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Photocatalytic Degradation of Tetracycline under Visible Light Irradiation on BiVO₄ Microballs Modified with Noble Metals

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Abstract: Monoclinic scheelite bismuth vanadate (BVO) microballs were prepared by a facile hydrothermal method and subsequently modified with 2 wt% of noble metals (NM = Au, Ag, Cu, Pt and Pd) by a photodeposition route. All materials were characterized by diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR). The photocatalytic performance was investigated by degradation of tetracycline antibiotic under visible light irradiation. Moreover, photocurrent generation under UV/vis was also examined. It was found that BVO modification with all tested NMs resulted in a significant improvement in photocatalytic performance. The highest activity was obtained for Cu/BVO with mainly oxidized forms of copper. Based on scavenger tests ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$ as the main responsible species for TC degradation) and redox properties, it was proposed that the Z-scheme mechanism between copper oxides and BVO was responsible for enhanced photocatalytic activity. However, the co-participation of zero-valent forms of NMs should also be considered, either as electron scavengers, plasmonic sensitizers or conductors. Presented data reveal that porous microballs, highly attractive for practical applications due to micro-sized diameter and efficient light harvesting inside the structure, could be efficiently used for environmental and energy purposes under solar radiation.

Keywords: photocatalysis; BiVO₄; degradation of pollutants; noble metals; photocurrent; surface modification



Citation: Wu, L.; Yue, X.; Chang, Y.; Wang, K.; Zhang, J.; Sun, J.; Wei, Z.; Kowalska, E. Photocatalytic Degradation of Tetracycline under Visible Light Irradiation on BiVO₄ Microballs Modified with Noble Metals. *Catalysts* **2022**, *12*, 1293. <https://doi.org/10.3390/catal12111293>

Academic Editors: Pedro B. Tavares and Roberto Fiorenza

Received: 29 August 2022

Accepted: 19 October 2022

Published: 22 October 2022

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1. Introduction

The acceleration of global industrialization and the rapid growth of the world population have caused the depletion of fossil resources and serious energy and environmental problems [1–3]. For example, the content of antibiotics in the environment has been continuously growing, which is associated with a high risk of antimicrobial resistance as microorganisms develop the ability to defeat the medicaments designed to kill them. As a promising “green” technology, semiconductor photocatalysis exhibits great potential in pollutants’ degradation [4,5], air purification [6,7], water treatment [8,9], hydrogen generation [10–12] and other applications [13] and thus could open up a new strategy for solar energy utilization [14]. Titanium(IV) oxide (titania) is probably the most famous photocatalyst because of high activity, stability, abundance and low price, but it is only active under UV irradiation [15]. Accordingly, its common use is limited to the world regions with high intensity of solar radiation, but even at such conditions, only ca. 3% of sunlight (UV) could be used efficiently. Therefore, it is important to find efficient visible light (vis)-responsive photocatalysts. For example, bismuth vanadate (BiVO₄, BVO) exhibits many advantages,

e.g., good stability, low price, vis response and eco-friendliness, and thus is considered an interesting choice for further study [16–18].

BVO might exist in one of three polymorphs, i.e., monoclinic scheelite, tetragonal zircon and tetragonal scheelite, or as an amorphous phase [19–21]. The monoclinic scheelite structure is generally considered the most active [22–24]. However, the photocatalytic activity of common BVO materials is usually low due to the fast recombination of photogenerated electrons and holes [25–28]. Therefore, a variety of methods have been employed to improve photocatalytic performance, including doping [29–32], morphology design [33–36], surface modification [37–39] and so on.

Many procedures have already been proposed for the fabrication of BVO photocatalysts. For example, a hydrothermal method under neutral conditions in the presence of CTAB as an additive and a dilute solution of nitric acid and sodium hydroxide for adjusting the pH value was proposed by Chen et al. [40]. They found that the crystalline properties of BVO changed from a mixed-crystalline form to a monoclinic phase by extending the reaction time. As already mentioned, the monoclinic phase of BVO has the best photocatalytic performance but also high crystallinity and the strongest light absorption ability. BVO photocatalysts were also synthesized by Soriya et al. through a hydrothermal method with the addition of sodium hydroxide and nitric acid as a pH-controlling agent [41]. It was confirmed that the pure monoclinic crystalline phase had significantly higher photodegradation efficiency than the mixed-crystal form.

Here, a BVO photocatalyst, prepared by the hydrothermal method, was modified with nanoparticles (NPs) of noble metals (NMs) to achieve high photocatalytic activity, especially at the vis range of the solar spectrum. It is well known that NMs work as scavengers for photogenerated electrons, hindering their recombination with photogenerated holes [42]. Although many reports have been published for titania and ZnO modifications, there are only a few studies on the deposition of NMs on BVO [43,44]. For example, Shi et al. prepared BVO by the hydrothermal method and then deposited Au/Pd (different mass ratios) by photoinduced reduction. Indeed, Au/Pd deposited on the surface of BVO improved its photocatalytic performance and stability [45]. However, the lack of comprehensive comparison between different NMs deposited on the same BVO material makes it impossible to draw the final conclusions (about the best properties and kind of NM).

Moreover, due to the plasmonic feature of NMs, another mechanism has been proposed under longer wavelengths than the absorption edge of semiconductors, i.e., plasmonic photocatalysis [46–49]. Accordingly, high photocatalytic activity is expected for NM-modified BVO materials at a wide range of irradiation, which indeed was found and shown in this paper. Moreover, the difference between gold, silver, platinum, palladium and copper as BVO modifiers was investigated for the first time to find the best BVO material for broad application. Tetracycline (TC) was selected for photocatalytic activity testing, as a typical antibiotic pollutant, i.e., characterized by persistence, bioaccumulation and potential ecotoxicity [4,5]. Its massive discharge poses a serious threat to aquatic and terrestrial ecosystems. Therefore, its quick removal from water has become a research hotspot in water environmental remediation and has important social value and far-reaching practical significance.

