



Article

Synthesis of Co_3O_4 Nanoparticles-Decorated $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ Hierarchical Microspheres for Enhanced Photocatalytic Degradation of RhB and BPA

Syed Taj Ud Din ¹, Wan-Feng Xie ^{1,2} and Woochul Yang ^{1,*}

¹ Department of Physics, Dongguk University, Seoul 04620, Republic of Korea

² School of Electronics and Information, University-Industry Joint Center for Ocean Observation and Broadband Communication, Qingdao University, Qingdao 266071, China

* Correspondence: wyang@dongguk.edu; Tel.: +82-02-2260-3444

Abstract: Three-dimensional (3D) hierarchical microspheres of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ (BOC) were prepared via a facile solvothermal method using a binary solvent for the photocatalytic degradation of Rhodamine-B (RhB) and Bisphenol-A (BPA). Co_3O_4 nanoparticles (NPs)-decorated BOC ($\text{Co}_3\text{O}_4/\text{BOC}$) heterostructures were synthesized to further enhance their photocatalytic performance. The microstructural, morphological, and compositional characterization showed that the BOC microspheres are composed of thin (~20 nm thick) nanosheets with a 3D hierarchical morphology and a high surface area. Compared to the pure BOC photocatalyst, the 20- $\text{Co}_3\text{O}_4/\text{BOC}$ heterostructure showed enhanced degradation efficiency of RhB (97.4%) and BPA (88.4%). The radical trapping experiments confirmed that superoxide ($\bullet\text{O}_2^-$) radicals played a primary role in the photocatalytic degradation of RhB and BPA. The enhanced photocatalytic performances of the hierarchical $\text{Co}_3\text{O}_4/\text{BOC}$ heterostructure are attributable to the synergetic effects of the highly specific surface area, the extension of light absorption to the more visible light region, and the suppression of photoexcited electron-hole recombination. Our developed nanocomposites are beneficial for the construction of other bismuth-based compounds and their heterostructure for use in high-performance photocatalytic applications.

Keywords: $\text{Co}_3\text{O}_4/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$; heterojunction; photocatalysis; Rhodamine-B; Bisphenol-A



Citation: Din, S.T.U.; Xie, W.-F.; Yang, W. Synthesis of Co_3O_4 Nanoparticles-Decorated $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ Hierarchical Microspheres for Enhanced Photocatalytic Degradation of RhB and BPA. *Int. J. Mol. Sci.* **2022**, *23*, 15028. <https://doi.org/10.3390/ijms232315028>

Academic Editors: Paschalis Alexandridis and Junjiang Zhu

Received: 21 October 2022

Accepted: 28 November 2022

Published: 30 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Rapid industrialization and population growth has led to a tremendous increase in environmental pollutions. These pollutants mostly consist of hazardous Azo dyes and phenolic compounds. Rhodamine-B (RhB) cationic Azo dye is an anthraquinone derivative. It is highly stable and non-biodegradable in nature and is classified as a carcinogenic and neurotoxic substance [1]. Aside from dyes, the other frequently used compound is the colorless Bisphenol-A. It is a diphenylmethane derivative and a raw material that is widely used in the fabrication of numerous polymeric materials [2]. Long-term exposure of BPA causes endocrine, neurological, and reproductive developmental disorders [3]. Therefore, it is crucial to eradicate RhB and BPA before waste is discharged into water reservoirs and landfills. Pollution-free environmental remediation technologies to degrade these organic pollutants have attracted substantial attention [4]. Among them, visible-light-driven photocatalytic technology has emerged as the most promising approach for wastewater cleaning and pollutant removal [5].

Recently, bismuth-based nanomaterials, such as BiPO_4 [6], $\text{Bi}_2\text{O}_2\text{CO}_3$ [7–9], $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [10], Bi_2MoO_6 [11], Bi_2WO_6 [12], Bi_2O_3 [13], and BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [14,15], have attracted substantial attention for their use in photocatalytic applications, because O 2p and Bi 6s valence band hybridization not only narrows the bandgap but also enhances the mobility of photo-generated holes in the valence band. Similarly, a bismuth and oxygen-enriched bismuth-oxyhalide ($\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ (BOC)) is a typical tetragonal phase compound composed

of a layered structure with an alternate stacking of $[\text{Bi}_2\text{O}_2]^{2+}$ sheets interleaved with $[\text{Cl}]^-$ groups, and it represents an important class of bismuth-based photocatalysts. The photocatalytic properties of nanobelts-like BOC were first reported by Xiao et al. in 2013 [16]. Since then, there have been many research efforts focused on the preparation of BOC with different morphologies, including nanobelts, nanosheets, and flower-like morphologies. For instance, Wang and colleagues [17] prepared BOC nanobelts through a solvothermal treatment using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, NH_4Cl , and NaOH as precursors in a solvent consisting of ethylene glycol (EG) and water for the photocatalytic degradation of BPA. Liu et al. [18] presented two-dimensional (2D)-BOC nanosheets oriented along the [002] direction which showed enhanced photocatalytic RhB degradation. Similarly, Fang et al. [19] prepared 3D BOC hierarchical nanostructures using a coprecipitation method followed by calcination, and these nanostructures demonstrated high photocatalytic efficiency for RhB degradation. Among the morphologies detailed above, the flower-shaped BOC has excellent characteristics, including high surface area, good adsorption capability, and maximum light absorption. Therefore, it is essential to develop a facile method to fabricate a 3D flower-like BOC. Despite these advantages, the 3D BOC still need to resolve the issues of a rapid electron-hole recombination rate and inappropriate redox potentials. Therefore, various research strategies have been developed to overcome these issues, including the fabrication of heterojunctions [20], element doping [21], noble metal deposition [22], and graphene decoration [23]. Among these methods, heterojunction preparation is the most effective approach because of the fast transfer rate of photo-generated electron and holes (e^- - h^+), which facilitates the separation of the photo-generated e^- - h^+ pairs in the photocatalysts, which play quite an important role in enhancing the photocatalytic activity of photocatalysts. For instance, He et al. [24] obtained a BOC/ β - Bi_2O_3 composite with flower-like micro/nano architectures that demonstrated good photocatalytic activity for the degradation of 4-tert-butylphenol under visible light. In another study, Huang et al. [25] prepared BiOI@BOC heterojunction photocatalysts with high exposure of the active BiOI (001) facet, which exhibited excellent photocatalytic performance for RhB and BPA degradation. Moreover, BOC heterostructures with non-bismuth-based compounds, such as CoAl-LDH/BOC [26] and Ag_2O /BOC *p-n* junction catalysts [27], have also been reported; both exhibit significant photo-degradation efficiency under visible light irradiation.

Co_3O_4 is a traditional *p*-type semiconductor (band gap, $E_g = 1.2\sim 2.6$ eV) with interesting electronic, magnetic, sensing, and catalytic properties [28]. In particular, Co_3O_4 -based heterojunctions have yielded high photocatalytic activity; for example, the 0D/2D $\text{Co}_3\text{O}_4/\text{TiO}_2$ heterojunction photocatalyst has exhibited enhanced photocatalytic activity under visible light irradiations [29]. In another study, Dai et al. [30] synthesized a Co_3O_4 /BOC photocatalyst that showed effective visible-light-driven RhB photodegradation due to the more positive value of the valence band potential of Co_3O_4 relative to BOC. However, BOC is an *n*-type semiconductor, as indicated by its positive slope in the Mott-Schottky plot [31], and the more positive valence band (VB) potential than that of the Co_3O_4 counterpart. Therefore, the combination of Co_3O_4 with BOC is favorable for the formation of the *p-n* heterojunction. As a result, the photo-generated holes on the VB of BOC could be easily transferred to the VB of Co_3O_4 under light illumination, thus resulting in practical separation of photo-generated e^- - h^+ pairs of BOC and Co_3O_4 , which would be beneficial for a photocatalyst in terms of photo-degradation efficiency. However, to our knowledge, there is a lack of research into using a Co_3O_4 /BOC hierarchical microsphere photocatalyst for the degradation of RhB and BPA.

Herein, the synthesis of a BOC hierarchical microsphere and its decoration with Co_3O_4 nanoparticles (NPs) via a solvothermal method have been reported. The heterojunction formation of the Co_3O_4 NPs-decorated BOC (Co_3O_4 /BOC) was evaluated through structural, morphological, spectroscopic, and electrochemical investigations. The photocatalytic degradation efficiency of the hierarchical microsphere Co_3O_4 /BOC heterojunction was evaluated against RhB and BPA aqueous pollutants. The results showed that the 20- Co_3O_4 /BOC heterostructure had an outstanding degradation efficiency of RhB (97.4%) and BPA (88.4%)

after 140 min and 175 min of visible light irradiation, respectively, compared to pure BOC and other composite samples. The improved photocatalytic degradation performance could be ascribed to the synergetic effects of the larger active area of hierarchical microsphere, the extended light absorption to visible light range with Co_3O_4 NPs, and the suppression of e^-h^+ recombination caused by the p - n junction formation of $\text{Co}_3\text{O}_4/\text{BOC}$.

2. Results and Discussion

2.1. Structural, Morphological, and Elemental Analyses

Figure 1 shows the morphology of the BOC fabricated with different volume ratios of ethylene glycol (EG) and ethyl alcohol (EtOH). BOC-1 (Figure 1a) synthesized in EG only and BOC-3 (Figure 1c) prepared in mixtures of EG and EtOH both have uniform 3D architectures, whereas BOC-2 (Figure 1b) prepared in pure EtOH solution shows a nanoparticle-like morphology with almost no agglomeration. Compared to BOC-1, the morphology of BOC-3 was more regular with a flower-like shape, and the size of the microflower was about $4\ \mu\text{m}$ (Figure 1c). In addition, BOC-3 was also prepared with different solvothermal reaction times to understand the microspherical morphology growth and optimize the reaction time (discussed in Appendix A). BOC-3 synthesized following 6 h of solvothermal treatment was composed of many ultrathin nanosheets (inset of Figure 1), which is beneficial for photocatalytic degradation due to the increased specific surface area. Figure 1d shows the N_2 adsorption-desorption isotherms of BOC-1 (dark), BOC-2 (red), and BOC-3 (blue). The isotherm plots showed type-IV isotherm and hysteresis loop curves [32]. The S_{BET} values of BOC-1, BOC-2, and BOC-3 were 8.914, 8.160, and $15.720\ \text{m}^2/\text{g}$, respectively, indicating that BOC-3 had the largest specific surface area.

