Visible-Light-Active CuO\textsubscript{x}-Loaded Mo-BiVO\textsubscript{4} Photocatalyst for Inactivation of Harmful Bacteria (Escherichia coli and Staphylococcus aureus) and Degradation of Orange II Dye

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ABSTRACT: In the present study, Mo-BiVO\textsubscript{4}-loaded and metal oxide (MO: Ag\textsubscript{2}O\textsubscript{x}, CoO\textsubscript{x}, and CuO\textsubscript{x})-loaded Mo-BiVO\textsubscript{4} photocatalysts were synthesized using a wet impregnation method and applied for microbial inactivation (Escherichia coli and Staphylococcus aureus) and orange II dye degradation under visible-light (VL) conditions (\(\lambda \geq 420\) nm). The amount of MO cocatalysts loaded onto the surface of the Mo-BiVO\textsubscript{4} photocatalysts was effectively controlled by varying their weight percentages (i.e., 1−3 wt %). Among the pure Mo-BiVO\textsubscript{4}, Ag\textsubscript{2}O\textsubscript{x}, CoO\textsubscript{x}, and CuO\textsubscript{x}-loaded Mo-BiVO\textsubscript{4} photocatalysts used in bacterial E. coli and S. aureus inactivation under VL irradiation, the 2 wt % CuO\textsubscript{x}-loaded Mo-BiVO\textsubscript{4} photocatalyst showed the highest degradation efficiency of E. coli (97%) and S. aureus (99%). Additionally, the maximum orange II dye degradation efficiency (80.2%) was achieved over the CuO\textsubscript{x} (2 wt %)-loaded Mo-BiVO\textsubscript{4} photocatalysts after 5 h of radiation. The bacterial inactivation results also suggested that the CuO\textsubscript{x}-loaded Mo-BiVO\textsubscript{4} nanostructure has significantly improved antimicrobial ability as compared to CuO\textsubscript{x}/BiVO\textsubscript{4}. The enhancement of the inactivation performance of CuO\textsubscript{x}-loaded Mo-BiVO\textsubscript{4} can be attributed to the synergistic effect of Mo doping and Cu\textsuperscript{2+} ions in CuO\textsubscript{x}, which further acted as an electron trap on the surface of Mo-BiVO\textsubscript{4} and promoted fast transfer and separation of the photoelectron (e\textsuperscript{−})/hole (h\textsuperscript{+}) pairs for growth of reactive oxygen species (ROS). Furthermore, during the bacterial inactivation process, the ROS can disrupt the plasma membrane and destroy metabolic pathways, leading to bacterial cell death. Therefore, we provide a novel idea for visible-light-activated photocatalytic antibacterial approach for future disinfection applications.

1. INTRODUCTION

The world is facing serious water scarcity. The increasing population decreases the per capita availability of water. In addition to the expanding population, available water quality is deteriorating owing to the organic and inorganic pollutants released into the water resources from industries and other anthropogenic activities.\(^1\) The issue takes a serious turn with the data that about 1.8 million deaths are caused worldwide every year due to waterborne illnesses.\(^2\) Furthermore, in the past few years, several waterborne diseases such as cholera, diarrhea, typhoid, and hepatitis were reported and remain as leading causes of human sickness and death worldwide.\(^3\) Therefore, researchers are looking for effective methods to eliminate pathogens and organic pollutants from the wastewater ecosystem.\(^4\) Previously, several physical, chemical, and biological methods have been used to remove organic and microbial pollutants from aqueous systems.\(^5\) Unfortunately, these kinds of wastewater treatment methods cannot completely remove the organic pollutants and produce harmful disinfection byproducts. Thus, finding out an effective water treatment technology without harmful treatment byproducts has become an urgent need. The semiconductor-based innovative photocatalytic inactivation method recently has attracted considerable attention for the inactivation of harmful pathogens and as a method for the degradation of dye in wastewater.\(^6\)

A variety of metal oxide-based semiconductors has been used as photocatalysts due to their suitable band potentials effective in photocatalytic reactions. In particular, metal oxide-based semiconductors have been proposed for use in hospitals, hotels, and commercial facilities due to their ability to kill harmful bacteria.\(^3,6\) TiO\textsubscript{2} photocatalysts are widely used for
bacterial inactivation experiments. Nevertheless, TiO₂-based semiconductors have a wide bandgap (3.2 eV) and therefore limit their activity for UV light.⁶ Therefore, it is important to find effective visible-light-active photocatalysts for the inactivation of harmful bacteria in wastewater.

In the past few years, visible-light-active BiVO₄ has been broadly studied as a visible-light-active photocatalyst for photocatalytic degradation of organic impurities in wastewater due to its suitable bandgap (2.4 eV).⁷ Recently, Regmi et al.⁸ stated that Ag/BiVO₄ photocatalysts are a safe and sustainable approach for the disinfection of bacteria in water. Nevertheless, single-component BiVO₄ semiconductors as photocatalysts have limitations of high electron–hole pair recombination.⁹ To solve this problem, several strategic modifications have been developed, such as the formation of heterojunctions and doping/loading with different metals. The use of noble metal oxides on visible-light-driven BiVO₄ as a support material increased the inactivation capacity and induced the bonding tendency of the organic substrate around the catalyst.¹⁰ Previously, Ganeshbabu et al.¹¹ developed BiVO₄ using a chemical precipitation method and stated that the nanocomposite indicated significant photocatalytic activity in the inactivation of pathogenic bacteria. However, bare BiVO₄ photocatalysts show low antimicrobial activity due to inefficient electron–hole separation. However, the photocatalytic inactivation performance can be improved by metal doping in the crystal lattice of BiVO₄. The main purpose of Mo doping in BiVO₄ is to increase the charge separation and enhance the inactivation capability of the BiVO₄ composite.