2. Results and Discussion

2.1. Characterization and Analysis

The successful synthesis of pristine and modified BVO samples was confirmed by XRD and FR-IR analyses, as shown in Figure 1. The obvious diffraction peaks (Figure 1a), at 18.988° , 28.823° and 30.549° correspond to the (011), (121) and (040) crystal planes, respectively, of monoclinic scheelite BVO (PDF#14-0688). The intense and sharp peaks as well as the lack of other phases, such as vanadium oxide and bismuth oxide, suggest good crystallinity and purity of the obtained samples. Unfortunately, the lack of another phase means also the impossibility to confirm the presence of NMs (at least by XRD), which could be caused by either their low content, the small size of NPs or the formation of an amorphous phase (highly possible for less noble metals, such as silver and copper, usually

co-present in oxide forms when stored under aerobic conditions [50]). However, the lack of any shift in XRD peaks confirms also that the crystalline structure of BVO was not changed by modification with NMs, and thus only the surface modification of BVO rather than any kind of doping was achieved.

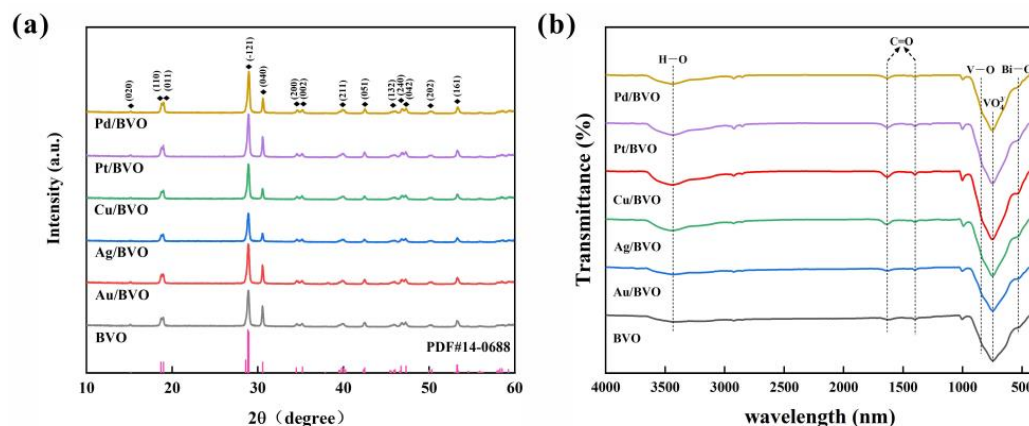


Figure 1. (a) XRD patterns and (b) FTIR spectra of bare and modified BVO samples.

Similar to XRD data, FTIR results do not confirm the presence of NMs, because of their low content, as shown in Figure 1b. However, the chemical composition of BVO was verified, as clearly observed by the peaks at 531.12, 850.07 and 745 cm^{-1} , related to the bending vibration mode of Bi-O, V-O (with low intensity indicating that V-O on the surface was disconnected and replaced by Bi-O) and the asymmetric and symmetric stretching vibrations of VO_4^{3-} , respectively. The absorption peak at 3431.62 cm^{-1} is associated with O-H, whereas two characteristic peaks at 1644.61 cm^{-1} and 1395.42 cm^{-1} are assigned to the stretching vibrations of C=O due to the adsorption of H_2O and CO_2 on the sample surface under air atmosphere. Although there is no proof of the NM presence, FTIR analysis confirmed that NMs were not incorporated inside the lattice of BVO. Accordingly, NMs should be present only on the BVO surface, which is consistent with XRD results.

Interestingly, it was found that BVO NPs formed aggregated microstructures, as shown in Figure 2. The SEM images reveal that pristine BVO forms mesoporous microballs, assembled by irregular NPs with a smooth surface. The size of the microballs varies from 1 to 1.5 microns.

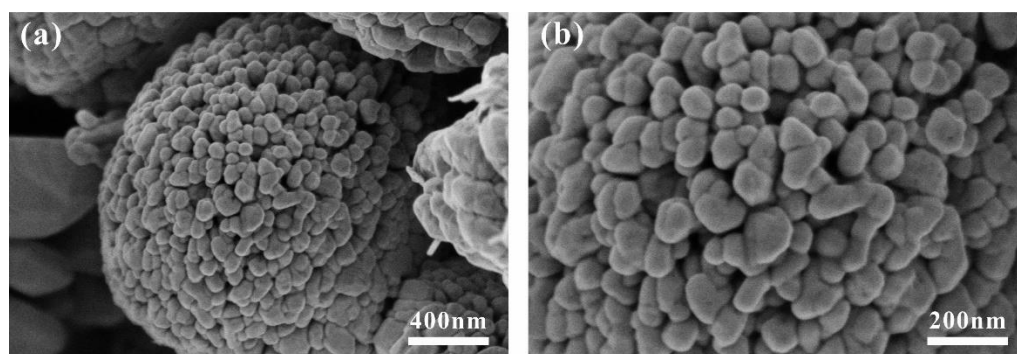


Figure 2. SEM images ((a) low magnification; (b) high magnification) of BVO sample.

DRS spectra (Figure 3) confirmed the vis response of all synthesized materials as the bandgap of BVO is ca. 2.3 eV [18]. The stronger absorption at the vis range for modified samples is caused by the NM presence. Unfortunately, it is impossible to observe clear plasmonic peaks, which could be caused by their overlapping with BVO and light scattering on the large microballs (clearly observed by high “light absorption” intensity in the whole studied range even for the pristine sample). The bandgap narrowing was not expected

(no doping), and indeed all samples show almost the same bandgap values of ca. 2.3 eV (the slight differences could be caused by the mentioned overlapping with plasmonic peaks).

