist plots revealed that the PPB-0.5 composite exhibited the smallest radius of the impedance arc among all samples. This indicates that the PPB-0.5 composite facilitated more efficient charge carrier separation and transfer, thereby enhancing the oxidation reaction kinetics. Moreover, the emission band observed at 490-510 nm (**Fig. S**3) corresponds to the band-band photoluminescence (PL) phenomenon characteristic of $BiVO_4$. Notably, Pt-Pd/$BiVO_4$ exhibits significant PL emission quenching compared to pristine $BiVO_4$, demonstrating that the built-in potential effectively suppresses charge recombination. The PL intensity was further decreased upon ultrasound application, clearly indicating that the piezoelectric field effectively facilitated the separation and migration of photogenerated charge carriers.

3.3. Piezo-photocatalytic degradation of TC

The catalytic performance of the as-prepared samples was evaluated by monitoring the variation in tetracycline (TC) concentration over time under different conditions (i.e., light irradiation, ultrasound, and combined light irradiation with ultrasound). Compared to individual piezocatalysis and photocatalysis, the piezo-photocatalysis system demonstrated significantly enhanced degradation activity. Among all the catalysts, PPB-0.5 exhibited the highest catalytic efficiency for TC degradation (**Fig.** 7a, c, e). Notably, 99.9% of TC was degraded over PPB-0.5 under simultaneous ultrasonic vibration and visible light irradiation within 50 minutes, while the degradation efficiency for pure $BiVO_4$ was only 65.4%. This remarkable improvement can be attributed to the synergistic effects of surface plasmon resonance (SPR), photocatalysis, and piezoelectric properties resulting from the loading of Pt and Pd nanoparticles (NPs) on the $BiVO_4$ surface. The corresponding pseudo-first-order reaction kinetics for TC degradation are presented in **Fig. 7**b, d, f. The high reaction rate constant (K) of Pt-Pd/$BiVO_4$ under photocatalysis, piezocatalysis, and piezo-photocatalysis further confirmed its superior degradation efficiency. These results highlight that the enhanced catalytic performance is primarily due to the formation of intimate interfaces between Pt-Pd NPs and $BiVO_4$, which establish a continuous pathway for charge migration. Additionally, the composite maintained approximately 89% of its initial activity after four consecutive cycles (Fig. 8a), demonstrating a reasonable degree of operational stability. The XRD and XPS patterns of PPB-0.5 before and after use (**Figs. S**4 and **S**5) remained nearly identical, confirming its structural stability and reusability. The efficiency decline is likely attributed to the progressive coverage of active sites by strongly adsorbed organic intermediates generated during the incomplete mineralization of TC. A comparison of the piezo-photocatalytic performance of PPB-0.5 with various catalysts reported in the literature is summarized in **Table 2**[49-54]. The results indicate that the PPB-0.5 composite exhibits superior TC degradation efficiency compared to most other catalytic systems, underscoring its potential for practical applications in pollutant degradation.

3.4. Mechanism study

To identify the active species generated during the piezo-enhanced photocatalytic reaction, trapping experiments were conducted using PPB-0.5. Ethylenediaminetetraacetic acid (EDTA), tert-butanol (t-BuOH), and benzoquinone (BQ) were employed as scavengers to trap h^+, $\cdot OH$, and $\cdot O_2^-$ species, respectively. The time-dependent piezo-photocatalytic degradation curves of TC are shown in **Fig. 8**b, revealing that the addition of scavengers suppressed the TC degradation efficiency to varying degrees. Notably, the introduction of BQ, as a $\cdot O_2^-$ quencher, had the most significant inhibitory effect, indicating that $\cdot O_2^-$ played a dominant role in the TC degradation process. To further validate the catalytic mechanism, electron spin resonance (ESR) measurements were performed. As illustrated in **Fig. S6** and **Fig. 8**c-d, characteristic signals corresponding to DMPO-$\cdot OH$ and DMPO-$\cdot O_2^-$ were detected for $BiVO_4$, $Pt/BiVO_4$, $Pd/BiVO_4$, and PPB-0.5, confirming the generation of reactive species. No radical signals were observed under dark conditions. When only ultrasonic vibration was applied, weak radical signals emerged, suggesting a limited piezocatalytic effect. However, under light irradiation, a significant enhancement in radical signal intensity was observed, highlighting the dominant role of photocatalytic activity in radical generation. Importantly, the signal intensities of $\cdot OH$ and $\cdot O_2^-$ for PPB-0.5 were the strongest among all samples under combined vibration and light irradiation, demonstrating that more reactive radicals ($\cdot OH$ and $\cdot O_2^-$) were generated during the piezo-photocatalytic reaction. These results indicate that the PPB-0.5 piezo-photocatalysis system efficiently generates more photogenerated charge carriers, which participate in redox reactions through the built-in polarization field, thereby enhancing the overall catalytic performance. The identified radical-based mechanism ($\cdot OH$ and $\cdot O_2^-$), known for its non-selective oxidation of diverse organic compounds, indicates that PPB-0.5 holds inherent potential for broad-spectrum environmental remediation, including the removal of dyes and pharmaceuticals.

