Understanding the Structural-Dependent Photocatalytic Antibacterial Activity: a Case Study of Ag Modified BiVO₄

Hailin Guan, Yuefeng Tian, Alideertu Dong* and Yiguo Su*

Abstract
In this work, Ag/BiVO₄ heterostructural photocatalysts were developed in order to reveal exceptional structural-dependent photoinduced charge migration kinetics as well as the underlying photocatalytic antibacterial dynamic process. The structure-dependent interface of BiVO₄ and Ag nanoparticles was successfully constructed to improve the photoinduced interface charge transfer efficiency and interface correlation. DFT calculation indicated that a net charge of about 0.33 e between Ag and tz-BiVO₄ was achieved by extraordinary interface charge transfer, being far larger than that between Ag and ms-BiVO₄. Larger net charge has consequences on mobility of charge carriers of tz-BiVO₄ that can raise the migration and separation of charge carriers for Ag/tz-BiVO₄ heterojunction. Fine interfacial contact between Ag and tz-BiVO₄ led to the optimized photocatalytic performance toward E. coli inactivation, being predominately higher than that of tz-BiVO₄, ms-BiVO₄, and Ag/ms-BiVO₄ catalysts. Besides photocatalytic activity, the thermocatalytic inactivation activity of Ag/tz-BiVO₄ also exhibited a factor of about 7.2 and 3.1 times higher than that of tz-BiVO₄ and Ag/ms-BiVO₄. Trapping and EPR measurements suggested that the structural-dependent photocatalytic activity of Ag/BiVO₄ mainly originated from the pronounced variation of the capability to produce H₂O₂ active species, where the capability of generating H₂O₂ over Ag/tz-BiVO₄ is highly accelerated. Moreover, it cannot be ignored that this study provides an ideal candidate for many aspects, such as environmental and water pollution caused by pathogenic microorganisms and disinfection of medical materials, food packaging, household materials, and public places, etc.

Keywords: Ag/BiVO₄, Photocatalysis, Structural dependent, E. coli inactivation, DFT calculation

Background
Utilization of solar light and semiconductors for photocatalytic purpose is still a research hotspot, which is found wide applications in energy conversion and environmental remediation [1, 2]. Nano-heterojunctions have also received attention that has to be taken seriously, because they can be applied to various aspects and have achieved extraordinary results in many potential applications [3–8]. Furthermore, due to its advantages of high efficiency, environmentally friendly, and renewable energy, photocatalytic antibacterial technology has an irreplaceable role in environmental governance and sterilization [9, 10]. Recently, BiVO₄ emerges an excellent candidate because of its tunable crystal structure and appropriate electronic structure [11, 12]. However, despite the favorable structural characteristics of BiVO₄, inefficient charge carrier transmission and short length of carrier diffusion are hindrance of its application in practice. From solid state physics viewpoint, the photocatalytic performance is thought to be predominately regulated by the distortion of microstructure. The tetragonal zircon (tz-) BiVO₄ synthesized by ethylene-glycol colloidal path controllable at room temperature induces strongly improved photocatalytic activity over monoclinic scheelite (ms-) BiVO₄, yet the underlying

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mechanism remains ambiguous [13]. Therefore, the modification of BiVO<sub>4</sub> is not limited to improving the photocatalytic activity; it is also absolutely necessary to explain the kinetics of photoinduced charge transfer from the microstructure.

Frequently, localizations of excess charge carriers as the so-called localized polarons accompanied by microstructural and interfacial regulation have intensely emotional impact on charge carrier mobility of oxide semiconductors. Localized polarons in BiVO<sub>4</sub> either inhibit the kinetics of charge mobility or influence the photocatalytic activity at surfaces [14, 15]. The reconstruction of surface or interface structures can drive the variation of polaron extension that affects the mobility of charge carriers as well as the photocatalytic performance. Noble metals, like Ag, Au, and et al., can act as photosensitizers to absorb visible light and regulate the generation of charge carrier through direct electron transfer or dipole-dipole coupling connection [16, 17].