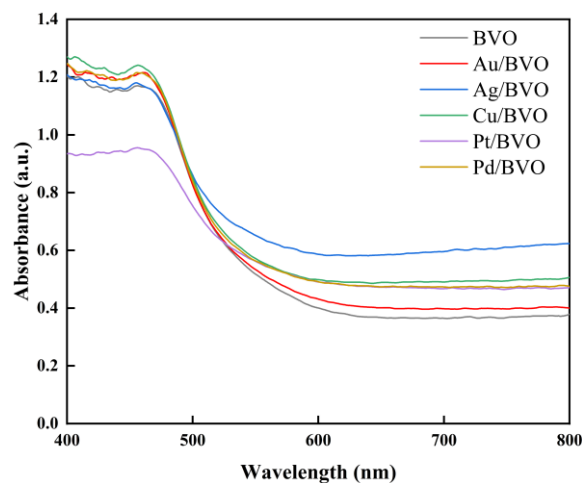


Figure 3. UV-Vis absorption spectra.

Since all previous methods do not confirm directly the successful deposition of NMs on the surface of BVO, XPS analysis was performed, and the obtained results are shown in Figures 4 and 5 and Tables 1 and 2.

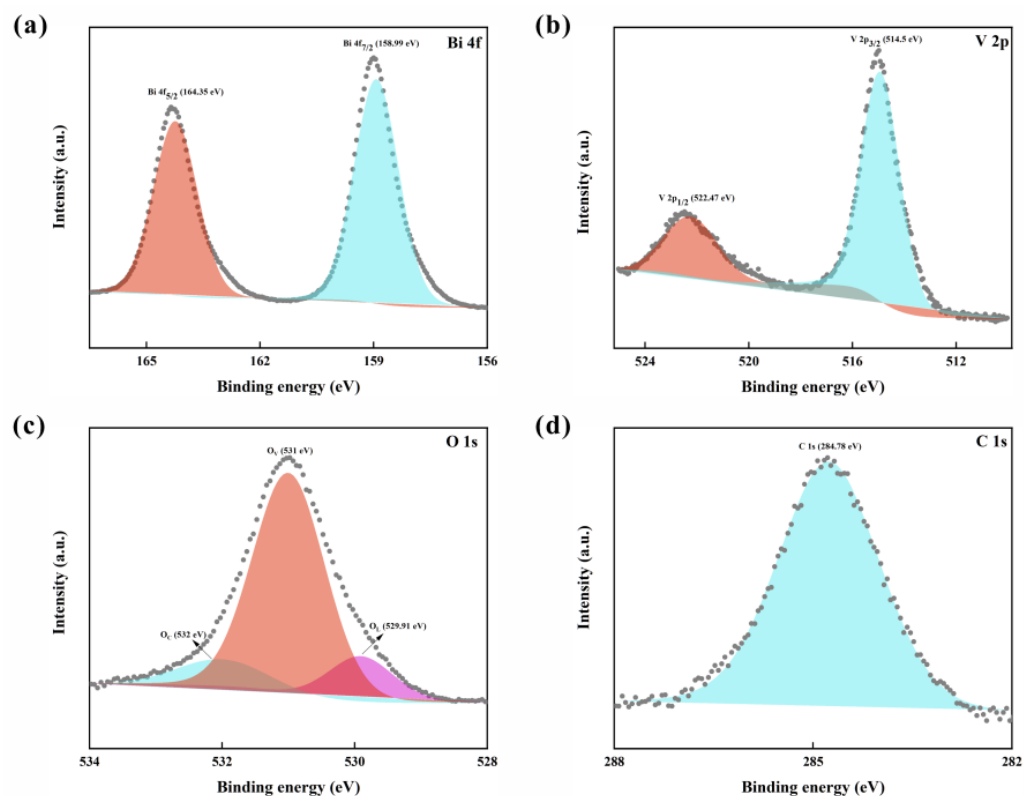


Figure 4. XPS spectra of BVO sample: (a) Bi 4f, (b) V 2p, (c) O 1s, (d) C 1s.

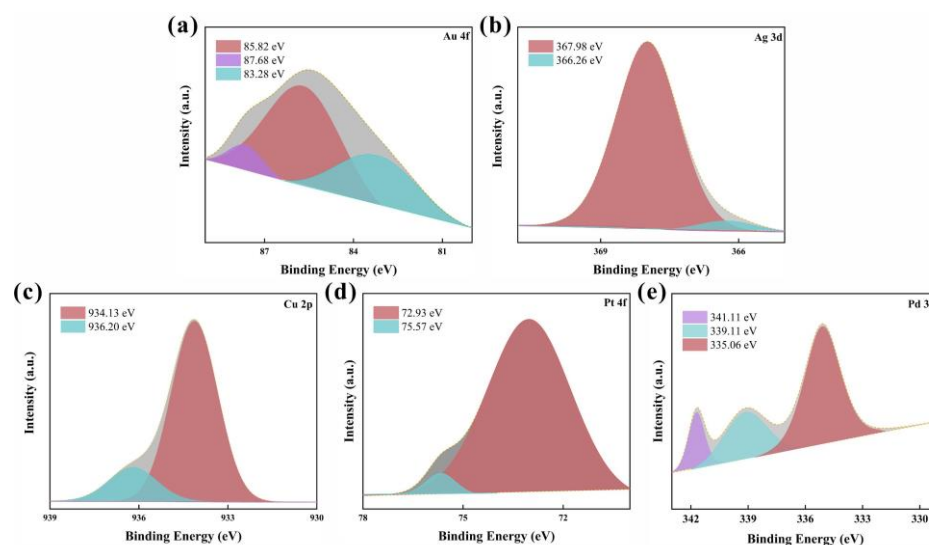


Figure 5. XPS spectra of NM/BVO samples: (a) Au 4f, (b) Ag 3d, (c) Cu 2p, (d) Pt 4f, (e) Pd 3d.

Table 1. Surface composition of bare and modified BVO samples determined by XPS analysis.