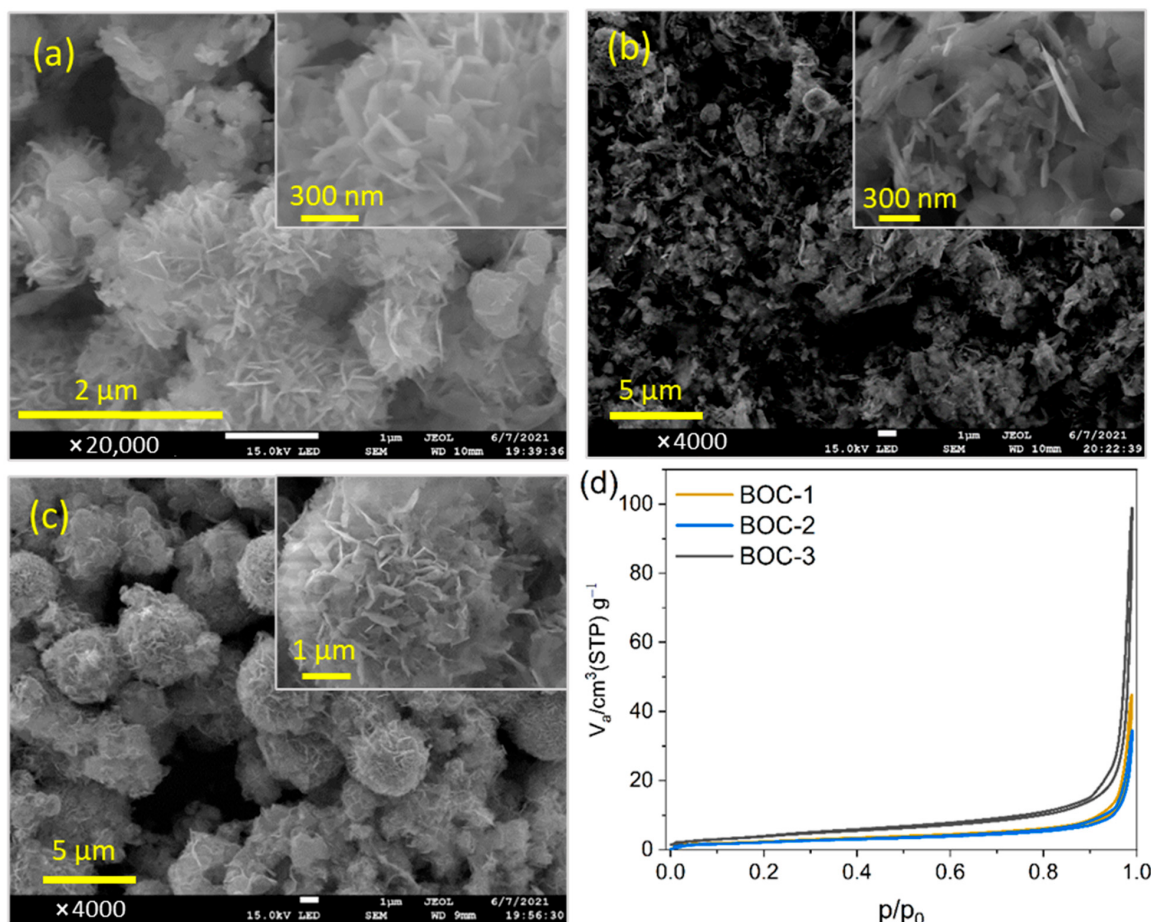


Figure 1. FESEM images of (a) BOC-1, (b) BOC-2, and (c) BOC-3; insets show the respective SEM image with high resolution. (d) N_2 adsorption–desorption isotherms of all samples.

Figure 2a shows a FESEM image of the 20-Co₃O₄/BOC synthesized with 20 mg of Co₃O₄ NPs and BOC-3. Its hierarchical morphology was almost identical to that of BOC-3, and it was not affected by the incorporation of Co₃O₄ NPs during the synthesis process. To investigate the existence of the nanosized Co₃O₄ in the BOC hierarchical morphology, HRTEM measurements of 20-Co₃O₄/BOC were performed, as shown in Figure 2b. The results confirmed that the Co₃O₄ NPs, which had an approximate diameter of 10 nm, were decorated on the surface of BOC. In the HRTEM, the fringe spacing of 0.23 nm belonged to the (222) crystal plane of Co₃O₄. By contrast, the fringe spacings of 0.272 nm and 0.31 nm, which respectively refer to the (200) and (117) crystal planes of BOC, have also been observed. Further, a high-angle annular dark-field (HAADF) image of 20-Co₃O₄/BOC was obtained (Figure 2c), in which the tiny black spots identified across the BOC surface indicated Co₃O₄ NPs; this finding was further confirmed by EDX analysis in Figure 2d,e. These results confirmed the 0D/3D morphology of the prepared photocatalyst might be conducive to the photocatalytic performance of the Co₃O₄/BOC heterostructure. Moreover, the obtained EDS mapping spectrum (Figure A2 in Appendix B) confirmed the presence of bismuth (Bi), oxygen (O), chlorine (Cl), and cobalt (Co) elements in the 20-Co₃O₄/BOC sample. The at.% and wt.% of the elements are also shown (inset table in Figure A2). Figure 2f presents the N₂ adsorption–desorption isotherm plots for 20-Co₃O₄/BOC. The estimated S_{BET} using N₂ isotherms was found to be 14.873 m²/g, which was close to the S_{BET} value of BOC-3. This result shows that the surface area of 20-Co₃O₄/BOC was slightly affected by the incorporation of Co₃O₄ NPs.

The XRD patterns of the pristine BOC-3, Co₃O₄, and 20-Co₃O₄/BOC are shown in Figure 2g. The observed peaks in the XRD patterns of BOC-3 and Co₃O₄ matched the BOC and Co₃O₄ crystallites (JCPDS cards #37-0702 and #42-1467), respectively. The 20-Co₃O₄/BOC samples showed all characteristic peaks of BOC-3. However, the characteristic peaks of Co₃O₄ were not observed in the prepared composite samples. The absence of Co₃O₄ characteristic peaks was attributed to the low amount of Co₃O₄ compared to BOC in 20-Co₃O₄/BOC composite samples. The structural properties of 20-Co₃O₄/BOC were further investigated using Raman spectroscopy, as shown in Figure 2h. All characteristic peaks of BOC have been observed in the Raman spectrum of pure BOC-3 [33]. The observed peak at 165.80 cm^{−1} belonged to the A_{1g} internal stretching of the Bi-Cl bond [33,34]. Because of the oxygen-rich nature of BOC-3, the observed peaks in the range from 200 cm^{−1} to 500 cm^{−1} belong to the vibrational modes of Bi and O bonding. Among them, The peak at 470.51 cm^{−1} is the characteristic vibrational mode of BOC-3, which belongs to O-Bi-O bending modes. Further, the peak at 598.80 cm^{−1} represents Cl-Cl stretching modes [35]. Regarding Co₃O₄ NPs, all the characteristic peaks of Co₃O₄ appeared in the Raman spectra, indicating the successful formation of Co₃O₄ NPs, along with an extra peak at 481.15 cm^{−1} from the glass substrate. These observed peaks belonged to the F_{2g} and E_g modes of the combined vibrations of the tetrahedral site and octahedral oxygen vibrations [36,37]. The Raman spectra of Co₃O₄ NPs-decorated BOC were also obtained. The Raman spectra of 20-Co₃O₄/BOC showed all the characteristic peaks of both Co₃O₄ and BOC-3 samples, along with an extra peak at 307.50 cm^{−1}. Since both Co₃O₄ and BOC-3 are oxygen-rich compounds, the interconnection of Co₃O₄ and BOC through oxygen bonding led to a new peak formation in the 20-Co₃O₄/BOC sample. The observed intense peak belongs to the Bi-O(1) rocking and weak O(2) breathing modes in the 20-Co₃O₄/BOC heterostructures, thus confirming the successful heterojunction formation [38].