The junction of noble metal with semiconductor to establish interfacial charge transfer provides an efficient approach to influence the polaron extension as well as the mobility of charge carriers that can raise the migration and separation of charge carriers. For instance, Au nanosphere decorated Mo:BiVO<sub>4</sub> photoanode displays increased photocurrent intensity of about 2.2 times in comparison to Mo:BiVO<sub>4</sub> [18]. Recent investigations on Ag/BiVO<sub>4</sub> nanostructures demonstrate highly improved photocatalytic performance toward water oxidation, organic dye degradation, and so forth [19, 20]. Most reports very often merely concentrated on fine characterization of photocatalytic response but did not focus on the microstructural analyses which profoundly governed the native photophysical and photochemical performance of semiconductors. Considering to uncovering the structural-dependent native properties, experimental identification of phase structure as well as surface/interface feature of Ag/BiVO<sub>4</sub> nanostructure is essential and advantageous to regulate the native properties and provides some hints to various structural-linked semiconductors.

Herein, this work means to deliver a proof by rationally controlling the phase structure of BiVO<sub>4</sub> and assembling Ag nanoparticles for photocatalytic antibacterial purpose in order to reveal structural-dependent photoinduced charge migration as well as the underlying photocatalytic antibacterial dynamic process.

**Methods/Experimental**

**Chemicals**

Bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) (purity 99%), silver nitrate (AgNO<sub>3</sub>) (purity 99.8%), and absolute ethanol (purity 99.7%) were obtained from Wind ship in Tianjin chemical reagent Co. Ltd (Tianjin, China). Ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) (purity 99.9%) was purchased from Adamas Reagent Co. Ltd (Shanghai, China). Distilled water was also needed. All reagents were used without further purification.

**Synthesis of BiVO<sub>4</sub> and Ag-Loaded BiVO<sub>4</sub>**

**Synthesis of BiVO<sub>4</sub>**

BiVO<sub>4</sub> samples were prepared by hydrothermal method. One millimole of Bi(NO<sub>3</sub>)<sub>3</sub> was added into 20 mL of distilled water under mild stirring, and a white suspension was formed for 30 min. One millimole of NH<sub>4</sub>VO<sub>3</sub> was added into 40 mL of distilled water to form a white suspension with stirring for 30 min. Then, NH<sub>4</sub>VO<sub>3</sub> suspension was dropwishe into the Bi(NO<sub>3</sub>)<sub>3</sub> solution to form an orange suspension. The pH value of the orange suspension is 0.59. Sodium hydroxide solution was adopted to adjust the pH value from 0 to 12 for the above suspension. And the suspension was loaded into a 100 Teflon-lined autoclave. The autoclave was sealed and heated in an oven at 180 °C for 12 h. The pH value of the suspension after the reaction was maintained. The autoclave was then naturally cooled to room temperature, where the obtained yellow powder was collected and washed with distilled water and ethanol several times to remove ions and possible remnants until the pH value near neutral and vacuum-dried for further characterization.

**Synthesis of Ag-Loaded BiVO<sub>4</sub>**

A set of five identical solutions was prepared, each of which contains 1 g BiVO<sub>4</sub> mixed in 40 mL of ethanol and sonicated for 10 min. Another set of solutions containing an appropriate amount of AgNO<sub>3</sub> was obtained. Then, AgNO<sub>3</sub> aqueous solution was carefully dropped into BiVO<sub>4</sub> solution and kept in the dark for 1 h with constant stirring. After that, the mixture of AgNO<sub>3</sub> and BiVO<sub>4</sub> was exposed to UV light for 2 h with stirring so as to Ag nanoparticles loaded BiVO<sub>4</sub> samples. The samples were then dried overnight at 60 °C. The initial Ag loading content was fixed to be 1 wt%, 3 wt%, 5 wt%, 7 wt%, and 10 wt%.