Samples	Content (at.%)					Ratio			
	Bi	V	O	C	Me	V/Bi	O/Bi	C/Bi	Me/Bi
BVO	11.6	17.4	38.6	32.2	-	1.5	3.3	2.8	-
Au/BVO	11.0	12.4	38.2	39.9	1.0	1.1	3.5	3.6	9.1
Ag/BVO	10.2	11.3	39.7	38.4	1.1	1.1	3.9	3.8	10.9
Cu/BVO	7.4	15.9	48.3	33.2	1.0	2.2	6.5	4.5	13.5
Pt/BVO	7.1	6.3	39.6	45.3	0.7	0.9	5.6	6.4	9.9
Pd/BVO	10.4	14.0	39.4	35.3	0.1	1.4	3.8	3.4	0.9

Table 2. Fraction of oxidation states of Au, Ag, Cu, Pt and Pd from deconvolution of XPS peaks of Au 4f_{7/2}, Ag 3d_{5/2}, Cu 2p_{3/2}, Pt 4f_{7/2} and Pd 3d_{5/2}.

Element	Au			Ag		Cu	
Form	Au(δ^+)	Au(0)	Au(δ^-)	Ag(+)	Ag(0)	Cu(2+)	Cu(+)
content	6.5%	55.8%	37.7%	93.0%	7.0%	17.2%	82.8%
Element	Pd			Pt			
Form	Pd(4+)	Pd(2+)	Pd(0)	Pt(2+)	Pt(0)		
content	11.9%	29%	59.1%	15.9%	84.1%		

First, the pristine sample was analyzed, and all obtained data (Figure 4) confirmed the chemical composition of BVO, as follows. Two distinct peaks at 158.99 eV and 164.35 eV, corresponding to Bi4f_{7/2} and Bi4f_{5/2}, respectively, indicate that bismuth exists in the Bi³⁺ oxidation state. The peaks of vanadate (V2p) at 514.5 eV and 522.47 eV, corresponding to V2p_{3/2} and V2p_{1/2}, respectively, relate to V⁵⁺ in BVO. In the case of oxygen, XPS spectra of O 1s could be deconvoluted into three peaks at around 530, 531 and 532 eV relating to O²⁻ species in the lattice (O_L), oxygen vacancies or defects (O_V) and chemisorbed or dissociated oxygen (O_C), respectively. Additionally, carbon (C1s) was analyzed, and an obvious C-C bond at ca. 284.78 eV was detected.

Finally, the presence of NMs could be confirmed, as shown in Figure 5. All NMs exist in mixed-oxidation states, as follows. Deconvolution of the gold (4f_{7/2}) peak into three parts with binding energies of 83.28 eV, 85.82 eV and 87.68 eV indicates the presence of

three valence states of gold, i.e., $\text{Au}(\delta+)$, $\text{Au}(0)$ and $\text{Au}(\delta-)$, respectively, with the zero-valent one being predominant (ca. 56%). Similarly, three forms of palladium ($3d_{5/2}$), i.e., $\text{Pd}(4+)$, $\text{Pd}(2+)$ and $\text{Pd}(0)$, reaching 11.9%, 29.0% and 59.1%, respectively, could be found, among which the zero-valent form is also the main one. In the case of platinum ($4f_{7/2}$), the zero-valent form is also predominant (84.1%), and the rest is $\text{Pt}(2+)$. Interestingly, less noble metals, i.e., silver and copper, exist mainly in oxidized forms. Of course, XPS analysis describes only the surface composition, and thus the co-presence of the metallic core is more than probable (also in the case of copper), as confirmed in other studies for NM-modified titania samples, prepared also by the photodeposition method [37]. Here, two valence states of silver ($\text{Ag}3d_{5/2}$), i.e., $\text{Ag}(+)$ and $\text{Ag}(0)$, corresponding to 367.98 eV and 366.26 eV, respectively, were detected, with the majority of the positively charged one (ca. 93.0%). However, copper exists only in oxidized forms, i.e., $\text{Cu}(+)$ and $\text{Cu}(2+)$ at ca. 936.2 eV and 934.13 eV, respectively, with $\text{Cu}(+)$ being predominant (ca. 82.8%).

Additionally, SEM observations and EDS analysis for NM-modified BVO samples were also performed. Although the formed NPs are very small (mainly 1–2 nm), and thus hardly detectable, as shown in Figure 6 for Ag/BVO and Cu/BVO, it could be confirmed that NMs are deposited on the BVO surface.

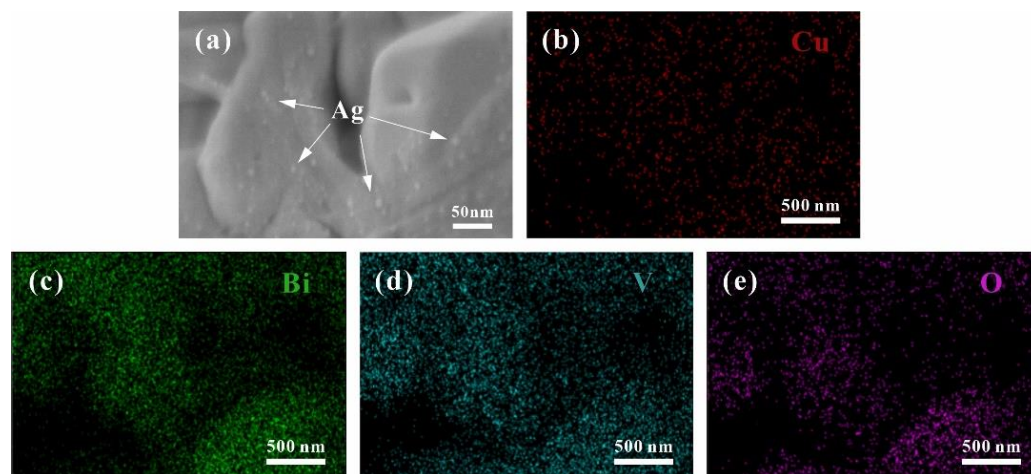


Figure 6. SEM (a) and EDS (b–e) analyses for: (a) Ag/BVO; (b–e) Cu/BVO for Cu (b), Bi (c), V (d) and O (e).