For this kind of advantage, for the first time, we synthesized visible-light-active CuOₓ-loaded Mo-BiVO₄ photocatalysts using a wet impregnation method. The main aim of this study is to develop a highly efficient VLA CuOₓ-loaded Mo-BiVO₄ photocatalysts for enhanced photocatalytic inactivation of Escherichia coli and Staphylococcus aureus and degradation of orange II dye under VL irradiation (λ ≥ 420 nm). A visible-light-active CuOₓ-loaded Mo-BiVO₄ photocatalyst for simultaneous removal of targeted model pollutants E. coli, S. aureus, and orange II dye) would be helpful from an environmental viewpoint. Moreover, the effects of different transition metal oxides (2 wt % Ag₂O, CoOₓ, and CuO) on bacterial degradation were studied. To identify the key reactive oxygen species (ROS) in photocatalytic degradation experiments with CuOₓ-loaded Mo-BiVO₄ photocatalysts, controlled tests using different radical scavengers were carried out during degradation of orange II dye. Based on the free radical capture experiments, the active species and photocatalytic degradation mechanism involved in pollutant degradation were proposed.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Bismuth(III) oxide (Bi₂O₃), vanadium(V) oxide (V₂O₅), and molybdenum trioxide (MoO₃) were used for the synthesis of Mo-BiVO₄. For transition metal oxide loading, silver nitrate (AgNO₃), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), and copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) were used as precursors of the respective transition metal oxides Ag₂O, CoOₓ, and CuO. Orange II dye (Sigma-Aldrich) was used for photocatalytic experiments. Luria–Bertani (LB) broth and agar were obtained from MB Cell, Seoul, South Korea, for the bacterial inactivation study. The waterborne pathogens of E. coli and S. aureus were procured from the Korean Agriculture Culture Collection (KACC) in Suwon, South Korea. All these precursor reagents used were of analytical grade and applied without further purification.

2.2. Synthesis of Mo-BiVO₄ Photocatalysts. Mo-BiVO₄ photocatalysts were synthesized using a wet impregnation method.¹² In a typical synthesis process to obtain homogeneous Mo-BiVO₄ photocatalysts, quantified amounts of MoO₃, Bi₂O₃, and V₂O₅ were mixed into 3 mL of ethanol, and the mixture was ground using a mortar and pestle. Then, the well-mixed yellow-colored powder was calcinated in a muffle furnace with a two-step process (600 °C, 5 h; 800 °C, 5 h) and a 5 °C min⁻¹ fixed heating rate. The samples were allowed to cool to room temperature, and the powders were collected from the box furnace and ground for further experiments.

2.3. Preparation of Metal Oxide-Loaded Mo-BiVO₄ Photocatalysts. Metal oxide (MO = CuOₓ, CoOₓ, and Ag₂Oₓ)-loaded Mo-BiVO₄ photocatalysts were synthesized using a wet impregnation method. For a typical experiment, a 1 wt % metal nitrate (silver nitrate, cobalt(II) nitrate hexahydrate, and copper(II) nitrate trihydrate) precursor was dissolved in 15 mL of deionized water. The Mo-BiVO₄ sample (110 mg), 3 mL of ethanol, and 100 μL of 1% metal nitrate precursor solution were added to the agate mortar. To achieve homogeneous metal nitrate-loaded Mo-BiVO₄ photocatalysts, they were ground 3 times and calcined at 300 °C for 2 h. These prepared samples were labeled as 1 wt % CuOₓ-, CoOₓ-, and Ag₂Oₓ-loaded Mo-BiVO₄ photocatalysts. To prepare 2 wt % MO-loaded Mo-BiVO₄, we used twice the amount of 1 wt % metal nitrate precursor solution during the grinding process, and the samples were denoted as 2 wt % CuOₓ-, CoOₓ-, and Ag₂Oₓ-loaded Mo-BiVO₄ photocatalysts. These same procedures were followed for three additional weight loads of MO on photocatalysts. The synthesis process for the Mo-BiVO₄- and metal oxide-loaded Mo-BiVO₄ photocatalysts is illustrated in Scheme 1.