**Bacteria Preparation**

The lyophilized powder was dissolved, and 1 mL of the bacterial suspension was adhered to the solid culture plate with a hot-sterilized toothpick. The inoculated solid culture plate was inverted and placed in a 37 °C incubator for 12 h. Then, the selection of the single colony and the expansion of the culture are carried out. The final cell density was adjusted to about 1 x 10<sup>7</sup>–1 x 10<sup>9</sup> colony forming unit (CFU) mL<sup>−1</sup>.
**Photocatalytic Bacterial Inactivation**

The VLD photocatalytic inactivation of *Escherichia coli* (*E. coli* ATCC 8099, Gram-negative bacteria) and *Staphylococcus aureus* (*S. aureus* ATCC 25923, Gram-positive bacteria) by Ag/tz-BiVO₄ was conducted under fluorescent tubes (PCX50C Discover) irradiation. A suspension (40 mL) containing the bacterial cells and the photocatalyst (40 mg). Then, the solution was turned on to start the photocatalytic inactivation experiments. At different time intervals, aliquots of the samples were collected and serially diluted with sterilized aqueous solution. Then, 1 mL of the diluted samples was immediately spread on Nutrient Agar plates and incubated at 37 °C for 12 h to determine the number of survival cells. *S. aureus* cultured at 54 °C for 24 h. For the comparison, light control (bacterial cells and light without photocatalyst) and dark control (photocatalyst and bacterial cells without light) were also conducted in the study.

The photocatalytic degradation performance of the prepared samples was evaluated by photodegradation of the MB (Methylene Blue) dye solution (5 mg/L, 30 mL) under visible light irradiation. A 300 W Xenon lamp equipped with a 420-nm cutoff filter was used as the light source. In the photodegradation experiment, 15 mg of photocatalysts was dispersed in 30 mL of the MB dye solution. To ensure the balance of adsorption and desorption, the quartz tube containing the solution was kept in the dark for 1 h before irradiation. At specific time intervals, 4 mL of the suspension was collected and analyzed by UV-visible diffuse reflectance spectrometer. The absorption peaks at 672 nm were employed to determine the concentration of the residual MB solution.

To identify the dominant reactive species accounting for the photocatalytic bacterial inactivation, specific compounds (i.e., respective scavengers) at predetermined optimized concentration were individually added into reaction solution with identical conditions mentioned above. All the above experiments were repeated in triplicates. At the same time, the capture experiment of photocatalytic degradation of MB solution was also performed.

**Preparation Procedure for SEM Observation of Bacteria**

The mixtures of photocatalyst *E. coli* before and after the inactivation were firstly sampled and centrifuged and wash the bacteria solution twice with PBS (phosphate buffer saline). After this, the harvested cells were prefixed in 2.5% glutaraldehyde for 12 h. After washed with 0.1 M PBS, the specimens were dehydrated in a graded series of ethanol (20% for once, 50% for once, 80% for one time, 100% for one time) each for 10 min and then wash the sides with t-butanol. Finally, drop it onto a clean silicon wafer for SEM observation.