2.2. Photocatalytic Activities of Samples

The photocatalytic activity of bare and NM-modified BVO was evaluated by photodegradation of the TC antibiotic under vis irradiation, and the obtained data are shown in Figure 7. It is clear that TC could not be decomposed by simple photolysis (black line in Figure 7a), whereas photocatalysis might result in its ca. 40% degradation. All modified samples show much higher activity than the pristine one, confirming that modification with NMs could effectively improve the photocatalytic performance. Interestingly, Cu/BVO (the sample with only oxidized forms of NMs) is the most active, which could be caused by the possible Z-scheme mechanism between copper oxides and BVO, as proposed for other semiconductors modified with copper [51]. Of course, for the overall removal of pollutants, adsorption ability on the surface of photocatalysts should also be considered. Here, it is clear that all modified samples exhibit better adsorption ability than the pristine one (Figure 7b), indicating that NMs could effectively enhance the TC adsorption, which is helpful for the subsequent photodegradation process. The total TC removal on bare BVO is only 51.2%, whereas the TC removal efficiencies on NM-modified samples are much higher, reaching ca. 61%, 56%, 69%, 58% and 53%, for BVO modified with Au, Ag, Cu, Pt and Pd, respectively. The reaction rate constants (k), estimated from the Langmuir-Hinshelwood (L-H) model, are shown in Figure 7c. It is obvious that the fastest degradation occurs on the Cu/BVO sample, being ca. 1.6 times faster than that on bare BVO.

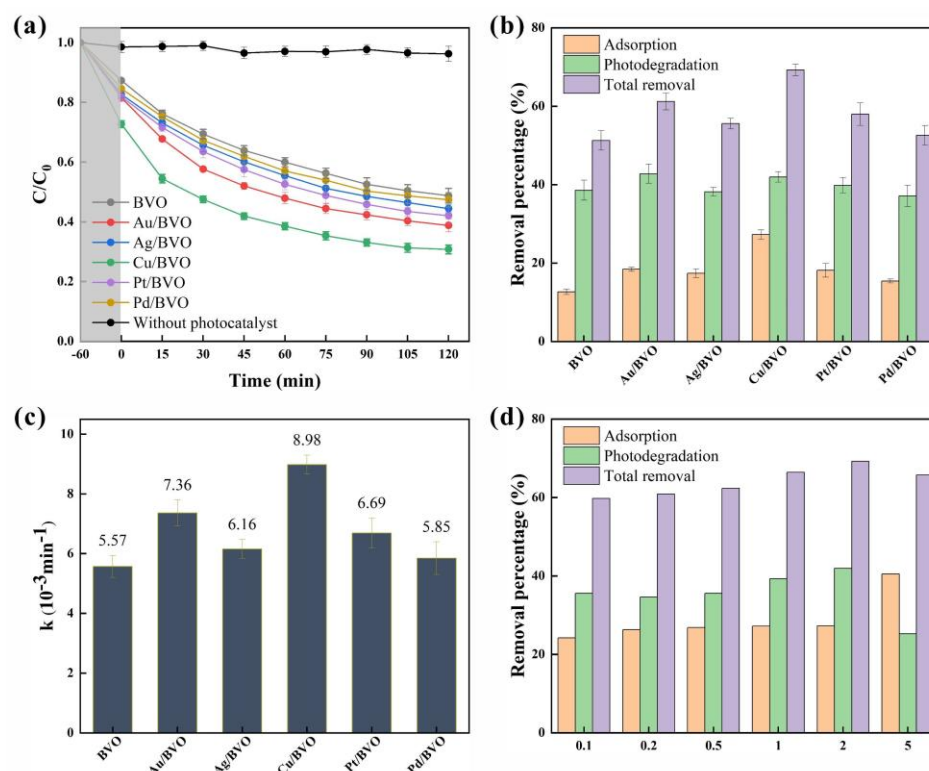


Figure 7. The photocatalytic performances of bare and modified BVO in the degradation of TC: (a) adsorption–photocatalytic degradation process; (b) removal rate; (c) the histogram of first-order rate constant k ; (d) influence of copper content on the photocatalytic performance of Cu/BVO.

Additionally, the best content of copper was investigated, and the obtained data for six different samples, containing 0.1 wt%, 0.2 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt% of copper, are shown in Figure 7d. As expected, it was confirmed that there is an optimal content of copper (exactly the same as that selected for all other experiments), and with an increase in copper content (from 0.1 to 2 wt%), both adsorption and photodegradation accelerate, reaching the best performance for 2 wt%. However, for larger copper content (5 wt%), though adsorption still increases, the photodegradation efficiency is worsened, which might be explained by the common “shielding effect” by excessive copper deposits on the surface of BVO and thus a decrease in the light harvesting by BVO.

In order to further explore the reaction mechanism on the Cu/BVO sample, the scavenger tests were carried out, and the obtained data are shown in Figure 8. Four different scavengers were used, i.e., P-benzoquinone (BQ), disodium ethylenediaminetetraacetic acid (EDTA-2Na), isopropanol (IPA) and silver nitrate (AgNO_3), to capture superoxide radicals ($\cdot\text{O}_2^-$), holes (h^+), hydroxyl radicals ($\cdot\text{OH}$) and electrons (e^-), respectively. Interestingly, it was found that photogenerated charge carriers (both electrons and holes) do not play a direct role in the photodegradation of TC since the addition of their scavengers hardly decreased the removal efficiency, i.e., from 69.23% to 67.48% and 67.53%, respectively. Accordingly, it might be concluded that the reaction does not occur directly on the photocatalyst surface. However, a significant function of reactive oxygen species (ROS), i.e., ($\cdot\text{O}_2^-$) and $\cdot\text{OH}$, was revealed. It should be pointed out that the formation of superoxide radicals from the direct reduction of oxygen by photogenerated electrons is not expected for BVO, because of the too-positive position of the conduction band level [52]. Accordingly, the Z-scheme mechanism between copper oxides and BVO might be expected, i.e., photogenerated electrons from BVO recombine with photogenerated holes from Cu_xO , and thus photogenerated electrons and holes from Cu_xO and BVO might further participate in the formation of respective ROS, i.e., superoxide and hydroxyl radicals, respectively.