Scheme 1. Schematic Diagram of the Synthesis of Mo-BiVO₄ and Transition Metal Oxide (CoOₓ, CuOₓ, and Ag₂Oₓ)-loaded Mo-BiVO₄ Photocatalysts
spectrometer, Thermo Scientific) was done to evaluate the electronic elements and valence states of the as-prepared samples. The HR-TEM images, EDS, and elemental mapping of photocatalysts were obtained via transmission electron microscopy (TEM, JEOL ARM-200F). The photocatalytic degradation spectra of orange II dye were measured using a UV–vis spectrophotometer (Shimadzu, UV-2600). Steady-state and time-resolved PL studies were achieved using a confocal microscope (MicroTime-200, PicoQuant, Germany). A 375 nm pulsed diode laser (30 ps pulse width and ~10 μW average power) was used as an excitation source, and emission photons were detected using an avalanche photodiode (PDM series, MPD) and a time-correlated-single-photon counting system (PicoHarp300, PicoQuant GmbH, Germany). Exponential fitting for the obtained emission decays was accomplished using Symphotime-64 software (Ver. 2.2). The time-resolved PL intensity is defined as \( I(t) = \sum A_i e^{-\mu_i \tau_i} \), where \( I(t) \) is the PL intensity as a function of time, \( A \) is the amplitude, and \( \tau \) is the PL lifetime. The average lifetime can be calculated using the following equation: \( \langle \tau \rangle = \sum A_i \tau_i^2 / \sum A_i \tau_i \). The steady-state PL spectrum was obtained by dividing and guiding emission photons through an optical fiber to the external spectrometer (F-7000, Hitachi). In addition, a bacterial sample that had antibiotic interaction with photocatalysts was examined using bio-TEM (H-7650, Hitachi, Japan) and fluorescence microscopy.

2.5. Photodegradation Experiments. The photodegradation study of orange II dye was carried out in a specially designed Pyrex glass vessel under VL illumination at room temperature. The reaction mixture was prepared by adding 100 mg of the optimized photocatalyst to a 45 mL aqueous solution of 25 μM orange II dye. Before starting the photocatalytic reaction, the reaction mixture was stirred for 30 min under dark conditions to allow equilibrium adsorption between the dye and nanocomposites. The reaction mixtures were continuously stirred using a magnetic stirrer during the photocatalytic reaction. After 30 min, the suspension was irradiated with visible light (cutoff filter, \( \lambda \geq 420 \text{ nm} \)) under continuous stirring. Over a 5 h period, 1.5 mL of the aliquot solution was withdrawn from the reaction vessel at each 30 min interval. During sampling, the photocatalysts were separated from the aqueous solution using a syringe filter (pore size: 0.2 μm). The photodegradation of orange II dye was analyzed by UV–vis spectroscopy (Shimadzu UV-2600) and HPLC-MS. The absorbance of orange II dye was measured at a wavelength (\( \lambda_{max} \)) of 484 nm. The degradation percentage of orange II dye was calculated using eq 1 as follows:

\[
\text{photodegradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \( C_0 \) is the initial concentration of orange II dye and \( C_t \) is the dye concentration at irradiation time (t).

2.6. Bacterial Culture and Analysis of E. coli and S. aureus. The waterborne pathogens E. coli (Gram negative) and S. aureus (Gram positive) were used for the photocatalytic disinfection experiment under dark and visible-light conditions. Harmful strains of E. coli and S. aureus were cultivated and measured as described by Cho et al.16 In summary, 100 mL of Luria–Bertani (LB) broth was inoculated with E. coli and S. aureus cultures and incubated for 24 h at 200 rpm and 37 °C in a shaking incubator. The bacterial cells were harvested by centrifugation at 4000 rpm for 10 min (three times) in phosphate-buffered solution (pH = 7.2, PBS, Sigma Co.). Typical E. coli and S. aureus solutions (1 × 10^10 CFU/mL) were prepared by resuspending washed pellets in 30 mL of PBS. In the photocatalytic inactivation experiments, the initial population of the target bacterial cultures (\( [N_0] \)) was adjusted to \( \sim 1 \times 10^5 \text{ CFU/mL} \) by dilution with a typical solution. One milliliter of the initial solution was serially diluted to 1/1, 1/10, and 1/100 in different tubes. Finally, 0.1 mL of the treated solution was dispensed on three replicate LB agar plates by using the spread plate technique, and then the viable cell counts were measured following incubation at 37 °C for 24 h.

2.7. Inactivation Experiments of E. coli and S. aureus. Photocatalytic inactivation tests were conducted in a 50 mL quartz reactor using 30 mL bacterial suspensions of the photocatalyst (Mo-BiVO_4- and MO-loaded Mo-BiVO_4 photocatalysts, 0.5 g/L), 1,4-piperazinediethanesulfonic acid (PIPES, 1 mM) buffer, and E. coli and S. aureus (1 × 10^5 CFU/mL), which were continuously stirred using a magnetic stirrer. All the disinfection experiments were conducted under dark and visible-light conditions with a UV cutoff filter (\( \lambda \geq 420 \text{ nm} \)). To monitor the bacterial inactivation process, the bacterial suspension was collected and promptly diluted using sterile saline solution (0.9%) at certain time intervals. The bacteria solution was uniformly dispersed on a Luria–Bertani agar plate and incubated at 37 °C for 24 h. At the end of the incubation period, the total number of colonies was counted to determine the number of viable cells on the agar plate. All the reagents and apparatus were sterilized at 121 °C for 20 min before the experiment to prevent background contamination.