**Morphology, Structure, and Optical Properties Characterizations**

Phase purity of all samples was characterized by X-ray diffraction (XRD) on Rigaku DMAX2500 X-ray diffractometer using a copper target (λ = 0.15406 nm). The scanning speed was 1° per minute, the scanning step was 0.05°, and the scanning range was set to 5–80°. Morphology of the samples was determined using scanning electron microscopy (SEM) on S4800 apparatus working at 10 kV and transmission electron microscopy (TEM) on a DHG-9240B FEI apparatus with an acceleration voltage of 200 kV. Appropriate amount of catalyst to be tested was dispersed it in absolute ethanol by ultrasonic dispersion. In the SEM test, the dispersed sample was dropped on a clean silicon wafer, and in the TEM test, it was dropped on a copper mesh supported by a carbon film. X-ray photoelectron spectroscopy (XPS) measurement were performed on a Thermo ESCALAB 250 with Al Ka (1486.6 eV) line at 150 W. To compensate for surface charges effects, the binding energies were calibrated using the C 1s peak at 284.60 eV as the reference; the casaXPS program was used to realize the quantification of the elements. UV-visible diffuse spectra of the samples were measured using Lambda 750 s UV/vis spectrometer. Barium sulfate was chosen as the reference substrate, and the scanning test range was set to 200–800 nm. Surface photovoltage spectrum (SPV) was obtained by a self-assembly system consisting of a sample chamber, a lock-in amplifier with a light chopper, and a 300 W Xenon lamp as light source. The photo-electrochemical performance of the samples was recorded on AUT302N electrochemical workstation (Metrohm) with standard three-electrode cell. Among them, the electrodes of catalyst sample, standard Ag/AgCl, and platinum were defined as the electrode of working, reference, and counter, respectively. The electrolyte solution was sodium sulfate (Na₂SO₄) solution with the concentration of 0.2 M, and the light source was LED light. Photoluminescence spectra analysis was carried out on an Edinburgh Instruments FLS920 spectrophotometer. Electron Paramagnetic Resonance (EPR) spectra for hydroxyl radicals (sample, 4 mg; DMPO, 0.22 M; aqueous solution volume, 2.0 mL) and superoxide radicals (sample, 4 mg; DMPO, 0.22 M; methanol solution volume, 2.0 mL) were provided both in dark and visible light irradiation at 3186 G and 9056.895 MHz by an ER200-SRC electron spin resonance spectrometer (Bruker, Germany). The magnetic field strength, microwave strength, and scan width were set to 0.2 mT, 1 mW, and 250 mT, respectively. The sample to be tested was placed inside the NMR tube, and the test was performed in air at room temperature. All structural optimization and property calculations were performed using the CASTEP program package based on density
functional theory (DFT) in the Materials Studio 2017 R2. The Perdew Burke Ernzerh (PBE) of generalized gradient approximation (GGA) was selected for exchange correlation of the interaction between electrons. The kinetic cut-off energy of 380 eV was set. The plane wave function was used as basis sets. The calculations of the electronic state and state density were performed based on the optimized crystal structure.

Results and Discussion

XRD data imply that a phase structure variation from monoclinic scheelite (ms-) to tetragonal zircon (tz-) structure of BiVO₄ can be achieved (Fig. S1). The junction of Ag nanoparticles led to no obvious alteration of the diffraction peaks of BiVO₄ (Fig. S1). However, from Rietveld’s refined results, it is noted that either Ag/tz-BiVO₄ or Ag/ms-BiVO₄ showed an apparent lattice expansion in comparison to pristine tz-BiVO₄ and ms-BiVO₄ samples, which is summarized in Table S1. Lattice variation of BiVO₄ matrix promised fine interfacial contact between Ag and BiVO₄ nanoparticles, which is also proved by TEM observations. TEM and HRTEM images were given in Fig. 1b. Apparently, either ms-BiVO₄ or tz-BiVO₄ can act as a support to bind highly dispersed Ag nanoparticles, where the content of Ag nanoparticles is close to initial value as verified by EDS data (Fig. S3) [21, 22]. The d-spacing of 0.239 nm corresponds to the (111) plane of Ag (JCPDS No. 87-0597), whereas the adjacent lattice fringes of 0.308 nm and 0.484 nm are closely related to the (112) plane of ms-BiVO₄ and (200) plane of tz-BiVO₄, respectively.