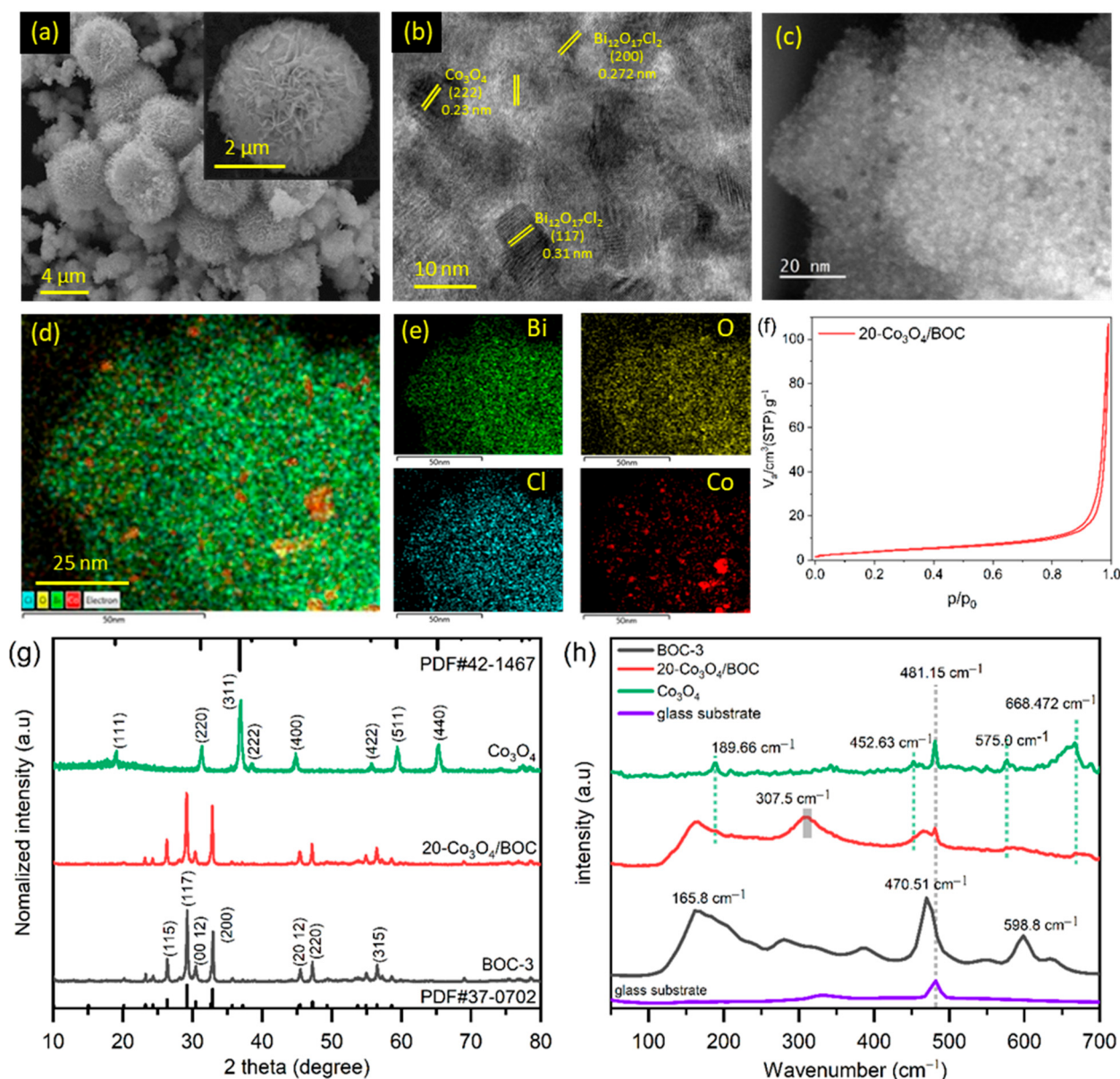


Figure 2. (a) FESEM image, (b) HRTEM image, (c) HAADF image, (d) EDX mapping, and (e) elemental EDX mapping of 20- $\text{Co}_3\text{O}_4/\text{BOC}$ sample, (f) N_2 adsorption-desorption isotherm of 20- $\text{Co}_3\text{O}_4/\text{BOC}$, (g) XRD patterns, and (h) Raman spectra of Co_3O_4 , BOC-3, and 20- $\text{Co}_3\text{O}_4/\text{BOC}$ micro flowers.

To analyze the chemical composition and chemical state of the elements, we performed X-ray photoelectron spectroscopy (XPS) of the 20- $\text{Co}_3\text{O}_4/\text{BOC}$ heterostructure photocatalyst (Appendix C). The XPS survey spectrum clearly demonstrated that all peaks were attributable to Bi, O, Cl, and Co elements, revealing that the heterostructure consisted of Bi, O, Cl, and Co elements, as shown in Figure A3 (See Appendix C). The high-resolution XPS spectra of Bi 4f, C 1s, O 1s, and Co 2p for the heterostructure are respectively shown in Figure A3b–e. The two strong peaks at 159.63 and 164.93 eV were assigned to Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, which are the features of Bi³⁺ in BOC (Figure A3b). As depicted in Figure A3c, the O 1s profile could be deconvoluted into three peaks, thus indicating the existence of three different kinds of O species in the sample. The peaks observed at 529.674 and 530.568 eV were assigned to the lattice oxygen metal bonds and hydroxyl (•OH) functional groups in 20- $\text{Co}_3\text{O}_4/\text{BOC}$, respectively [39]; the peak at 531.592 eV corresponded to oxygen vacancies in Co_3O_4 in the 20- $\text{Co}_3\text{O}_4/\text{BOC}$ composite sample [40]. Figure A3d

shows the spectrum of Cl 2p, which contained diverse peaks at 198.58 and 200.139 eV, respectively. These can be attributed to Cl 2p_{3/2} and Cl 2p_{1/2} of the Cl[−] ions in the corresponding 20-Co₃O₄/BOC sample [41]. In Figure A3e, the Co 2p peak of 20-Co₃O₄/BOC showed Co 2p_{3/2} and Co 2p_{1/2} spin-orbit doublets. The peaks at 782.25 and 793.50 eV in 20-Co₃O₄/BOC corresponded to Co²⁺ ions, whereas the peaks observed at 779.50 and 792.50 eV were assigned to Co³⁺ ions, therefore indicating the coexistence of Co²⁺ and Co³⁺ in both samples [42].

2.2. Photocatalytic Performance

The photocatalytic performance of BOC-1, BOC-3, 10-Co₃O₄/BOC, 20-Co₃O₄/BOC, and 40-Co₃O₄/BOC was explored by degrading RhB dye in aqueous solution under visible light, as shown in Figure 3a,b. Figure 3a indicates that 20-Co₃O₄/BOC outperformed BOC-3, 10-Co₃O₄/BOC, and 40-Co₃O₄/BOC by decomposing RhB dye solution in 140 min. Further, the degradation rate of RhB in the presence of each photocatalyst could be determined by the pseudo-first-order kinetic model, as expressed in Equation (1).

$$\ln C/C_0 = kt, \quad (1)$$

where k , C_0 , and C represent the reaction rate constant, initial concentration, and remaining concentration at time t , respectively. Figure 3b shows the reaction rate and degradation efficiency of all photocatalysts used for RhB degradation after 140 min. 20-Co₃O₄/BOC had the highest degradation rate of 2.21×10^{-2} /min and an efficiency of 97.4%. Moreover, we compared the RhB photocatalytic degradation performance of the single BOC and 20-Co₃O₄/BOC photocatalyst with previously reported, similarly structured semiconducting photocatalysts, as shown in Table A1 (In Appendix E). Both synthesized BOC and Co₃O₄/BOC hierarchical microspheres possessed relatively higher degradation performance under similar test conditions. This enhanced efficiency might be related to the high surface area of hierarchically structured BOC and the formation of a Co₃O₄/BOC heterojunction with Co₃O₄ NPs-decoration.

Moreover, the photocatalytic degradation of BPA was performed to evaluate the photocatalytic activity of BOC and Co₃O₄/BOC, as shown in Figure 3c,d. The BPA degradation results showed that 20-Co₃O₄/BOC efficiently decomposed BPA aqueous pollutant solution in 170 min. Moreover, the degradation of BPA in the presence of each photocatalyst followed the 1st-order reaction kinetic model. Figure 3d shows the reaction rate and degradation efficiency after 110 min for all the photocatalysts used for BPA degradation. 20-Co₃O₄/BOC had the highest degradation rate of 1.66×10^{-2} /min and an efficiency of 88.4%, followed by BOC-3, BOC-1, and BOC-2.

We further conducted a reusability test for the 20-Co₃O₄/BOC in the presence of RhB and BPA pollutants, as shown in Figure A4 (in Appendix D). During RhB and BPA degradation, a consistent decrease in the degradation of RhB and BPA occurred after the 3rd cycle of degradation, and its degradation performance was slightly reduced. This slight reduction in photocatalytic degradation may be attributable to the adsorption of RhB and BPA molecules on the surface of the 20-Co₃O₄/BOC sample.

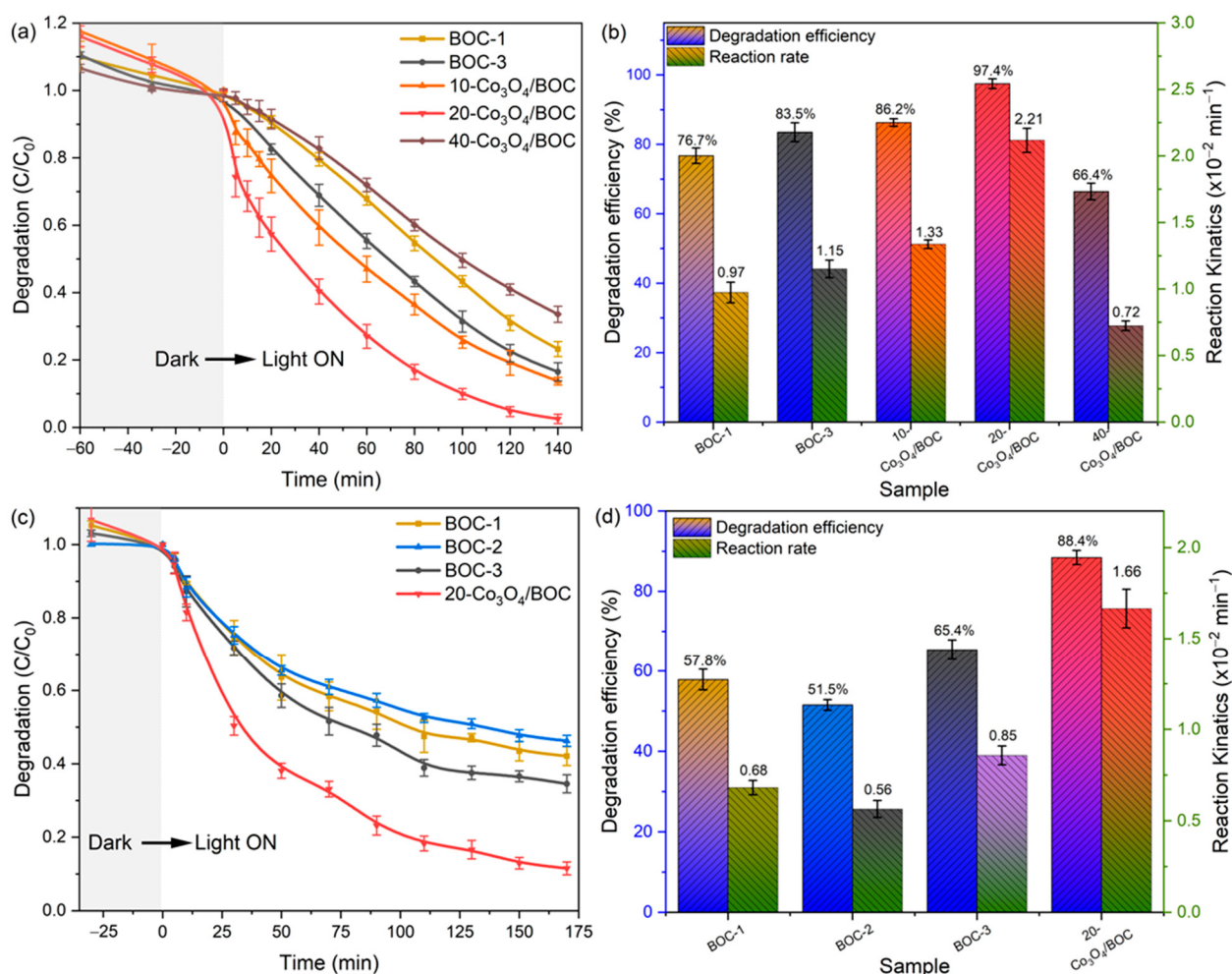


Figure 3. (a) Photocatalytic degradation curves of RhB, (b) its degradation efficiency with reaction rate constant, in the presence of BOC-1, BOC-3, 10-Co₃O₄/BOC, 20-Co₃O₄/BOC, and 40-Co₃O₄/BOC, (c) photocatalytic degradation of BPA, and (d) its degradation efficiency with reaction rate constant in the presence of BOC-1, BOC-2, BOC-3, and 20-Co₃O₄/BOC.