2.8. Bacterial Live/Dead Cell Analysis. The bacterial strains treated with CuO_2 (2 wt %)/Mo-BiVO_4 photocatalysts were assessed using fluorescent staining with the dyes of a Live/Dead BacLight bacterial viability kit (L7012, Molecular Probes, Inc.) following the manufacturer’s instructions. The samples were recorded using fluorescence microscopy (Nikon ECLIPSE 80i, Japan) equipped with a filter block N UV-2A, an excitation filter Ex 330–380 (Nikon, Japan), and a Spot-K slider CCD camera (Diagnostic Instruments, Inc., USA). The live bacteria were stained with green dye, and the dead bacteria were stained with red dye. All experiments were performed in triplicate.

2.9. Antibiotic Interaction of CuO_2 (2 wt %)/Mo-BiVO_4 Photocatalysts in the E. coli Cell Membranes. The antibiotic interaction of the CuO_2 (2 wt %)/Mo-BiVO_4 photocatalysts in the E. coli cell wall membranes was evaluated using bio-TEM (H-7650, Hitachi, Japan). In this study, 10 mL of mature cell cultures were centrifuged at 10,000 rpm for 5 min, and the pellet was suspended in sterile deionized water. Five milliliters of this bacteria suspension was exposed to 1 mL of CuO_2 (2 wt %)/Mo-BiVO_4 photocatalysts for 2 h and incubated under typical conditions. After incubation, the treated samples were imaged with bio-TEM analysis.

2.10. Photoelectrochemical Measurements. The photocurrent–time (j–t) curves and electrochemical impedance spectra (EIS) analyses were measured on a portable potentiostat (CompactStat, Ivium, and Chronoamperometry, Netherlands) equipped with an electrochemical interface using a specially designed three-electrode cell. A xenon arc lamp with an irradiation intensity of 100 mW cm^{-2} was used as the illumination light source, and 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. During photoelectrochemical analyses, the Mo-BiVO_4 and CuO_2 (2 wt %)/Mo-BiVO_4...
photocatalysts were used as working electrodes (in a separate set of experiments), and saturated Ag/AgCl and platinum mesh electrodes were utilized as the reference and counter electrodes, respectively. Working electrodes were synthesized using the following steps. First, 10 mg of Mo-BiVO₄ photocatalyst powder was suspended in 0.5 mL of isopropyl alcohol. Then, the solution was sonicated for 15 min, and 80 μL of the solution was drop-coated onto a 2.5 × 1 cm² FTO substrate and dried at 60 °C in an electric oven for 12 h. The samples were drop-coated with an 80 μL titanium butoxide-ethanol (2 mM) solution. Finally, the samples were quenched at 450 °C for 2 h in a box furnace. The photocurrent–time curves were measured at 0.4 V vs Ag/AgCl (applied bias potential). Furthermore, EIS measurements were carried out at 0.4 V vs Ag/AgCl potential with a frequency range from 23 kHz to 0.01 Hz and an AC voltage amplitude of 0.01 V.

2.11. Radical Scavenger Tests. Four radical scavengers, silver nitrate (5 mM AgNO₃), isopropyl alcohol (5 mM IPA), ammonium oxalate (5 mM AO), and benzoquinone (5 μM BQ), were investigated for the presence of hydroxyl radicals (OH·), holes (h⁺), electrons (e⁻), and superoxide radicals (O₂⁻²), respectively. A quantified amount of scavenger was added into 45 mL of orange II dye solution (25 μg L⁻¹), and the mixed suspension was used for photocatalytic degradation tests in visible-light irradiation.