To acquire the surface chemical composition and oxidation states of the as-prepared samples, XPS technique was adopted. XPS results can fully verified that the Ag/BiVO₄ catalyst was successfully prepared by the analyses of the binding energies over Bi, V, O, and Ag elements, as illustrated in Fig. 2 and Fig. S4. From Fig. 2a, it is seen that the Bi 4f orbital of tz-BiVO₄ can be well-reproduced to two peaks with binding energies of 164.1 eV and 158.8 eV, which can be ascribed to the Bi 4f₅/₂ and Bi 4f₇/₂ orbitals, being close to the previous reported value [23, 24]. As for Ag/tz-BiVO₄, a slight toward lower binding energy of about 0.3 eV was observed for Bi 4f orbital. Figure 2b shows the high-resolution XPS data of V element. It is clearly that the binding energies of V 2p₁/₂ and V 2p₃/₂ locate at ~ 524.2 eV and 516.6 eV for pristine tz-BiVO₄. Similar to that of Bi 4f orbital, V 2p orbital also gave a red shift of the binding energies for Ag/tz-BiVO₄ heterojunction. Moreover, the O 1s XPS analysis was also illustrated in Fig. 2c. Three typical binding energies of O 1s orbital for tz-BiVO₄ appears at 529.6 eV, 531.6 eV, and 533 eV, respectively, which can be assigned to the lattice oxygen, oxygen of surface hydration as well as the chemical-absorbed molecular O₂, respectively [25]. As for Ag/tz-BiVO₄, a red shift of ~0.2 eV was observed for the lattice oxygen in comparison to pristine tz-BiVO₄. Such a behavior is supposed to be related to lattice expansion as well as the interfacial interaction between Ag and tz-BiVO₄. Very often, the lattice expansion accompanies with elongated average lattice bonds and weakened strength of these bonds, which leads to the decrease of binding energies [26]. On the other hand, the variation of binding energies reflects the rearrangement of electron density near atoms, which can be influenced by surface modification. The decrease of the binding energies also implies the fine interfacial contact between Ag and tz-BiVO₄, predicting an interfacial transfer may occur, which resulted in the variation of electron density [27]. This suspension can be verified by the following theoretical results. Moreover, XPS data also confirmed the metallic feature of Ag nanoparticles, and no evidence of Ag⁺ was observed in Ag/tz-BiVO₄ heterojunction (Fig. 2d) [28]. On the other hand, the XPS results of Ag/ms-BiVO₄ were also given in Fig. S4.
Similar to that of Ag/tz-BiVO₄ heterojunction, the binding energies of Bi 4f, V 2p, and O 1s orbitals in Ag/ms-BiVO₄ also exhibited a tiny redshift of about 0.1~0.2 eV. The slight variation of the binding energy shift in Ag/tz-BiVO₄ and Ag/ms-BiVO₄ is likely to be ascribed to the structural-dependent interfacial feature of BiVO₄ and Ag nanoparticles.

Since the lattice expansion of BiVO₄ occurred after Ag modification, the electronic structure may also be influenced, which can be verified by density functional theory (DFT) calculations. Because of large lattice mismatch between Ag and BiVO₄, the convergence and structural optimization of Ag/BiVO₄ is inaccessible. Thereby, a cluster/surface model was established to reveal the interfacial correlations between Ag and BiVO₄ (Fig. S5 and Fig. S6). The band gap energy of tz-BiVO₄ was estimated to be 2.59 eV, which is larger than that of 2.17 eV for ms-BiVO₄ (Fig. S7), being in accordance to

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**Fig. 2** XPS spectra of tz-BiVO₄ and Ag/tz-BiVO₄ samples: (a) Bi 4f, (b) V 2p, (c) O 1s, and (d) Ag 3d orbital

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**Fig. 3** UV-visible diffuse reflectance spectra (a) and surface photovoltage spectra (b) of the as-prepared samples
previous reported results [13, 29]. The anchoring of Ag cluster on BiVO$_4$ surfaces has no obvious consequences on the typical electronic transitions from O 2p to V 3d orbital, as illustrated by the UV-visible diffuse reflectance spectra of the as-prepared samples (Fig. 3a). From Fig. 3a, it is seen that both ms-BiVO$_4$ and tz-BiVO$_4$ showed visible light response. According to Kubelka-Munk theory, the band gap energy of the samples can be calculated from the relationship between light absorption and band gap.

\[
(\alpha h\nu)^2 = A(h\nu - E_g)
\]

where \(\alpha\), \(h\), \(\nu\), \(E_g\), and \(A\) mean absorption rate, Planck constant, frequency, band gap, and constant, respectively. The band gap energy of ms-BiVO$_4$ and tz-BiVO$_4$ was estimated to be 2.40 eV and 2.69 eV, respectively (Fig. S8), being close to the DFT results. It is noted the modification of Ag nanoparticles on BiVO$_4$ surfaces led to an extension of the visible light absorption (Fig. S9).