2.3. Analysis of Enhanced Photocatalytic Activity of Co₃O₄/BOC

Photocatalytic activity is mainly attributed to light absorption capacity and the separation and transfer efficiency of photoinduced charge carriers. Firstly, photoluminescence (PL) measurements were conducted to investigate the recombination rate of photo-induced e^-h^+ pairs in BOC-3 and 20-Co₃O₄/BOC photocatalysts, as shown in Figure 4a. The PL emission intensity of 20-Co₃O₄/BOC was lower than that of BOC-3, thus indicating reduced recombination of e^-h^+ pairs in the 20-Co₃O₄/BOC photocatalyst. The transient photocurrent response was also measured to provide further support to the efficient separation of photo-generated charges, as shown in Figure 4b. The 20-Co₃O₄/BOC had a higher photocurrent response than BOC-3. The higher photocurrent response of 20-Co₃O₄/BOC was attributed to the higher separation efficiency of the excitons and its longer lifetime. Moreover, the EIS Nyquist plot was obtained to examine the electrode/electrolyte interfacial charge transfer resistance, as shown in Figure 4c. 20-Co₃O₄/BOC showed a smaller arc radius than BOC-3. The inset in Figure 4c shows the circuit of the sample-solution in the EIS measurements. According to the model of the circuit, R_s is related to uncompensated solution resistance, R_p is related to the porosity of the electrode, and R_{ct} represents the charge transfer resistance at the interface [43]. The R_{ct} values for BOC and 20-Co₃O₄/BOC are $1.58 \times 10^{-4} \Omega$ and $82.93 \times 10^{-4} \Omega$, respectively. The smaller R_{ct} value of 20-Co₃O₄/BOC

represents its lower charge transfer resistance, which is beneficial for high redox reactions during photocatalysis.

Further, the UV-vis DRS of Co_3O_4 , BOC-3, and $20\text{-Co}_3\text{O}_4/\text{BOC}$ were measured to investigate the optical absorption ability, as shown in Figure 4d. Co_3O_4 showed absorption throughout the whole UV and visible range. The absorption edges for BOC-3 were located around 520 nm. In comparison, $20\text{-Co}_3\text{O}_4/\text{BOC}$ showed enhanced absorption in the visible range after loading Co_3O_4 NPs on BOC. The high absorption of $20\text{-Co}_3\text{O}_4/\text{BOC}$ was attributed to the strong contribution of Co_3O_4 in $20\text{-Co}_3\text{O}_4/\text{BOC}$ to the absorption of visible light. Ultimately, these results suggest that the formation of the heterojunction in $20\text{-Co}_3\text{O}_4/\text{BOC}$ heterostructure could effectively suppress the recombination of the photoexcited charge carriers and enhance the visible light absorption ability. Therefore, the photocatalytic performance could effectively be improved by the $20\text{-Co}_3\text{O}_4/\text{BOC}$ heterostructure.

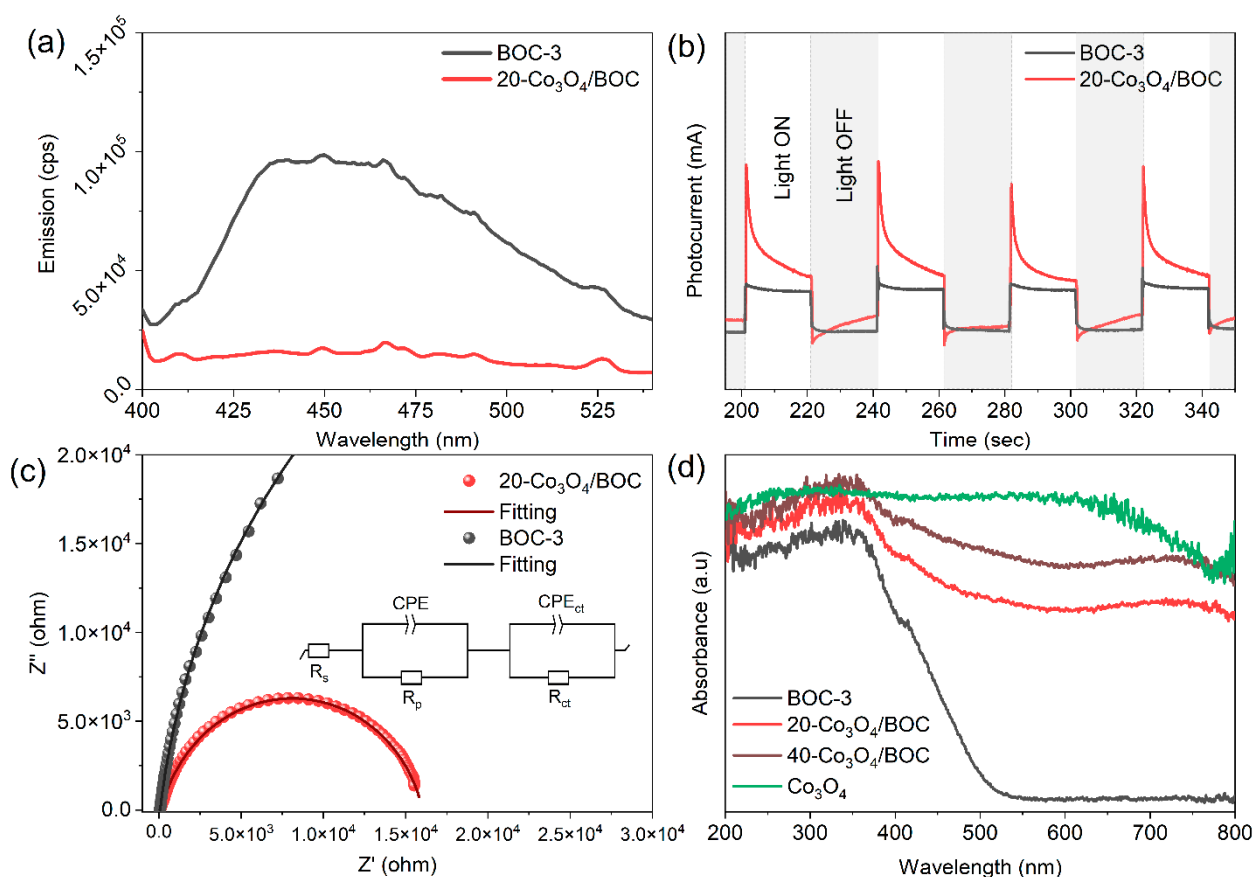


Figure 4. (a) Photoluminescence spectra, (b) Transient photocurrent response, (c) EIS Nyquist plots of BOC-3 and $20\text{-Co}_3\text{O}_4/\text{BOC}$ samples, and (d) UV-Vis diffuse reflectance spectra of Co_3O_4 , BOC-3, $20\text{-Co}_3\text{O}_4/\text{BOC}$, and $40\text{-Co}_3\text{O}_4/\text{BOC}$.

2.4. Interfacial Charge Transfer Behavior and Photocatalytic Reaction Mechanism

The electronic structures of Co_3O_4 , BOC, and $\text{Co}_3\text{O}_4/\text{BOC}$ were analyzed by UV-Vis diffuse reflectance spectra (DRS), the Mott-Schottky (MS) plot, and valence band (VB) XPS measurements to elucidate the photocatalytic mechanism of the $20\text{-Co}_3\text{O}_4/\text{BOC}$ heterostructure during the photodegradation of RhB and BPA, as shown in Figure 5. First, the optical bandgap energies of BOC-3 and Co_3O_4 could be obtained through curve fitting of the Tauc plot of $(\alpha h\nu)^{n/2}$ versus $h\nu$ (Figure 5a), where $n = 4$ for the Co_3O_4 direct band gap semiconductor and $n = 1$ for the indirect band gap semiconductor [44,45]. The obtained bandgap energies were 2.34 and 2.25 eV for BOC-3 and Co_3O_4 , respectively.

Secondly, the Fermi energy (E_f) levels of the prepared Co_3O_4 and BOC-3 were obtained using MS analysis, as shown in Figure 5b,c, respectively. The MS plots of Co_3O_4 and BOC-3

showed negative and positive slopes, thus indicating p-type and n-type semiconducting behaviors, respectively [46,47]. Further, by extrapolating MS plots, the flatband potentials of Co_3O_4 and BOC-3 were found to be +0.037 and −0.51 V, respectively, vs. the standard calomel electrode (SCE). Note that the flatband potential (E_{fb}) of the n-type and p-type semiconductors represents the E_f level. The E_f level vs. the normal hydrogen electrode (NHE) scale could be calculated using Equation (2). The resultant E_f of Co_3O_4 and BOC-3 were +0.277 and −0.266 eV vs. NHE, respectively

$$E_{fb} \text{ (vs. NHE)} = E_{fb} \text{ (vs. SCE)} + 0.244 \text{ (eV)}, \quad (2)$$

Valence band (VB) XPS measurement was conducted to determine the VB potentials of Co_3O_4 and BOC-3, as shown in Figure 5d. The VB XPS spectra revealed the VB maxima of 0.86 and 1.69 eV for Co_3O_4 and BOC-3, respectively. Thus, the VB potentials with respect to the E_f level were calculated to be 1.137 and 1.424 eV vs. NHE, respectively (Figure 6a). The CB minima of Co_3O_4 and BOC-3 were determined using the following Equation (3).

$$E_{CB} \text{ (vs. NHE)} = E_{VB} \text{ (vs. NHE)} - E_g, \quad (3)$$

where E_{CB} , E_{VB} , and E_g denote the sample's CB potential, VB potential, and bandgap, respectively. As a result, the calculated CB potentials for Co_3O_4 and BOC-3 were −1.113 and −0.916 eV vs. NHE, respectively.