3. RESULTS AND DISCUSSION

Figure 1A(a–d) illustrates the XRD patterns of Mo-BiVO₄ and MO-loaded (CuOₓ, CoOₓ, and Ag₂Oₓ) Mo-BiVO₄ photocatalysts. The diffraction peaks obtained at the 2θ angles of 18.95, 28.94, 30.58, 34.62, 35.23, 40.04, 42.55, 45.99, 47.32, 50.23, 53.37, and 58.52° were assigned to the corresponding planes (011), (121), (040), (200), (022), (211), (051), (231), (042), (202), (161), and (321), respectively, which indicated its crystallinity. All the MO-loaded Mo-BiVO₄ photocatalysts exhibited the same crystal structure. In our study, the combination pattern of all assigned diffraction peaks in the MO-loaded Mo-BiVO₄ photocatalysts indicated enhanced photocatalytic inactivation/disinfection compared to that in the bare Mo-BiVO₄ due to the presence of the crystalline phase. The UV–vis DRS spectra of bare Mo-BiVO₄ and 2 wt % MO (CuOₓ, CoOₓ, and Ag₂Oₓ)-loaded Mo-BiVO₄ photocatalysts are shown in Figure 1B. The UV-DRS graphs do not show significant changes in the bandgap energy after the metal oxide was loaded on Mo-BiVO₄, suggesting the presence of the lower amount of metal oxide on the surface of Mo-BiVO₄ photocatalysts. Further, the bandgap energy of bare and MO-loaded Mo-BiVO₄ photocatalysts was estimated from the extrapolated Kubelka–Munk (KM) plot, and the results are displayed in Figure 1B. The calculated band gap energy values of the pure Mo-BiVO₄ and 2 wt % MO-loaded Mo-BiVO₄ photocatalysts (CuOₓ, CoOₓ, and Ag₂Oₓ) are 2.379, 2.377, 2.382, and 2.375 eV, respectively. The surface morphologies of Mo-BiVO₄ and 2 wt % MO (CuOₓ, CoOₓ, and Ag₂Oₓ)-loaded Mo-BiVO₄ photocatalysts were examined using FESEM as shown in Figure 2A–D. By careful study of the FESEM micrographs, the morphology of bare Mo-BiVO₄ and 2 wt % MO-loaded Mo-BiVO₄ photocatalysts was observed as a quasi-spherical shape. The FESEM images of Mo-BiVO₄ showed that the surface was smooth and fragmented due to the wet impregnation method. The FESEM microstructures of 2 wt % MO-loaded Mo-BiVO₄ photocatalysts are illustrated in Figure 2B–D. The surface of Mo-BiVO₄ was covered with nanosized and irregularly shaped CuOₓ, CoOₓ, and Ag₂Oₓ grains, displaying a good combination between MO and Mo-BiVO₄. Furthermore, the elemental composition of MO-loaded Mo-BiVO₄ photocatalysts was determined using energy-dispersive X-ray spectroscopy (EDS) as shown in Figure S1A–D. The chemical composition presented in the MO-loaded Mo-BiVO₄ photocatalysts indicates that MO nanoparticles were well dispersed in the Mo-BiVO₄ photocatalysts. TEM analyses were carried out to understand the structure of the CuOₓ (2 wt %)/Mo-BiVO₄ photocatalysts in detail. Figure 3A shows a TEM image of CuOₓ (2 wt %)/Mo-BiVO₄ photocatalysts, revealing that the particles had an irregular cubic or rectangular shape, and the CuOₓ particles were well dispersed on the surface of Mo-BiVO₄. Figure 3B clearly shows lattice fringes with a distance between adjacent lines of about 0.375 nm, corresponding to (200) lattice planes of cubic BiVO₄. Figure 3C–I shows the scanning TEM energy-dispersive X-ray spectroscopy (STEM-EDS) and element mapping images. It is seen that Mo, Bi, V, Cu, and O were homogeneously distributed over the tested area of CuOₓ (2 wt %)-loaded Mo-BiVO₄ photocatalysts. However, the amount of Mo and Cu was relatively smaller than that of other elements of CuOₓ (2 wt %)/Mo-BiVO₄ photocatalysts. The chemical compositions and valence states of the prepared 2 wt % CuOₓ-loaded Mo-BiVO₄ photocatalysts were studied using the high-resolution XPS spectra of Mo 3d, Bi 4f, V 2p, O 1s, and Cu 2p. As shown in Figure 4A, the XPS spectra...
survey spectra of 2 wt % CuO$_x$-loaded Mo-BiVO$_4$ photocatalysts showed that the major elements of the prepared samples were Mo, Bi, V, O, and Cu. The high-resolution XPS spectra of Mo 3d contained doublet peaks at binding energies around 232.09 and 235.15 eV, which corresponded to Mo (3d$_{5/2}$) and Mo (3d$_{3/2}$), respectively (Figure 4B), suggesting that the Mo element was present in the +6 oxidation state.\textsuperscript{19}

Further, Figure 4C shows the Bi 4f spectrum of pristine BiVO$_4$, where peaks at the band edges of 163.7 and 158.5 eV corresponded to Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$, respectively, suggesting the +3 oxidation state of Bi species.\textsuperscript{26,27} Similarly, the V 2p spectrum showed double peaks at 523.4 and 516.6 eV corresponding to V 2p$_{1/2}$ and V 2p$_{3/2}$, respectively, for the presence of the V$^{5+}$ state in the BiVO$_4$ particles (Figure 2D).\textsuperscript{28}

The oxygen O 1s deconvoluted peaks appeared at 529.3, 531.3, and 535.8 eV and were attributed to the lattice oxygen atoms and surface hydroxyl groups of CuO$_x$-loaded Mo-BiVO$_4$ photocatalysts, respectively, which are shown in Figure 4E.\textsuperscript{28}

Figure 4F displays the main and satellite peaks of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ at binding energies of 931.1 and 953.2 eV, respectively, which corresponds to the +2 state of Cu in the 2 wt % CuO$_x$-loaded Mo-BiVO$_4$ photocatalysts.\textsuperscript{30}

Figure 5 shows the steady-state PL spectrum and time-resolved PL decay. The measured PL spectrum showed major emissions in the red wavelength region. In particular, the emission intensity was reduced in the case of 2 wt % Cu loading. To study the excited-state carrier dynamics, we further examined TRPL decay, which showed a decreased PL lifetime after 2 wt % CuO$_x$ loadings onto the Mo-BiVO$_4$ photocatalysts (Table 1). The decreased PL intensity and lifetime indicated that the nonradiative charge transfer process was facilitated more highly in the excited state of the CuO$_x$-loaded Mo-BiVO$_4$ phase than in the Mo-BiVO$_4$ phase without doping.\textsuperscript{31−33}