As illustrated by the surface photovoltage (SPV) signals in Fig. 3b, the maximal SPV signal of tz-BiVO$_4$ was achieved to 0.33 mV after Ag modification, which is about 91.7 times higher than that of pristine tz-BiVO$_4$. Moreover, it is noted that the intensity of SPV signal for Ag/tz-BiVO$_4$ is also much higher than that of Ag/ms-BiVO$_4$. Frequently, the SPV signal derived only from the photoinduced charge separation capability, the modification of Ag nanoparticle on BiVO$_4$ can also has great impact on the kinetics of photoinduced charge carriers.

Having the above-mentioned results in mind, Ag/BiVO$_4$ heterostructures would display structural-dependent photocatalytic performance. A wild bacterium, *E. coli*, was chosen as a model bacterium to study the photocatalytic inactivation activity of Ag/tz-BiVO$_4$ and Ag/ms-BiVO$_4$, respectively. Because *E. coli* is a Gram-negative bacterium, an auxiliary study was also carried out using a representative of Gram-positive bacteria with *S. aureus* (Fig. S10). A comparative study was firstly conducted to verify the inactivity of visible light...
toward the E. coli inactivation. As shown in Fig. 5a, the inactivation experiments of E. coli by tz-BiVO$_4$, Ag/tz-BiVO$_4$, ms-BiVO$_4$, and Ag/ms-BiVO$_4$ were carried out under visible light irradiation. It can be seen from Fig. 5a that the inactivation performance for E. coli over pristine tz-BiVO$_4$ and ms-BiVO$_4$ photocatalyst was merely detectable. However, anchoring of Ag nanoparticles can modulate the photocatalytic inactivation performance of BiVO$_4$ (Fig. S11). Meanwhile, a structural-dependent photocatalytic performance was observed. When the weight ratio of Ag reached to 7%, Ag/tz-BiVO$_4$ exhibited optimized photocatalytic inactivation efficiency over E. coli compared with some materials in the previous reports (Table S3). Within 90 min, the efficiency of bacterial inactivation reaches 100%, whereas Ag/ms-BiVO$_4$ hetero-photocatalyst displayed tiny photocatalytic activity toward E. coli inactivation under VL irradiation (Fig. S11). As reported previously, Ag nanoparticles have found that ms-BiVO$_4$ was inert to the inactivation of E. coli, while tz-BiVO$_4$ exhibited poor activity either under VL irradiation or in dark. After Ag nanoparticles modification, the thermocatalytic activity was greatly improved. For instance, the thermocatalytic inactivation activity of Ag/tz-BiVO$_4$ improved a factor of about 7.2 and 3.1 times higher than that of tz-BiVO$_4$ and Ag/ms-BiVO$_4$. Moreover, with VL irradiation, the catalytic activity of both Ag/tz-BiVO$_4$ and Ag/ms-BiVO$_4$ was predominately enhanced. The similar results can be obtained in the photocatalytic degradation of MB dye solution (Fig. S12a). After 7 h of visible light irradiation, the photocatalytic degradation rate of MB dye solution by 7Ag/tz-BiVO$_4$ can reach about 85%. So as to know the destruction process of E. coli by Ag/tz-BiVO$_4$, SEM observation was conducted to examine the morphology changes during the photocatalytic inactivation process as illustrated in Fig. 5c and d. As shown in Fig. 5c, when the bacterial was not in contact with the catalyst, E. coli exhibited a well-preserved rod shape and intact cell structure. After 2 h irradiation reaction, disorganized membrane structures are observed (Fig. 5d), which demonstrates that the cell is completely decomposed. This matches well with the previous studies that photocatalytic treatment can induce significant disorder in membrane permeability of bacterial cells.