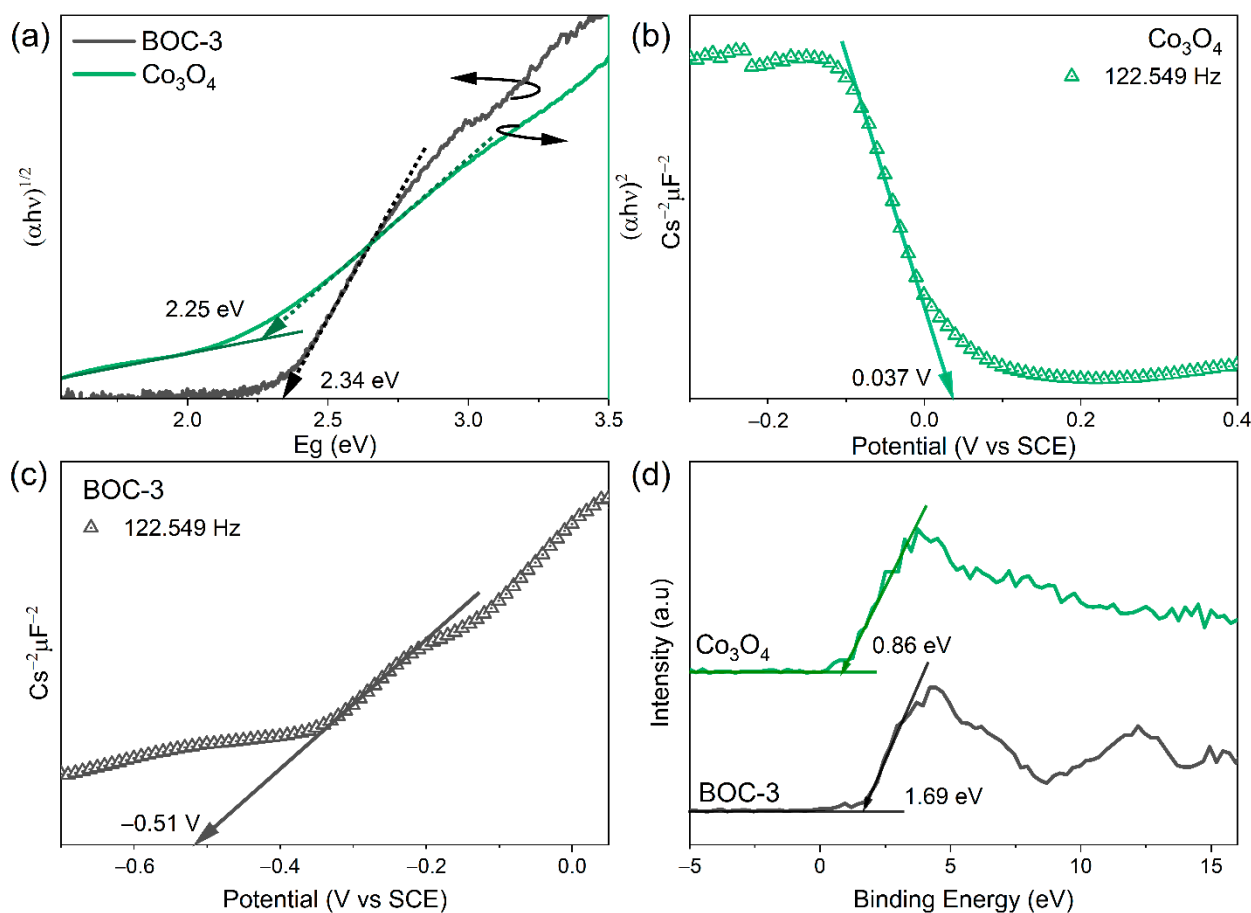


Figure 5. (a) Tauc plots, (b,c) Mott-Schottky plots, and (d) valence band XPS of Co_3O_4 and BOC-3.

Therefore, based on the above analysis, we can obtain the band structures of Co_3O_4 and BOC in NHE scale before contact, as shown in Figure 6. When Co_3O_4 and BOC form the Co_3O_4 /BOC heterojunction after they come into contact, the electrons will spontaneously

migrate from BOC to Co_3O_4 through the Co_3O_4 /BOC interface to align with the Fermi level because BOC has a higher E_f level than Co_3O_4 . The migration of these electrons results in the band bending upward for BOC and downward for Co_3O_4 , near the interface of BOC and Co_3O_4 , respectively, as shown in Figure 6b. These band bendings lead to a depletion region at the Co_3O_4 and BOC-3 interface, thus resulting in the generation of an internal electric field (IEF) from BOC toward Co_3O_4 at the interface. After light is irradiated on the photocatalyst, the charge carriers simultaneously excite from VB to the CB in Co_3O_4 and BOC-3 to produce photo-generated e^- and h^+ pairs. Then, the photoexcited electrons in the CB of Co_3O_4 will quickly migrate to the CB of BOC-3, whereas the remaining holes in the VB of BOC-3 will migrate to the VB of Co_3O_4 because of the IEF directed from BOC to Co_3O_4 in the 20- Co_3O_4 /BOC, which is a typical charge transport of a type-II heterostructure. As a result, the e^- - h^+ recombination is suppressed in the heterostructure system. Moreover, the unique 0D/3D morphology of 20- Co_3O_4 /BOC will provide more active catalytic reaction centers and increase the active sites. Thus, the developed heterostructure could be suggested to be beneficial in photocatalytic degradation.

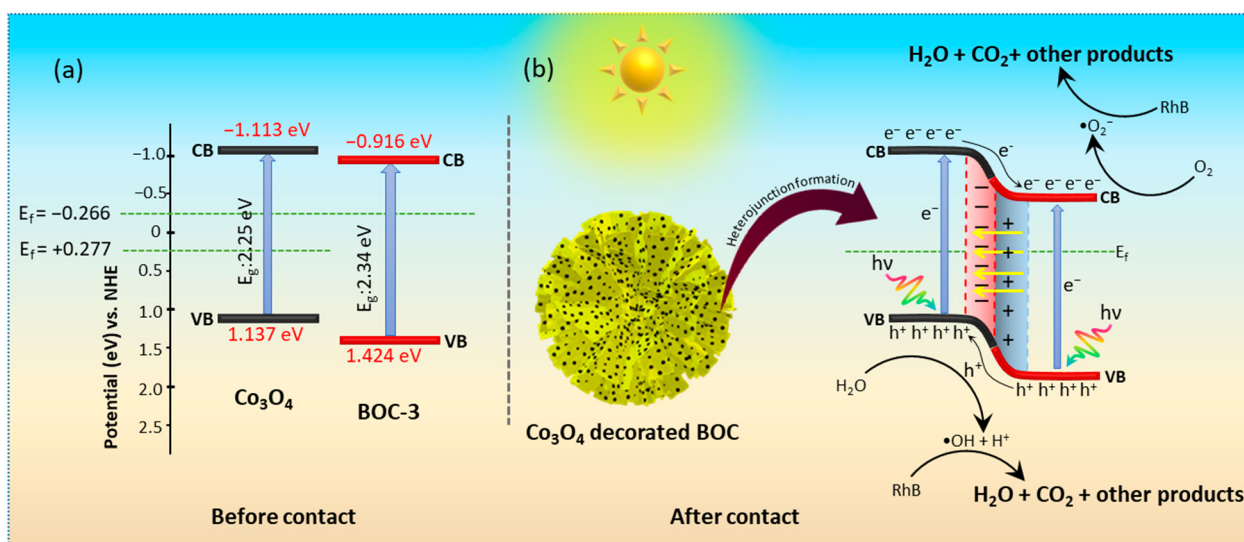


Figure 6. (a) Energy-level diagrams of Co_3O_4 and BOC and (b) interfacial charge transfer behavior and redox reaction process in 20- Co_3O_4 /BOC heterostructure under visible-light irradiation.

Finally, photocatalytic active radical detection experiments were conducted to investigate the photocatalytic reaction mechanism and validate our proposed heterojunction formation, as depicted in Figure 7. Here, BQ, IPA, and KI were used as scavengers of $\cdot\text{O}_2^-$ radicals, $\cdot\text{OH}$ radicals, and hole (h^+), respectively, which are produced during the photocatalytic degradation of RhB [48]. Since 20- Co_3O_4 /BOC composite decomposed the RhB dye efficiently compared to the other photocatalysts (shown in Figure 3a), a 20- Co_3O_4 /BOC photocatalyst sample was chosen for active radical detection. As shown in Figure 7, in the presence of BQ and IPA, the degradation efficiency of RhB was significantly reduced from 98% (no scavenger) to 68.5% and 86.2%, respectively. However, no effect on the degradation efficiency was observed when using KI as an h^+ scavenger. Therefore, $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals were found to be the reactive species with increased generation of $\cdot\text{O}_2^-$ during the photodegradation of RhB.

Based on the radical scavenger experiments, the possible reaction mechanism was proposed as shown in reaction (4)–(10); the excited electrons on BOC reduced the oxygen molecule (O_2) into $\cdot\text{O}_2^-$ radicals, and then the $\cdot\text{O}_2^-$ radicals reacted with e^- and hydrogen ions (H^+), ultimately resulting in the generation of hydrogen peroxide (H_2O_2) radical,

which was further reduced to $\bullet\text{OH}$ and hydroxyl ion (OH^-). Then, the $\bullet\text{O}_2^-$, $\bullet\text{OH}$, and OH^- finally decomposed RhB and BPA into small chain molecules.

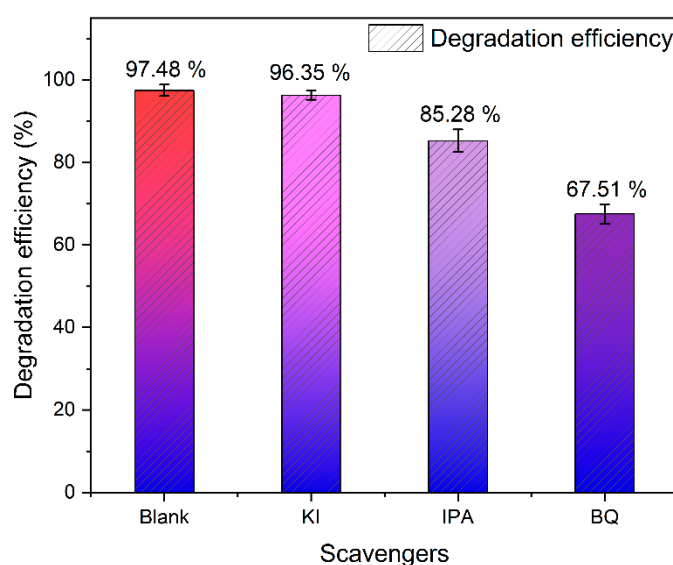
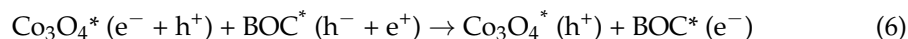
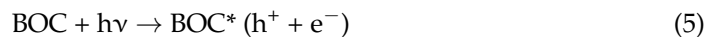
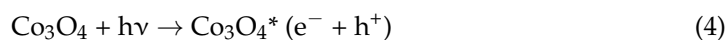


Figure 7. Active radicals detection in the presence of various scavengers during RhB degradation.