Figure 6A–D shows the photocatalytic inactivation of \textit{E. coli} and \textit{S. aureus} under dark and visible-light conditions using CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts. To precisely measure the antimicrobial properties of the CuO$_x$ (2 wt %)/Mo-BiVO$_4$ catalyst, two control experiments containing only the photocatalyst under dark and light conditions were conducted.\textsuperscript{34} The experimental results indicate that around 98% of the micro-organisms were degraded by the CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts within 120 min under visible-light conditions (Figure S2). On the other hand, the control (photocatalyst + bacteria under dark conditions) showed nonsignificant inactivation. These results imply that usage of CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts was incapable of killing \textit{E. coli} and \textit{S. aureus} bacteria in the absence of light. The slight inactivation of \textit{E. coli} and \textit{S. aureus} in the dark was due to the bactericidal activity of the Cu compound itself.\textsuperscript{35} In the absence of photocatalysts, only 3% of the \textit{E. coli} and \textit{S. aureus} bacteria were inactivated under visible-light irradiation for 120 min, suggesting that direct photo-killing is a very slow bactericidal process. Hence, it is evident from Figure 6A,B that the CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts were more effective for microbial inactivation than the other photocatalysts (bare Mo-BiVO$_4$ and different MO wt %-loaded photocatalysts). When CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts were used, about 90% of the \textit{E. coli} and \textit{S. aureus} were inactivated in visible-light irradiation within 90 min, and almost all micro-organisms were killed within 120 min (Figure 6C,D). The special heterojunction structure of CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts might be responsible for its enhanced inactivation.\textsuperscript{36} Also, the effect of Mo doping on the antimicrobial action of BiVO$_4$ was estimated for the inactivation of \textit{E. coli} bacteria. As shown in Figure S3, the inactivation results suggested that the Mo doping of CuO$_x$/BiVO$_4$ has improved the antimicrobial activity compared to

Figure 3. (A) TEM image, (B) HR-TEM, and (C–I) STEM-EDS element mapping images of CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts.
This is due to the fact that the doping of Mo improves the electron–hole separation, thereby enriching the electron transport properties. Therefore, the incorporation of Mo nanoparticles into BiVO₄ to form a single-crystal material is very useful for antibacterial infection studies.

It is generally accepted that the inactivation of E. coli and S. aureus is caused by the oxidative species (e.g., O₂⁻) generated on the surface of photocatalysts in visible-light irradiation, which could oxidize the bacterial cell membranes. These species invade the DNA structure to stop the functioning of minerals, proteins, and genetic materials that are leaked due to cell membrane disruption, ultimately causing cell death. With the above observations, the photocatalytic disinfection efficiency of our photocatalyst (CuOₓ (2 wt %)/Mo-BiVO₄ photocatalysts) was compared with previous reports (Table S1). These results prove that CuOₓ (2 wt %)/Mo-BiVO₄ photocatalysts are promising antimicrobial agents for the effective elimination of waterborne bacteria such as E. coli and S. aureus.

Table 1. TRPL Lifetime Parameters of the Specimens

| sample          | A₁ (%) | τ₁ (ns) | A₂ (%) | τ₂ (ns) | A₃ (%) | τ₃ (ns) | ⟨τ⟩ (ns) |
|-----------------|--------|---------|--------|---------|--------|---------|----------|
| Mo-BiVO₄       | 75.2   | 0.04    | 22.4   | 0.41    | 2.4    | 4.5     | 2.3      |
| 2 wt % Cu-Mo-BiVO₄ | 81.0   | 0.03    | 17.8   | 0.34    | 1.2    | 4.5     | 1.8      |
To study the causes of photocatalytic inactivation of CuO\(_x\) (2 wt %)/Mo-BiVO\(_4\) photocatalysts on E. coli, the cell viability of the bacterial cells was measured using BacLight Bacterial Viability Kit fluorescence microscopy, as shown in Figure 7A. The bacterial samples were stained with the two fluorescent dyes SYBR and propidium iodide (PI). As shown in Figure 7A, the live bacteria cells exhibited strong green fluorescence, and the dead bacteria cells displayed weak red fluorescence. These results show that after 120 min of irradiation of CuO\(_x\) (2 wt %)/Mo-BiVO\(_4\) photocatalysts, the bacteria cells showed strong red fluorescence, suggesting that the cell membranes of E. coli were damaged during the photocatalytic inactivation process. Based on these results, the synergistic mechanism of photo-inactivation using CuO\(_x\)-loaded Mo-BiVO\(_4\) photocatalysts is schematically shown in Figure 7B. The main disinfection mechanism of the photocatalytic materials was the production of ROS.\(^{39}\) Photocatalytic inactivation might have occurred due to oxidative attack on harmful bacteria by \(\cdot O_2^-\) radicals as a minor active species. In summary, CuO\(_x\) (2 wt %)/Mo-BiVO\(_4\) photocatalysts effectively accelerated the separation of photo-generated charges and reduced recombination during photocatalysis, which enabled efficient photocatalytic inactivation activity.\(^{40,41}\)

The morphological changes in the CuO\(_x\) (2 wt %)/Mo-BiVO\(_4\) photocatalysts-treated E. coli cells were visualized using bio-TEM (Figure 8A,B). The untreated E. coli cells were naturally rod-shaped and remained intact with no visible damage to the integrity of the cell surface (Figure 8A).
However, after treatment with CuO (2 wt %)/Mo-BiVO₄ photocatalysts, the E. coli cell surfaces were deformed, and cells were lysed and leaked intracellular materials (Figure 8B). The smaller CuO (2 wt %)/Mo-BiVO₄ photocatalysts were uniformly scattered inside the cells, while the larger-sized particles remained on the surface of the cell membrane. These results showed that the CuO (2 wt %)/Mo-BiVO₄ photocatalysts caused changes in the E. coli outer membrane structures. Figure 8C shows a schematic diagram of the inactivation of E. coli bacteria by CuO (2 wt %)/Mo-BiVO₄ photocatalysts.