![Fig. 5](image-url)
To get further information of the photocatalytic process as well as the radical oxygen species that determine the inactivation process of *E. coli*, several types of radical species scavengers were carefully introduced by repeating the photocatalytic process of *E. coli* inactivation. As shown in Fig. 6a, sodium oxalate, isopropanol, Cr(VI), Fe(II)-EDTA, and Tetramethylpiperidine (TEMPOL) were taken as the scavengers for holes (h⁺), hydroxyl radicals (•OH), electrons (e⁻), H₂O₂, and superoxide radicals (•O₂⁻) [33, 34]. Before the scavenger experiment was performed, the concentrations of different scavengers were optimized in earlier research. When no scavenger was added, 10⁶ cfu mL⁻¹ of *E. coli* could be completely inactivated within 90 min. The bacterial inactivation is virtually suppressed with the addition of TEMPOL and Fe(II)-EDTA as the scavenger of •O₂⁻ and H₂O₂, suggesting that •O₂⁻ and H₂O₂ played critical roles in the photocatalytic inactivation process. After the addition of sodium oxalate and isopropanol, it can be observed that the bactericidal inactivation efficiency over Ag/tz-BiVO₄ were partially inhibited, suggesting that h⁺ and •OH could directly destroy the *E. coli* cells with a powerful oxidation capability, whereas photoinduced electrons exhibited unobservable impact on the inactivation process of *E. coli*. And the capture experiment of photocatalytic degradation of MB dye solution was also carried out under visible light irradiation. In Fig. S12b, t-BuOH, silver nitrate (AgNO₃), ethylenediaminetetraacetic acid (EDTA), and Fe(II)-EDTA were taken as the scavengers for •OH, e⁻, h⁺, and H₂O₂, respectively. The results indicate that H₂O₂ is the main active species in the experiment of photocatalytic degradation of MB dye solution. The active species •OH, e⁻, and h⁺ also have different effects on the photocatalytic degradation process, which is different from the role of active species in the photocatalytic sterilization capture experiment caused by errors in the plate counting method.

To acquire further information of the active species, electron paramagnetic resonance (EPR) measurement was used. In brief, DMPO acted as a spin trapper to testify the existence of •O₂⁻ and •OH species [35, 36]. As displayed in Fig. 6b, very weak characteristic EPR signal of DMPO-•OH was detected for all as-prepared samples (Fig. S14). Similar result to the EPR signal of DMPO-•OH is that the intensity of DMPO-
\( \cdot O_2^- \) was also improved for Ag/tz-BiVO4 and Ag/ms-BiVO4 heterostructures. Interestingly, the EPR signal intensity of either DMPO-\( \cdot OH \) or DMPO-\( \cdot O_2^- \) for Ag/tz-BiVO4 is higher than that for Ag/ms-BiVO4. For photocatalytic process, the electronic band potential always plays dominate roles in modulating the active species as well as the photocatalytic activity. On the basis of Mulliken electronegativity and band gap energy [37], the conduction band potentials of tz-BiVO4 and ms-BiVO4 were calculated to be about 0.21 V and 0.30 V versus NHE (S15). Thereby, the valence band potentials tz-BiVO4 and ms-BiVO4 were determined to be 2.90 V and 2.70 V versus NHE. According to previous literatures, the redox potential of \( \cdot O_2^-/O_2 \) locate at 2.38 V versus NHE [38], suggesting the participation of \( \cdot OH \) in the photocatalytic process for the inactivation of E. coli. However, it is seen that the redox potential of \( \cdot O_2^-/O_2 \) \((-0.33 \text{ V versus NHE})\) is more negative than the conduction potential of tz-BiVO4 and ms-BiVO4, indicating both tz-BiVO4 and ms-BiVO4 are not capable to generate \( \cdot O_2^- \) reactive species. This result seems to be contrary to the trapping experiments. Then, it is necessary to specify the origination of the \( \cdot O_2^- \) reactive species. In aqueous solution, a photoinduced hole can oxidize \( H_2O_2 \) to produce one \( \cdot O_2^- \) via the following equation: \( H_2O_2 + h^+ \rightarrow \cdot O_2^- + 2H^+ [39] \). Moreover, the generation \( \cdot O_2^- \) can also be achieved by reaction of \( H_2O_2 \) with \( \cdot OH \) by the following equation: \( H_2O_2 + \cdot OH \rightarrow \cdot O_2^- + H_2O + H^+ [40] \). From this point, the capability for the generation of \( H_2O_2 \) over the as-prepared BiVO4 samples should be investigated. The concentration of \( H_2O_2 \) as a function of VL irradiation time was given in Fig. 5c. Clearly, \( H_2O_2 \) can be generated for all as-prepared samples under VL irradiation. Predominantly, \( H_2O_2 \) concentration gradually increased from 6.40 to 30.69 \( \mu \text{M} \) in initial 120 min under VL irradiation for Ag/tz-BiVO4 heterostructure, which is much higher than the other samples. Consequently, junction of Ag and tz-BiVO4 can greatly improve the capability of the photocatalysts to generate \( H_2O_2 \) due to the fine interfacial contact, which resulted in highly improved photocatalytic activity toward E. coli inactivation as well as the phase dependent photocatalytic activity of Ag modified BiVO4 heterostructures.