3. Materials and Methods

3.1. Chemicals

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99%), Cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), Potassium chloride (KCl, 99%), Ethylene glycol (EG) ($(\text{CH}_2\text{OH})_2$, 99%), Dimethylformamide (DMF) ($\text{C}_3\text{H}_7\text{NO}$), Rhodamine-B (RhB) ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$, 99%), Bisphenol-A (BPA) ($\text{C}_{15}\text{H}_{16}\text{O}_2$, 99%), 1,4-benzoquinone (BQ) ($\text{C}_6\text{H}_4\text{O}_2$, 99%), and Fluorine doped tin oxide (FTO) glass were purchased from Sigma Aldrich Inc. (St. Louis, MO, USA). Ethanol (EtOH) ($\text{C}_2\text{H}_5\text{OH}$, 99%) and Isopropyl alcohol (IPA) ($\text{C}_3\text{H}_8\text{O}$, 99%) were purchased from DAEJUN Co., Ltd (Daejun, Korea). All reagents were used without any further purification.

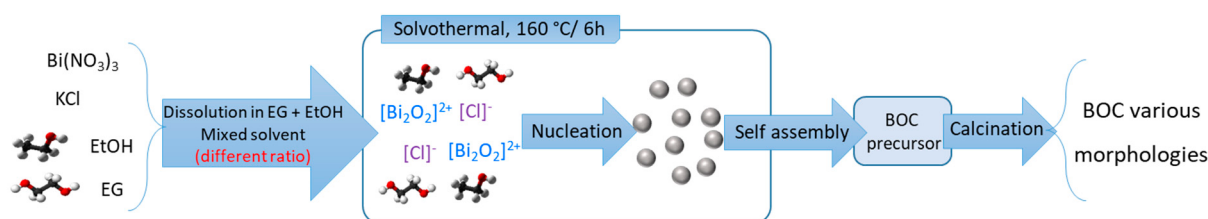
3.2. Preparation of Co_3O_4 Nanoparticles

The Co_3O_4 NPs were prepared by the solvothermal method [29]. In a typical synthesis, 80 mg of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 60 mL of EtOH using a magnetic stirrer. The prepared solution was then transferred to a 100 mL Teflon-lined autoclave and heated at 150 °C for 4 h in a thermal oven to initiate the solvothermal reaction. After completion of the reaction, the autoclave was allowed to cool down to room temperature, at which point the raw Co_3O_4 was washed with EtOH and centrifuged at 15,000 rpm for 30 min. Following centrifugation, the collected sample was dried at 60 °C overnight to obtain the Co_3O_4 NPs.

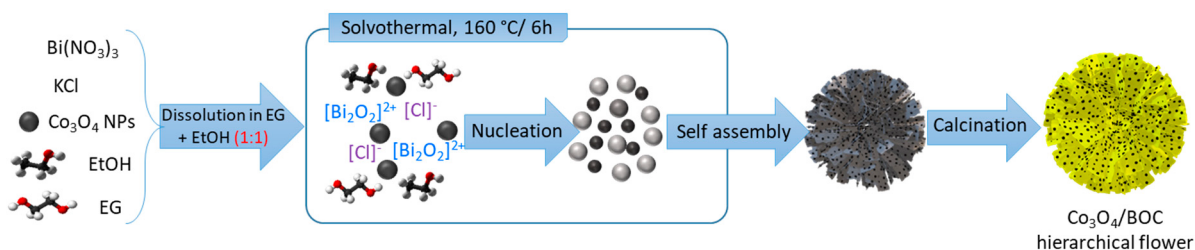
3.3. Preparation of BOC and $\text{Co}_3\text{O}_4/\text{BOC}$

BOC was prepared by a solvothermal method, as shown in Scheme 1a. In a typical synthesis method, 2.186 g (4.5 mmol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 17.5 mL of ethanol by ultrasonication, followed by stirring. The resulting solution was referred to as solution-A. At the same time, 1.5 mmol of KCl was dissolved in 17.5 mL of EG by ultrasonication, followed by stirring for 30 min. The resulting solution was referred to as solution-B. Next, solution-B was added dropwise to solution-A and then constantly stirred for 30 min. Then, the resulting combined solution was transferred to a 50 mL Teflon autoclave and heated for 6 h at 160 °C. The product obtained in this way was washed and dried overnight at 60 °C. Afterward, the gray powder was collected and calcinated in a muffle furnace at 450 °C for 1 h to obtain the targeted BOC hierarchical microspheres. The $\text{Co}_3\text{O}_4/\text{BOC}$ samples were prepared using the identical synthesis procedure with the addition of Co_3O_4 NPs (10, 20, and 40 mg) into the combined solution (see Scheme 1b). Moreover, the BOC sample was prepared in pure EG and EtOH solutions to investigate the roles of EG, EtOH, and EG-EtOH mixed solvents during BOC synthesis. The samples prepared in EG, EtOH, and EG-ETOH mixed solvents were labeled as BOC-1, BOC-2, and BOC-3, and the sample prepared with the addition of 10, 20, and 40 mg of Co_3O_4 NPs were labeled as 10- $\text{Co}_3\text{O}_4/\text{BOC}$, 20- $\text{Co}_3\text{O}_4/\text{BOC}$, and 40- $\text{Co}_3\text{O}_4/\text{BOC}$, respectively.

(a). BOC synthesis



(b). $\text{Co}_3\text{O}_4/\text{BOC}$ synthesis



Scheme 1. Synthesis of (a) nanoflower-like BOC, and (b) 0D/3D $\text{Co}_3\text{O}_4/\text{BOC}$ hierarchical micro flower.

3.4. Characterization of Samples

The crystal structure and phase purity were characterized by powder X-ray diffraction (XRD) in the 2θ range from 10–80° (2° min^{-1}) using an X-ray diffractometer (Rigaku D/MAX-2500) with a $\text{Cu K}\alpha$ irradiation source ($\lambda = 1.54178 \text{ \AA}$) and X-ray power of 40 kV/30 mA. Micro-Raman spectroscopy (XperRAM100, Nanobase Inc., Seoul, Korea) equipped with a monochromatic laser source (wavelength of 532 nm and power of 6 mW) was used to characterize the crystalline phase. The morphologies were examined using a field emission scanning electron microscope (SEM) (JSM-6700F, Jeol Ltd., Tokyo, Japan) and a transmission electron microscope (TEM) (“NEOARM “/JEM-ARM200F, Jeol Ltd.) equipped with an energy dispersive spectroscopy (EDX). X-ray photoemission spectroscopy (XPS) (Veresprobe II, ULVAC-PHI Inc., Kanagawa, Japan) with a Monochromatic $\text{Al K}\alpha$ X-ray source was used to examine the chemical compositions of the samples. The specific surface area was volumetrically assessed by measuring the nitrogen adsorption/desorption isotherms at 77 K using Microtrac, BELsorp-mini II. UV-vis diffuse reflectance spectra

(DRS) were obtained using a spectrometer (V-750, Jasco Inc., Tokyo, Japan) equipped with a 60 mm integrating sphere while using BaSO₄ as a reference. Photoluminescence spectra (PL) were collected using a spectrophotometer (FS5 fluorescence, Edinburg, United Kingdom) with an excitation wavelength of 375 nm. Electrochemical impedance spectroscopy (EIS) was performed using a three-electrode workstation (VSP Potentiostat, Biologic, Seyssinet-Pariset, France). A Pt square plate (1 × 2 cm²) and a standard calomel were used as counter and reference electrodes, respectively. A clean fluorine-doped tin oxide (FTO) glass with an active surface area of 0.8 cm² was used as a substrate for the working electrode, whereas an aqueous solution of 0.5 M Na₂SO₄ (80 mL) was used as the electrolyte. In the preparation of the working electrode, 0.1 mg of photocatalyst was added to 1 mL of DMF solution and sonicated for 1 h. Then, 50 µL of the dispersed solution was drop-casted on FTO and annealed at 160 °C for 1 h, which was further used in the electrochemical investigation.

3.5. Photocatalytic Activity Measurements

The photocatalytic characteristics of the samples were examined using a visible light source with a 300 W Xenon lamp (1000 W/m²) (CEL-HXF300, CEAULIGHT Co., Beijing, China) equipped with a UV-IR cutoff filter (420 nm > λ > 780 nm). A double wall jacket beaker with a surface area of 80 cm² connected to a water chiller was used to perform the photocatalytic degradation measurement of the photocatalysts. The height from the surface of the pollutant solution to the light source was kept at 30 cm. In this study, RhB dye and BPA colorless pollutants were used to evaluate the degradation efficiency of the synthesized photocatalysts. Briefly, 20 and 40 mg of photocatalyst was used to degrade 40 mL of RhB dye (20 ppm) and BPA colorless pollutant (10 ppm), respectively. Before initiating the photocatalytic experiment, the RhB and BPA aqueous solutions were stirred for 60 min and 30 min, respectively, in dark conditions to attain an adsorption–desorption equilibrium of the photocatalysts. To investigate the photocatalytic degradation rate, 2 mL solution was taken from the RhB or BPA solution after a specific interval, and this solution was then centrifuged for 3 min at 5000 rpm to separate the photocatalyst, after which the absorbance spectrum of the supernatant using UV-visible spectrophotometer was measured. Further, radical trapping experiments were conducted to determine the dominant radical species involved in the photocatalytic decomposition of RhB and BPA. IPA, BQ, and KI of 2 mmol were used as trapping reagents to explore the active species, such as, •O₂[−], •OH radicals, and h⁺, respectively.

4. Conclusions

In this work, we successfully developed a 3D hierarchical BOC microsphere and a 0D/3D-Co₃O₄/BOC heterojunction photocatalyst composed of BOC decorated with Co₃O₄ NPs using a simple solvothermal synthesis method. The developed heterostructure showed a conventional type II charge transport phenomenon across Co₃O₄ and BOC-3 by forming a *p-n* heterojunction. The 0D/3D hierarchical morphology of the Co₃O₄/BOC could increase active sites because of its high surface area, suppressing e[−]-h⁺ recombination, and improving visible light absorption. The results of mechanistic studies have proven that the generation of an IEF from BOC-3 to Co₃O₄ led to a *p-n* junction and the formation of a type II heterojunction. Thus, benefiting from the above properties, the Co₃O₄/BOC sample demonstrated a higher reaction rate and a higher degradation efficiency than bare Co₃O₄ and BOC during RhB and BPA degradation. Conclusively, our developed photocatalyst should be considered a good candidate for pollutant degradation.