To investigate the potential application of as-prepared CuO (2 wt %)/Mo-BiVO₄ photocatalysts, they were tested for photocatalytic efficiency for degradation of orange II dye in visible-light irradiation at various time intervals (Figure 9).

![Figure 9](https://doi.org/10.1021/acsomega.1c02379)

Figure 9. Photocatalytic degradation of orange II dye by CuO (2 wt %)/Mo-BiVO₄ photocatalysts under dark and visible-light irradiation.

These results showed very high degradation efficiency of orange II dye by CuO (2 wt %)/Mo-BiVO₄ photocatalysts under visible-light conditions, whereas that under dark conditions was much lower. Furthermore, we also observed a decrease in the degradation of orange II dye after removal when using CuO (2 wt %)/Mo-BiVO₄ photocatalysts. Concurrently, the color of the solution changed gradually, suggesting that the orange II dye was diverted by an oxidation process. The photocatalytic experiment was standardized for the photocatalytic reactions and eventually led to the degradation of organic pollutants in an aqueous solution.

The higher surface area also facilitated the degradation of dye molecules on the surface of the CuO (2 wt %)/Mo-BiVO₄ photocatalysts. In visible-light irradiation, orange II dye molecules were absorbed onto the surface of the nanocomposites and produced electrons. These electrons were captured by the surface adsorbed O₂ molecules to yield O₂⁻ and HO₂⁻ radicals, which increased the chance of contact with orange II dye by increasing the reaction speed. The orange II dyes could be mineralized over time by superoxide radical ions. Consequently, it can be concluded that the smaller crystalline size of the CuO (2 wt %)/Mo-BiVO₄ photocatalysts was favorable for reduction of O₂ and oxidation of H₂O molecules by trapping electrons and holes, which improved their photocatalytic activity in visible-light irradiation. Therefore, these results show that the CuO (2 wt %)/Mo-BiVO₄ photocatalyst had an excellent photocatalytic performance for removal of orange II dye in aqueous solution under visible-light irradiation. This improvement could be explained in terms of the synergistic effects on the specific adsorption properties and the efficient electron-hole separation at the coupled CuO (2 wt %)/Mo-BiVO₄ photocatalysts interface. No previous CuO (2 wt %)/Mo-BiVO₄ photocatalysts have been reported for the degradation of orange II dye pollutants.

In order to further understand the possible degradation products of orange II dye during the photocatalytic degradation process over CuO (2 wt %)/Mo-BiVO₄ photocatalysts, the 1 mL sample was collected every 1 h and was analyzed by HPLC-MS. Figure S5 shows the HPLC-MS chromatograms of orange II dye taken at different degradation intervals. It was seen that at 0 min degradation, HPLC-MS chromatograms have a major peak at a retention time (tᵣ) of 26.69 min, which is assigned to orange II dye. However, as the reaction proceeds further to 1, 2, 3, and 4 h, the intensity of the major peak at 26.69 min in HPLC-MS chromatograms decreases significantly, while the appearance of new peaks at retention times of 1.59, 2.68, 18.60, 21.32, and 22.52 min was clearly observed (Figure S5). As compared with the literature, these results confirm the breakdown of orange II dye into its five constituent products as listed in Table S2.