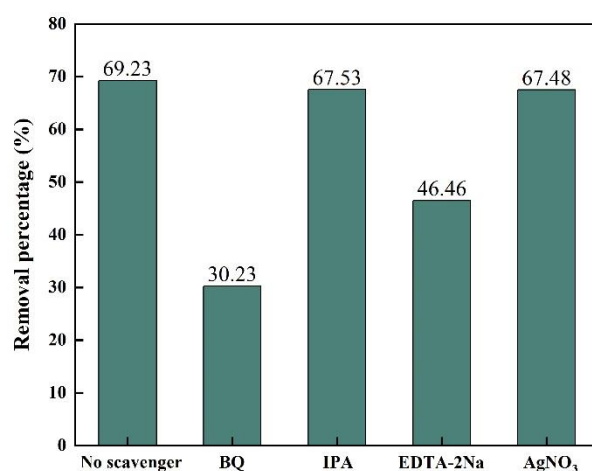


Figure 8. Trapping experiments of active species during photocatalytic degradation on Cu/BVO.

In order to further study the interfacial charge transfer and separation efficiency on the bare and modified BVO, photoelectrochemical tests were conducted, and the obtained data (EIS and IT) are shown in Figure 9. The instantaneous photocurrent curves of the prepared samples at four on-off cycles are shown in Figure 9a. All the samples showed photoelectric response with good reproducibility during the four switching intermittent irradiation cycles, indicating high photostability of obtained materials. Moreover, the photocurrent density of NM-modified BVO samples was much higher than that of bare BVO. It was found that the order of photocurrent density correlates well with photodegradation ability (Figure 8) as follows: Cu/BVO > Au/BVO > Pt/BVO > Ag/BVO > Pd/BVO > BVO. The highest photocurrent density was obtained for the Cu/BVO sample, reaching $0.37 \mu\text{A cm}^{-2}$, which was 6.5 times higher than that of bare BVO. Nyquist impedance plots of all samples are shown in Figure 9b. The transfer speed of electrons between the working electrode and the electrolyte solution was reflected by the curve, where a smaller radius of the arc suggests the faster speed of interfacial charge transfer. Similarly, for all other data, Cu/BVO and bare BVO exhibit the fastest and the slowest charge migration, respectively.

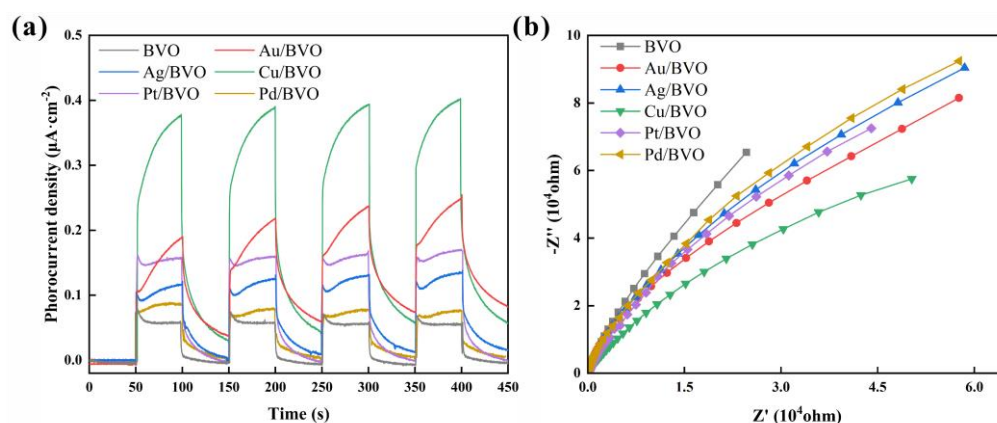


Figure 9. (a) Transient photocurrent responses and (b) Nyquist impedance plots of all samples.

2.3. Mechanism of the Photocatalytic Degradation of Organic Compounds on NM-Modified BVO

Based on the above experimental results, the possible photodegradation mechanism on the NM/BVO photocatalysts could be proposed as follows. First, BVO is excited with irradiation equal to and/or shorter than its bandgap edge ($\lambda < 520 \text{ nm}$). It should be pointed out that the microball porous structure allows efficient light harvesting, and thus all photons with proper energy (even scattered) could be eventually absorbed and used for photocatalytic reaction. Additionally, the co-existent NM oxides, especially in the case of less noble metals, such as copper and silver, could also be excited, resulting in the

formation of photogenerated charge carriers. The position of conduction and valent bands for both oxides suggests that either type II heterojunction or the Z-scheme mechanism is possible. However, it must be remembered that though heterojunction might hinder charge carriers' recombination, it is not recommended, considering redox properties, since photogenerated electrons and holes would have less negative and less positive potentials, respectively. Additionally, the transfer of electrons from the conduction band (CB) of copper oxide to the CB of BVO should result in the formation of hydrogen peroxide rather than superoxide radicals. However, scavenger tests (Figure 8) reveal that superoxide radicals are participating in the overall mechanism of TC degradation. Therefore, the Z-scheme mechanism seems the most probable and attractive, as presented in Figure 10.