Author Contributions: S.T.U.D. contributed to the main idea and the writing of the original draft. W.-F.X. contributed to the writing—review and editing. W.Y. contributed to the writing—review and editing, supervision, project management, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2022R1F1A1074441 and 2021H1D3A2A01100019).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

Appendix A

We also prepared BOC-3 in different solvothermal reaction times to explore the formation mechanism of the BOC microspherical morphology. Figure A1 represents the SEM images of the BOC samples prepared with solvothermal reaction times of 3, 6, 9, 12, and 18 h. The formation of a sphere-like morphology composed of ultrathin nanosheets could be observed after 3 h of solvothermal reaction (Figure A1a). When the solvothermal reaction time increased to 6 h, the nanosheets grew further, thus increasing the diameter of the microspheres with clear visibility of ultrathin nanosheets (Figure A1b). When the reaction time was increased to 9 h, the microspheres were covered with external BOC nanosheets, and the nanosheets did not grow further (Figure A1c). The BOC nanosheets were covered with BOC nanosheets after increasing the hydrothermal reaction time to 12 h and 18 h, respectively (Figure A1d,e). These results indicate that the formation of BOC microspheres quickly underwent nucleation, growth, and self-assembly.

Based on the above results, the formation of the BOC samples in the different solvent ratios proceeded as illustrated in Scheme 1. It could be concluded that $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ will be hydrolyzed into $[\text{Bi}_2\text{O}_2]^{2+}$ after dissolution in EtOH. Secondly, Cl^- ions generated from KCl in EG solution could react with $[\text{Bi}_2\text{O}_2]^{2+}$ to form Cl–Bi–O–Bi–Cl nuclei through the coulomb force during the solvothermal reaction [49], thus resulting in homogenous nucleation. As the reaction proceeded in the first 3 h of the solvothermal reaction time at 160 °C, the BOC nanosheets formed. These nanosheets formations could potentially have occurred due to the bonding of the OH functional group to Bi^{3+} ions in Cl–Bi–O–Bi–Cl complex, which grew vertically along the c axis due to its intrinsic crystal structure. Since BOC has a known silane-type structure with a space group of $P4/nmm$ and lattice constants of $a = 5.4 \text{ \AA}$ and $c = 35.20 \text{ \AA}$, which are related to $\sqrt{2}a_s \times \sqrt{2}b_s \times c_s$ supercell, its layered structure was constructed through the combination of the 6-fold metal-oxygen (Bi–O) layer separated by the Cl layer [50]. Therefore, the formation of the nanosheets and their regulation with the OH functional group were considered to be favorable [51]. Thirdly, as the reaction progressed, the obtained nanosheets were assembled into microspheres, which could decrease the surface energy and achieve a stable structure. Finally, the hierarchical microspheres grew further and the size of the samples gradually increased.

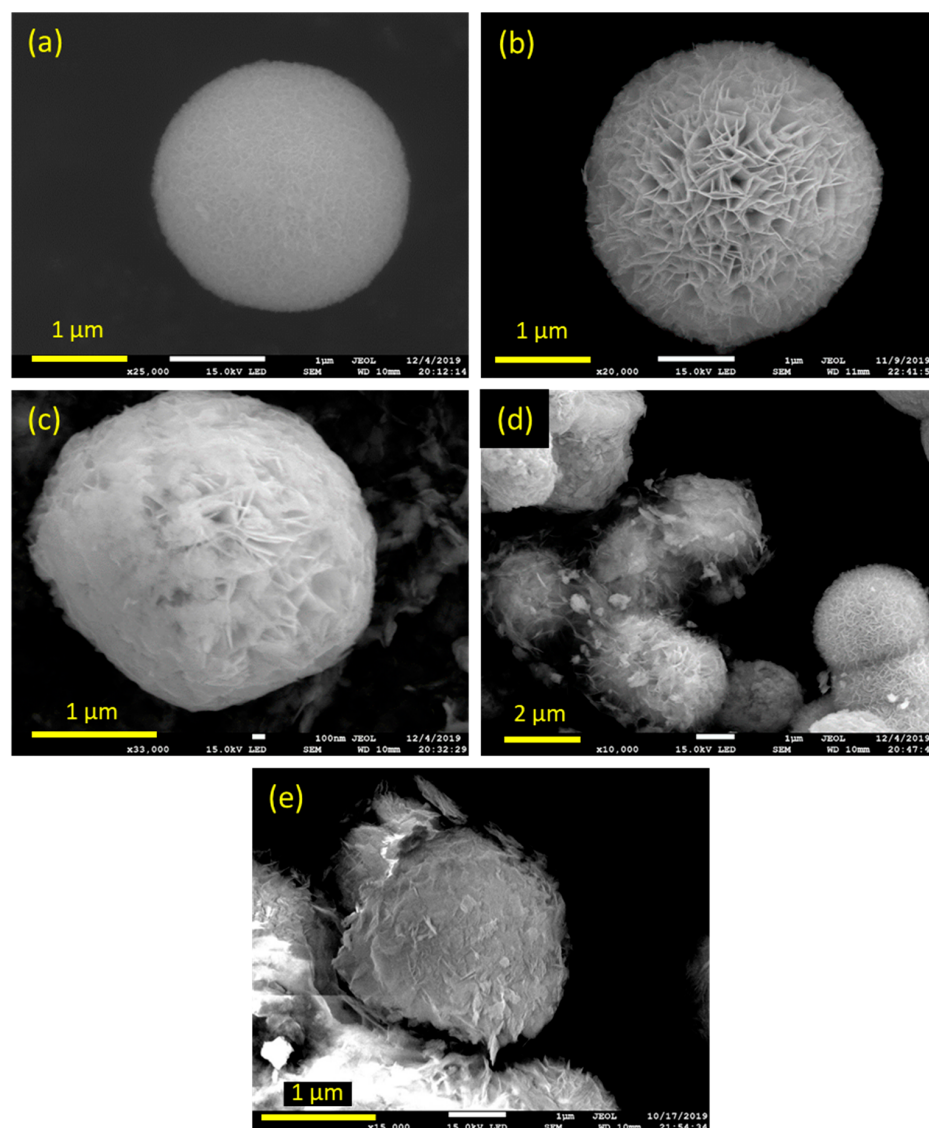


Figure A1. SEM images of BOC samples prepared after (a) 3, (b) 6, (c) 9, (d) 12, and (e) 18 h of solvothermal reaction time.

Appendix B

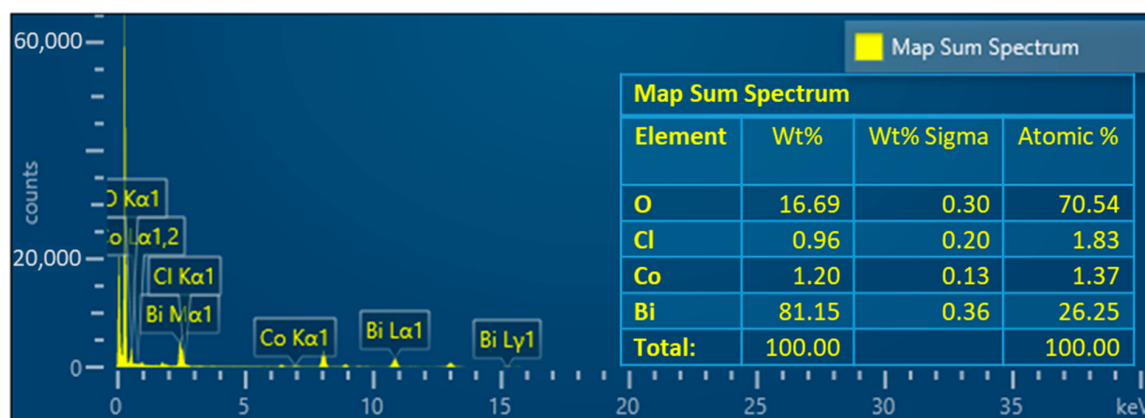


Figure A2. EDX spectrum of 20-Co₃O₄/BOC, and its elemental and atomic wt.% in the inset table.

Appendix C

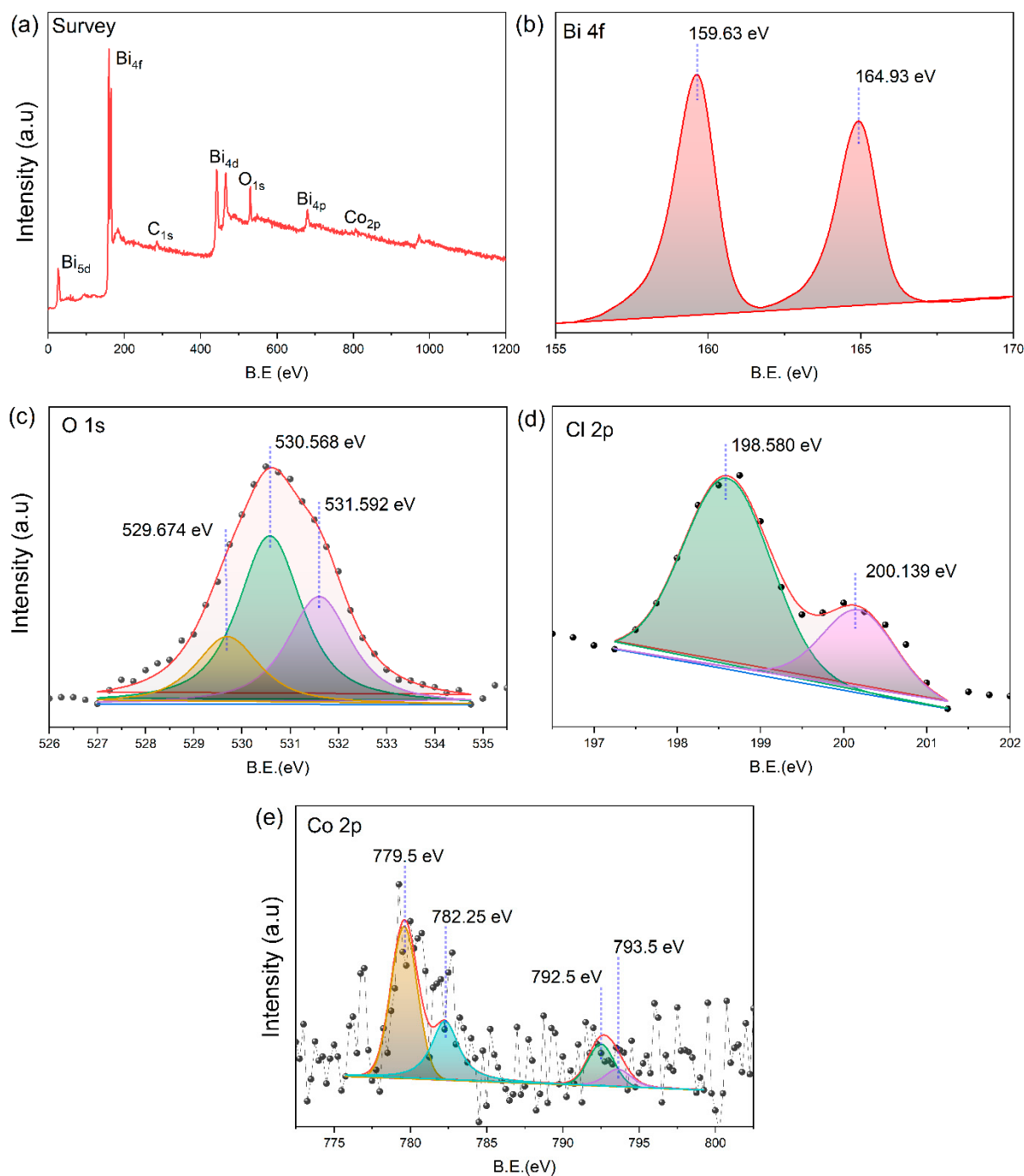


Figure A3. XPS survey spectra (a), core level spectra of (b) Bi 4f, (c) O 1s, (d) Cl 2p, and (e) Co 2p spectra for the prepared 20-Co₃O₄/BOC samples.