To determine the specific roles of the active species in the degradation of orange II dye using CuO (2 wt %)/Mo-BiVO₄ photocatalysts, controlled experiments were performed with in situ addition of different scavengers. AgNO₃, AO, BQ, and isopropanol alcohol (IPA) were used to capture electrons, holes, O₂⁻, and OH⁻, respectively. Figure S6 shows the variation in C/C₀ vs t during orange II dye degradation before and after the addition of scavengers to the photocatalytic system. In the absence of scavengers, 82.3% of orange II dye was degraded within 3 h. In contrast, only 67.4 and 37.4% dye degradation were observed when BQ and AO, respectively, were added to the system. The significant reduction in dye degradation upon the addition of BQ and AO was due to electron capture by O₂⁻ and holes. Furthermore, compared to the values observed for AO and BQ, lower dye degradation was achieved with the addition of IPA, indicating that a small amount of OH⁻ was generated during the reaction of OH⁻ with H⁺. No decrease in dye degradation was observed with the addition of AgNO₃, suggesting no direct interaction between the electrons and the dye molecules. Thus, it can be concluded that O₂⁻ and H⁺ are the major active species and OH⁻ is a minor active species responsible for photodegradation of orange II dye in visible-light irradiation.
The photodegradation mechanism of orange II dye by CuO$_2$-loaded Mo-BiVO$_4$ photocatalysts is shown based on the band diagram in Figure 10a,b. The photocatalytic process consisted of the generation of photogenerated electrons and holes and their transfer to the surface of the nanocomposites as well as the creation of active oxygen species. After visible-light irradiation, the reactions were initiated by forming an electron–hole pair on the surface of the photocatalysts. The energy supplied by the visible light assisted the electron in jumping into a conduction band from the valence band, leaving a hole. These photogenerated electron/hole pairs on the surface of the Mo-BiVO$_4$ photocatalyst reacted with electron acceptors, such as O$_2$ molecules, adsorbed onto the surface of the Mo-BiVO$_4$ and produced superoxide radical O$_2^\cdot$ through a reduction process. Similarly, the holes at the valence band combined with the OH$^\cdot$ radicals and oxidized them to form hydroxyl radicals, OH. The formed hydroxyl radical (OH$^\cdot$) and superoxide radical (O$_2^\cdot$) species were the major oxidizers capable of degrading the molecular structure of the orange II dye pollutants into harmless products as shown in Figure 10a,b. In this particular case, the existence of oxygen vacancies and the incorporation of CuO$_x$ into the Mo-BiVO$_4$ lattice acted as a reservoir for electrons/hole pairs and boosted the interfacial recombination, leading to superior photocatalytic degradation.$^{32}$ Bare Mo-BiVO$_4$ did not undergo a direct transition of excited state electrons to any intermediate states between the conduction and valence bands, allowing faster recombination and reduced photodegradation.$^{33}$ The diagram also shows that the holes and electrons were effectively separated from each other at the surface of the CuO$_2$-loaded Mo-BiVO$_4$ nanocomposites.

Figure 11A displays the transient photocurrent response for the Mo-BiVO$_4$ and CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photo-anodes under switch-on and switch-off cycles. It demonstrates that the CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photo-anodes exhibited a higher photocurrent density (8.53 $\mu$A·cm$^{-2}$) than the Mo-BiVO$_4$ photo-anodes (1.4 $\mu$A·cm$^{-2}$), signifying that the CuO$_x$ loading onto Mo-BiVO$_4$ (CuO$_x$ (2 wt %)/Mo-BiVO$_4$) had the best photogenerated charge separation efficiency. The 5-time improved photoelectrochemical performance of CuO$_x$ (2 wt %)/Mo-BiVO$_4$ revealed that Mo-BiVO$_4$ could serve as an effective photogenerated electron collector to enhance interfacial charge migration. To validate the ease of charge transfer in the bulk and at the electrode/electrolyte interface, EIS was performed. Figure 11B shows the Nyquist plots measured for the Mo-BiVO$_4$ and CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photo-anodes measured in light irradiation over a frequency range of 23 kHz to 0.1 Hz. The lower arc radius of the diameter of the EIS CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photo-electrode showed a decrease in charge-transfer resistance on the CuO$_x$ (2 wt %)/Mo-BiVO$_4$ surface, which led to effective electron–hole pair separation, consistent with the $J$–$t$ results.$^{14,54}$ Thus, the CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photo-anodes led to lower resistance than the Mo-BiVO$_4$ photo-anodes, suggesting effective charge separation at the CuO$_x$ (2 wt %)/Mo-BiVO$_4$ heterojunction and the electrode/electrolyte interface.$^{35,56}$ The photogenerated electrons were transferred to the counter electrode. Therefore, CuO$_x$ (2 wt %)/Mo-BiVO$_4$ exhibited dominant photocatalytic dye degradation activity.

4. CONCLUSIONS

In this study, we confirmed the effects of different MO (Ag$_2$O$_x$, CoO$_x$, and CuO$_x$) and different wt % loadings of CuO$_x$ in Mo-BiVO$_4$ photocatalysts on photocatalytic inactivation and degradation of orange II dye in visible-light irradiation. The CuO$_x$ loading significantly enhanced the photocatalytic degradation activity of Mo-BiVO$_4$ photocatalysts for bacteria and orange II dye because of appropriate charge separation and transfer at the Mo-BiVO$_4$ interface. The optimum CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts prepared using the wet impregnation methods exhibited the maximum inactivation efficiency (98%) for E. coli and S. aureus over 120 min. Scavenger effect analysis suggested that the observed superiority of the copper oxide-modified Mo-BiVO$_4$ photocatalysts arose from the significantly improved O$_2^\cdot$ and OH radical production. It was easier for O$_2^\cdot$ and OH radicals to destroy the bonds of the orange II dye under VL conditions. Moreover, the optimized CuO$_x$ (2 wt %)/Mo-BiVO$_4$ photocatalysts showed outstanding inactivation of E. coli and S. aureus (98%) compared to the other prepared photocatalysts. Thus, the results of this study reveal CuO$_x$-loaded Mo-BiVO$_4$ photocatalysts as highly reliable and that they could easily be used for quantitative removal of organic pollutants and harmful bacteria from wastewater.

ASSOCIATED CONTENT

* Supporting Information The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02879.
Supplementary results and discussion including EDS result, photograph of the antibacterial (E. coli and S. aureus) activity, effect of the Mo catalyst on the inactivation of E. coli, UV–vis absorbance spectra and HPLC-MS chromatograms of the orange II dye degradation, and comparison of photocatalytic degradation efficiency for different photocatalysts (PDF).

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