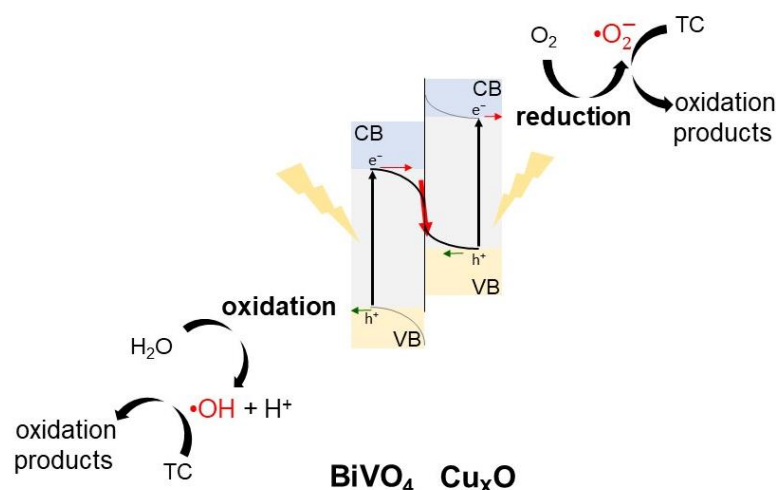


Figure 10. Schematic drawing of proposed Z-scheme mechanism for TC oxidation on Cu/BVO photocatalyst.

Moreover, the participation of the zero-valent form of NMs should be also considered, and thus various additional pathways might be proposed. First, NMs might work as scavengers for electrons generated on NM oxides (or BVO), and then superoxide radicals (or H_2O_2) are formed on their surface. Second, NMs might be a plasmonic sensitizer, especially those with plasmon resonance localized at longer wavelengths than the absorption edge of BVO. Accordingly, it is possible that in the case of gold with localized surface plasmon resonance (LSPR) at wavelengths longer than 520 nm (the position depending on the size and shape of NM NPs), plasmonic photocatalysis could happen. Here, both mechanisms suggested in the literature could be expected, i.e., electron and energy transfer, since even slight overlapping between the LSPR peak and BVO allows energy transfer [35]. Finally, the NM might work as a conductor between BVO and NM oxides for faster charge transfer (2nd-generation Z-scheme structures). However, further detailed studies, e.g., by action spectra analysis, are necessary for the clarification of these possibilities and are now under investigation. Moreover, the mechanism of TC decomposition should also be investigated to ensure that photodegradation products are not more toxic than TC, as pointed out by Zhang et al. [53] and Wang et al. [54]. The most advisable is to achieve complete oxidation (mineralization) or the conversion of TC into valuable chemical compounds (fuels).

Additionally, the stability of Cu/BVO was investigated, and the obtained data are shown in Figure 11. During five cycles, a slight decrease in the overall performance was observed, which could be caused by the photocatalyst lost during centrifugation. However, other possibilities, e.g., self-oxidation/reduction by photogenerated charge carriers, could not be neglected, and thus detailed studies are necessary before commercialization.

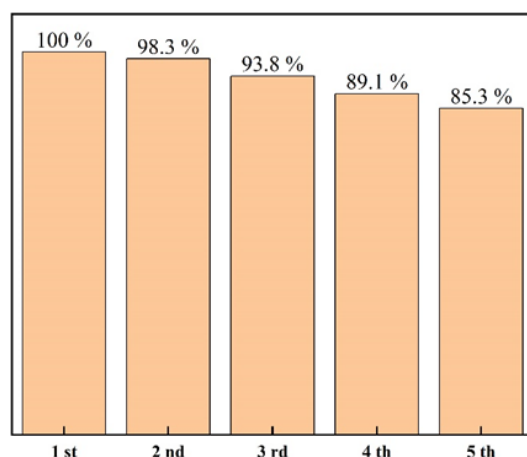


Figure 11. The stability tests for Cu/BVO photocatalysts.

To conclude, quite good stability of Cu/BVO was confirmed, suggesting its high potential for environmental applications, but the material needs further investigation. The most probable mechanism for Cu/BVO is based on the Z-scheme concept with efficient charge transfer between Cu_xO and BVO (as suggested by the scavenger tests and the redox properties). In the case of other photocatalysts (but also Cu/BVO), the co-participation of zero-valent NMs should also be considered.

3. Experiment

3.1. Preparation of BVO and NM/BVO

For the preparation of bare BVO, the chemical reagents, purchased from Aladdin company (Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China), were used without further treatment. The bare BVO was prepared as follows: 2.7164 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.682 g NaVO_3 and 0.2041 g CTAB were dissolved in deionized water (60 mL), and then after magnetic stirring for 30 min, a yellow suspension was obtained, which was transferred into an inner Teflon reactor (100 mL) with outer stainless steel shell for hydrothermal reaction (160 °C for 24 h). After the reaction was completed and the temperature inside the reactor was cooled down to room temperature, the precipitate was washed (first with ethanol and then with deionized water), centrifuged and freeze dried.

Next, for the surface modification, NM salts, i.e., $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, AgNO_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and K_2PdCl_6 , purchased from Aladdin company, were used to modify BVO with NPs of platinum, gold, silver, copper and palladium, respectively, and obtained photocatalysts were named accordingly, as follows: Pt/BVO, Au/BVO, Ag/BVO, Cu/BVO and Pd/BVO. The modification was carried out via photodeposition method. In brief, 500 mg of bare BVO powder was put into a glass bottle, and aqueous solution of weighted salt of NM precursor (2 wt% of BVO; 10 mg NM) was added to BVO powder; then, 25 mL of methanol aqueous solution (50 vol.%) was poured into the bottle, and the air inside the bottle was replaced by Ar through 15 min bubbling. Next, the bottle was sealed with a rubber septum and irradiated with high-pressure mercury lamp (300 W) for 1 h. After irradiation, the powder was collected after washing (three times with methanol and then with deionized water) and freeze drying. The obtained NM/BVO samples were named accordingly to the respective NM, e.g., Ag/BVO corresponds to silver-modified BVO sample. A brief diagram showing the preparation of NM-modified BVO is shown in Figure 12.