As a result, a plausible explanation for the inactivation of E. coli over Ag/tz-BiVO4 was proposed. As the CB edge potential of tz-BiVO4 is higher than that of the metallic Ag nanoparticles, the electrons in the CB of tz-BiVO4 can quickly transfer toward to Ag nanoparticles, inhibiting the recombinaton of electron–hole pairs between the VB and CB of BiVO4. The photogenerated holes migrate to the surface of the semiconductor and then directly contact with bacteria, or even produce \( H_2O_2 \) and \( \cdot OH \) with \( H_2O \) molecules. Simultaneously, the enrichment of electrons on the Ag nanoparticles may be subsequently scavenged by \( H_2O_2 \) to produce \( \cdot OH \) active species. The free radicals can react with the organic matter that constitutes the microbial organism and directly oxidize the organic matter into inorganic substances such as \( CO_2 \) and \( H_2O \). This process will change the original state and properties of the microbial organism, thereby directly hindering the proliferation of microbial cells and preventing bacteria.

Conclusions
In summary, Ag/BiVO4 heterostructural photocatalysts were developed with the aim to deliver a proof by rationally controlling the phase structure of BiVO4 and assembling Ag nanoparticles for photocatalytic antibacterial purpose in order to reveal structural-dependent photoinduced charge migration as well as the underlying photocatalytic antibacterial dynamic process. DFT theoretical calculation indicates an interfacial charge transfer between Ag and tz-BiVO4 with a net charge of about 0.33 e, which is far larger than that between Ag and ms-BiVO4, predicting fine interfacial contact and improved charge separation efficiency of Ag/tz-BiVO4. Relying on further experimental characterization, the optimized photocatalytic performance toward E. coli inactivation of Ag/tz-BiVO4 is predominately higher than that of tz-BiVO4, ms-BiVO4, and Ag/ms-BiVO4 catalysts. Besides photocatalytic activity, the thermocatalytic inactivation activity of Ag/tz-BiVO4 also exhibited a factor of about 7.2 and 3.1 times higher than that of tz-BiVO4 and Ag/ms-BiVO4. In combination with trapping experiment and EPR measurement, \( \cdot O_2^- \), \( \cdot OH \), and \( H_2O_2 \) active species played critical roles in the photocatalytic inactivation process. Moreover, detailed investigation suggested that the structural-dependent photocatalytic activity of Ag/BiVO4 mainly originated from the pronounced variation of the capability to produce \( H_2O_2 \) active species, where the capability of generating \( H_2O_2 \) over Ag/tz-BiVO41 is highly accelerated. This work provides hints for regulating the native properties of various structural-linked semiconductors.

Supplementary information
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The authors declare that they have no competing interests.

Availability of Data and Materials

The datasets supporting the conclusions of this article are included within the article.

Competing Interests

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