The piezo-photocatalytic reaction mechanism can be summarized as follows:

$$\text{PPB-0.5} + \text{light and ultrasound} \rightarrow e^- + h^+ \qquad (3)$$

$$e^- + O_2 \rightarrow \cdot O_2^- \qquad (4)$$

$$O_2^- + e^- + 2H^+ \rightarrow H_2O_2 \qquad (5)$$

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \qquad (6)$$

$$(\cdot OH + h^+ + \cdot O_2^-) + TC \rightarrow CO_2 + H_2O \qquad (7)$$

Based on theoretical insights and the experimental results, a plausible mechanism for the piezo-photocatalytic degradation of TC over Pt-Pd/$BiVO_4$ is proposed. As illustrated schematically in **Fig. 9**, the hydrothermally synthesized $BiVO_4$ nanosheets are considered as a moderate bandgap semiconductor, possessing a bandgap of $\approx$2.4 eV. Under visible light irradiation, PPB-0.5 is excited to generate electron-hole pairs. The photogenerated electrons in the conduction band (CB) of $BiVO_4$ rapidly migrate to the surface of Pt-Pd nanoparticles (NPs), while the photogenerated holes remain in the valence band (VB). Simultaneously, mechanical stress induces the formation of polarized electric fields in $BiVO_4$, which accumulate positive and negative charges on opposite crystal surfaces. The synergistic effects of piezoelectric polarization and the surface plasmon resonance (SPR) effect facilitate the effective separation and rapid transfer of photogenerated carriers to the catalyst surface, significantly reducing the recombination rate of electron-hole pairs. During the degradation process, the accumulated electrons on the surface activate TC to produce $\cdot O_2^-$ radicals, while the photogenerated holes in the VB react with OH^- in the solution to form $\cdot OH$ radicals. By integrating the SPR effect, photocatalytic activity, and piezoelectric properties, PPB-0.5 generates a higher concentration of active radicals, which actively participate in the TC degradation reaction. This synergistic mechanism results in significantly enhanced piezo-photocatalytic performance, demonstrating the superior efficiency of the PPB-0.5 system in pollutant degradation.

Conclusions

In this study, bimetallic Pt-Pd NP-decorated $BiVO_4$ piezo-photocatalysts (Pt-Pd/$BiVO_4$) were successfully synthesized using a facile hydrothermal and chemical reduction method. The prepared PPB-0.5 composites exhibited significantly enhanced piezo-photocatalytic activity for TC degradation compared to pure $BiVO_4$. This improved performance is primarily attributed to the synergistic effects of the surface plasmon resonance (SPR) effect, photocatalytic activity, and piezoelectric properties, which collectively enhance carrier transport efficiency. Notably, the PPB-0.5 heterojunction demonstrated the highest piezo-photocatalytic performance, achieving nearly complete degradation (99.9%) of TC in wastewater within 50 minutes. Furthermore, the PPB-0.5 catalysts maintained excellent stability, with only a minimal loss of activity after four consecutive cycles. While the noble metal cost challenges scale-up, the high performance and stability of PPB-0.5 provide a compelling proof-of-concept. This work provides new insights into the design of highly efficient piezo-photocatalysts for pollutant degradation, highlighting the significant contributions of the SPR effect and piezoelectric properties to the photocatalytic activity of piezoelectric materials. These findings pave the way for the development of advanced catalytic systems for environmental remediation.

CRediT authorship contribution statement

Hao Sun: Writing-original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Xu Zhao**: Supervision, Resources, Funding acquisition, Methodology, Writing-review & editing. **Martin R. Tillotson**: Writing-review & editing, Methodology, Investigation. **Wei Guo**: Writing-review & editing, Validation, Conceptualization.

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Data availability

Data will be made available on request.

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Fig. 1. XRD spectra of $BiVO_4$ and Pt-Pd/$BiVO_4$ with different Pt-Pd loading contents; (b) Raman spectra of the $BiVO_4$ and PPB-0.5 samples.

Fig. 2. (a-b) TEM of PPB-0.5 nanocomposites (c-h) elemental mapping patterns of PPB-0.5 samples.

Fig. 3. (a) Topographic images, (b) amplitude images, (c) phase images, (d) amplitude-voltage and (e) phase-voltage curves of PPB-0.5 samples.

Fig. 4. (a) Nitrogen adsorption-desorption isotherms of the synthesized samples; (b) pore size distributions of the synthesized samples.

Fig. 5. XPS spectra of $BiVO_4$, Pt/$BiVO_4$, Pd/$BiVO_4$ and PPB-0.5 samples. (a) Survey spectra; (b) Bi 4f; (c) V 2p; (d) O 1s (e) Pt 4f; (f) Pd 3d.

Fig. 6. (a) UV-vis DRS spectra of as-prepared samples; (b) Transient photocurrents of all samples under light irradiation (L) and ultrasound (U); (c) Transient photocurrents of PPB-0.5 in the presence or absence of ultrasound; (d) EIS of p$BiVO_4$, Pt/$BiVO_4$, Pd/$BiVO_4$ and PPB-0.5 composites.

Fig. 7. (a) TC degradation experiments for $BiVO_4$, Pt/$BiVO_4$, Pd/$BiVO_4$ and Pt-Pd/$BiVO_4$

catalysts for (a) Piezocatalytic, (c) photocatalytic, and (e) piezo-photocatalytic performance; and (b), (d) and (f) show the corresponding first-order kinetics plots of the different catalysts.

Fig. 8. (a) Recycling runs of PPB-0.5; (b) photocatalytic performance of PPB-0.5 with different species of quenchers (EDTA-2Na for h^+, *t*-BuOH for ·OH, *P*-benzoquinone for $\cdot O_2^-$); and (c-d) ESR spectra of $BiVO_4$, $Pt/BiVO_4$, $Pd/BiVO_4$ and PPB-0.5.

Fig. 9. Piezo-photocatalytic mechanism of TC degradation by PPB-0.5.