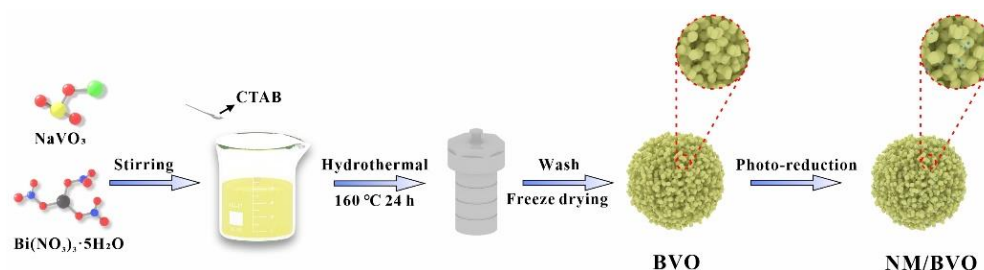


Figure 12. The schematic drawing showing the preparation procedure of NM-modified BVO.

3.2. Characterization

The crystalline phase and crystallinity of samples were analyzed by X-ray diffraction (XRD; PANalytical Empyrean, Almelo, The Netherlands, Cu-K α radiation, scanning rate of $10^\circ/\text{min}$). The morphology was observed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS, Hitachi SU8010, FESEM, Tokyo, Japan, BE + SBE, face scan). The surface composition and valence state of elements were evaluated by X-ray photoelectron spectroscopy (XPS; PHI5000 Versaprobe VersaProbe III, Chigasaki, Japan). The Fourier transform infrared (FTIR) spectrogram of samples was measured with a TensorII FTIR spectrophotometer (Bruker, Billerica, MA, USA) and the optical adsorption properties with a SHIMADZU UV-2600 UV-vis spectrometer (DRS, Tokyo, Japan).

3.3. Photocatalytic and Electrochemical Evaluation

The photocatalytic activities of samples were evaluated during photodegradation of tetracycline hydrochloride (TC) as a model organic pollutant under vis irradiation (300 W Xe lamp and 420 nm cutoff filter). The reaction temperature was maintained at 298 K with circulating cooling water.

In brief, 30 mg of sample was added to 100 mL of TC solution (25 mg/L), the obtained suspension was stirred first in the dark for 1 h to reach an equilibrium of adsorption-desorption and then irradiated for 2 h with 6 mL sampling at regular intervals of 15 min. The withdrawn samples were centrifuged (to remove the photocatalyst powder) at 4500 rpm for 5 min, and the supernatant was analyzed at 357 nm with UV-Vis spectrophotometer. Scavenger tests were carried out to explore the reaction mechanism on Cu/BVO sample, where four different scavengers were used, i.e., P-benzoquinone (BQ), disodium ethylenediaminetetraacetic acid (EDTA-2Na), isopropanol (IPA) and silver nitrate (AgNO_3), to capture superoxide radicals ($\cdot\text{O}_2^-$), holes (h^+), hydroxyl radicals ($\cdot\text{OH}$) and electrons (e^-), respectively. The concentrations of all scavengers were the same (0.2 mM). They were added to TC solution (25 mg/L) containing 30 mg of Cu/BVO powder. The photocatalytic stability of Cu/BVO was investigated during five subsequent cycles. After each cycle, the powder was centrifuged and used without any other treatment.

The photoelectrochemical (PEC) properties of samples were tested on a CHI760E electrochemical workstation in a conventional three-electrode system. The counter, the reference and the working electrodes were a platinum sheet, Ag/AgCl and fluorine-doped conductive glass (FTO) coated with the analyzed sample, respectively. The working electrode was prepared as follows: 4 mg of sample was added to the mixture of 125 μL ethanol, 375 μL deionized water and 50 μL nafion (5%) and sonicated for 1 h, and then 13.5 μL of the mixture was evenly coated on FTO, followed by drying at $40\text{ }^\circ\text{C}$ for 24 h. A 0.1 M Na_2SO_4 solution and a 200 W xenon lamp were used as electrolyte and excitation light source, respectively. Transient photocurrent densities and EIS plots of samples were measured at 0.2 V.

4. Conclusions

Mesoporous BVO microballs could be successfully prepared by a facile hydrothermal method, and a simple photodeposition process results in the fabrication of NM-modified photocatalysts.

BVO modification with NMs results in significant improvements in photoabsorption properties and thus the resultant photocatalytic performance for both experiments, i.e., degradation of TC and photocurrent generation. Among tested NMs, modification with copper (existing mainly in oxidized forms) results in the best photocatalytic activity. It is thought that TC photodegradation proceeds via ROS, i.e., superoxide and hydroxyl radicals, generated on the surface of copper oxides and BVO, respectively, according to the Z-scheme mechanism. The co-participation of zero-valent metals through various possible mechanisms (e.g., as scavengers of photogenerated electrons, plasmonic sensitizers and conductors) should also be considered but needs further clarification.

To conclude, it was found that all tested NMs (Au, Pt, Pd, Cu and Ag), even at low content (2 wt%), could efficiently improve the performance of the BVO photocatalyst. The facile synthesis allows one to prepare efficient, vis-responsive materials of large diameter (micro-sized range) and is thus highly convenient for practical applications (simple filtration after use). Additionally, the porous morphology seems to be highly attractive for efficient light capture inside the structure (light harvesting). It is thought that NM-based BVO of porous microball morphology could be broadly used for environmental and energy applications.

Author Contributions: Conceptualization, Z.W.; methodology, Z.W.; investigation, L.W., X.Y., J.S. and J.Z.; resources, Z.W.; writing—original draft preparation, Z.W., L.W. and X.Y.; writing—review and editing, E.K.; visualization, K.W.; supervision, Y.C., Z.W. and E.K.; funding acquisition, Z.W. and E.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (NSFC) (51802087), the Natural Science Foundation of the Hubei province of China (2019CFB524) and the Green Industry Leading Program of Hubei University of Technology (XJ2021002101). The project was co-financed by the Polish National Agency for Academic Exchange within the Polish Returns Program (BPN/PPO/2021/1/00037).

Data Availability Statement: The data presented in this study are available on request from the corresponding author (Z.W.).

Conflicts of Interest: The authors declare no conflict of interest.

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