Appendix D

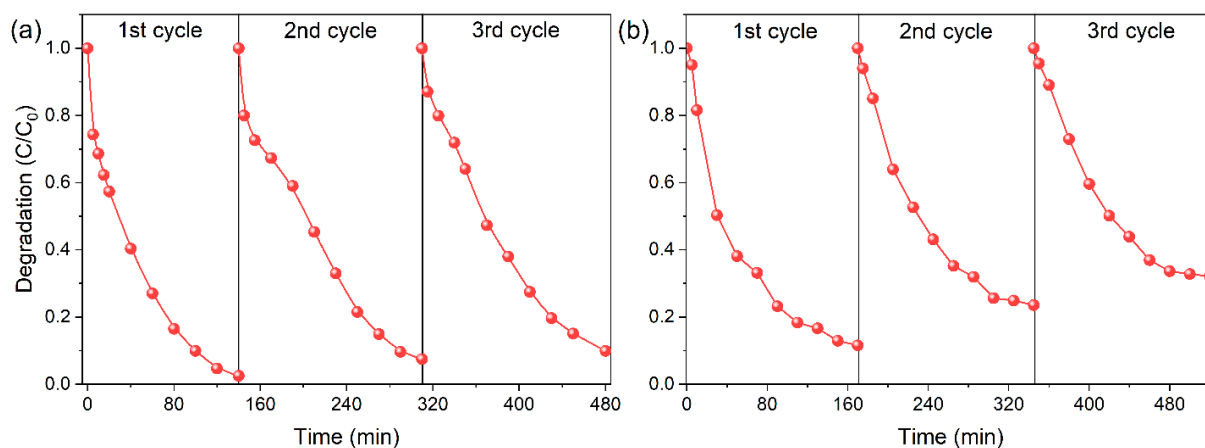


Figure A4. Cyclic photocatalytic degradation of (a) RhB and (b) BPA in the presence of 20- Co_3O_4 /BOC sample.

Appendix E

Table A1. Comparison of photocatalytic degradation of RhB in the presence of pure BOC and BOC composite sample with recently reported results.

Photocatalyst	Rate Constant (min^{-1})	Degradation Efficiency (%)	Degradation Time (min)	Lamp (C)	Amount of Catalyst (mg)	Solution Volume (mL)	Solution Concentration (mg/L)	Ref
$\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.0115 min^{-1}	83.5%	140	300 W Xenon lamp, (420–720 nm)	20	40	20	This work
$\text{Co}_3\text{O}_4/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.021 min^{-1}	97.4%						
$\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	$1.93 \times 10^{-3} \text{ min}^{-1}$	40%	240	300 W Xenon lamp, (420–720 nm)	40	80	15	[52]
$\text{Ag}/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	$10.3 \times 10^{-3} \text{ min}^{-1}$	93%						
$\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	$1.16 \times 10^{-2} \text{ min}^{-1}$	83%	150	300 W Xenon lamp, (400–780 nm)	80	80	20	[53]
$\text{Bi}-\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	$2.19 \times 10^{-2} \text{ min}^{-1}$	99%						
$\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.074 min^{-1}	–	20	300 W Xenon lamp, (400 nm)	10	50	10	[54]
Fe(III)-modified $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.157 min^{-1}	–						
$\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.0613 min^{-1}	78%	20	300 W Xenon lamp, (400 nm)	30	50	10	[23]
Graphene/ $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.160 min^{-1}	–						
$\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.102 min^{-1}	83%	20	300 W Xenon lamp, (400 nm)	30	50	5	[55]
2D/2D $\text{g}-\text{C}_3\text{N}_4/\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$	0.353 min^{-1}	99%						
ZnO/NiO	0.019 min^{-1}	–	120	320 mW/cm^2 . LED light	50	50	10	[56]
$\text{g}-\text{C}_3\text{N}_4$	1.11 min^{-1}	99%	90	150 watt halogen lamp	50	100	5	[57]
Carbon dot implanted $\text{g}-\text{C}_3\text{N}_4$	0.48 min^{-1}	–	80	300 W Xenon lamp, (320–780 nm)	10	30	15	[58]
$\text{BiVO}_4\text{-Ni}/\text{AgVO}_3$	0.133 min^{-1}	–	30	300 W Xenon lamp, (400 nm)	30	50	10	[59]
$\text{Fe}-\text{BiOBr} + \text{H}_2\text{O}_2$	0.0646 min^{-1}	98.23%	60	350 W xenon lamp (420 nm)	30	50	20	[60]
$\text{SrSnO}_3/\text{g}-\text{C}_3\text{N}_4$	k1: 0.0083^{-1} k2: 0.0348^{-1}	97.3	250	Sun Light	100	100	5	[61]

References

- Al-Buriah, A.K.; Al-Gheethi, A.A.; Senthil Kumar, P.; Radin Mohamed, R.M.S.; Yusof, H.; Alshalif, A.F.; Khalifa, N.A. Elimination of Rhodamine B from Textile Wastewater Using Nanoparticle Photocatalysts: A Review for Sustainable Approaches. *Chemosphere* **2022**, *287*, 132162. [\[CrossRef\]](#)
- Corrales, J.; Kristofco, L.A.; Steele, W.B.; Yates, B.S.; Breed, C.S.; Williams, E.S.; Brooks, B.W. Global Assessment of Bisphenol A in the Environment: Review and Analysis of Its Occurrence and Bioaccumulation. *Dose-Response* **2015**, *13*, 1559325815598308. [\[CrossRef\]](#)
- Wright-Walters, M.; Volz, C.; Talbott, E.; Davis, D. An Updated Weight of Evidence Approach to the Aquatic Hazard Assessment of Bisphenol A and the Derivation a New Predicted No Effect Concentration (Pnec) Using a Non-Parametric Methodology. *Sci. Total Environ.* **2011**, *409*, 676–685. [\[CrossRef\]](#)
- Sadeghfard, F.; Zalipour, Z.; Taghizadeh, M.; Taghizadeh, A.; Ghaedi, M. Chapter 2—Photodegradation Processes. In *Interface Science and Technology*; Ghaedi, M., Ed.; Photocatalysis: Fundamental Processes and Applications; Elsevier: Amsterdam, The Netherlands, 2021; Volume 32, pp. 55–124.
- Taghizadeh, A.; Taghizadeh, M.; Sabzehmeidani, M.M.; Sadeghfard, F.; Ghaedi, M. Chapter 1—Electronic Structure: From Basic Principles to Photocatalysis. In *Interface Science and Technology*; Ghaedi, M., Ed.; Photocatalysis: Fundamental Processes and Applications; Elsevier: Amsterdam, The Netherlands, 2021; Volume 32, pp. 1–53.
- Kumar, R.; Raizada, P.; Khan, A.A.P.; Nguyen, V.-H.; Van Le, Q.; Ghotekar, S.; Selvasembian, R.; Gandhi, V.; Singh, A.; Singh, P. Recent Progress in Emerging BiPO₄-Based Photocatalysts: Synthesis, Properties, Modification Strategies, and Photocatalytic Applications. *J. Mater. Sci. Technol.* **2022**, *108*, 208–225. [\[CrossRef\]](#)
- Li, L.; Gao, H.; Liu, G.; Wang, S.; Yi, Z.; Wu, X.; Yang, H. Synthesis of Carnation Flower-like Bi₂O₂CO₃ Photocatalyst and Its Promising Application for Photoreduction of Cr(VI). *Adv. Powder Technol.* **2022**, *33*, 103481. [\[CrossRef\]](#)
- Li, L.; Gao, H.; Yi, Z.; Wang, S.; Wu, X.; Li, R.; Yang, H. Comparative Investigation on Synthesis, Morphological Tailoring and Photocatalytic Activities of Bi₂O₂CO₃ Nanostructures. *Colloids Surf. A: Physicochem. Eng. Asp.* **2022**, *644*, 128758. [\[CrossRef\]](#)
- Li, L.; Sun, X.; Xian, T.; Gao, H.; Wang, S.; Yi, Z.; Wu, X.; Yang, H. Template-Free Synthesis of Bi₂O₂CO₃ Hierarchical Nanotubes Self-Assembled from Ordered Nanoplates for Promising Photocatalytic Applications. *Phys. Chem. Chem. Phys.* **2022**, *24*, 8279–8295. [\[CrossRef\]](#)
- Cheng, T.; Gao, H.; Liu, G.; Pu, Z.; Wang, S.; Yi, Z.; Wu, X.; Yang, H. Preparation of Core-Shell Heterojunction Photocatalysts by Coating CdS Nanoparticles onto Bi₄Ti₃O₁₂ Hierarchical Microspheres and Their Photocatalytic Removal of Organic Pollutants and Cr(VI) Ions. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *633*, 127918. [\[CrossRef\]](#)
- Guo, J.; Shi, L.; Zhao, J.; Wang, Y.; Tang, K.; Zhang, W.; Xie, C.; Yuan, X. Enhanced Visible-Light Photocatalytic Activity of Bi₂MoO₆ Nanoplates with Heterogeneous Bi₂MoO₆-X@Bi₂MoO₆ Core-Shell Structure. *Appl. Catal. B Environ.* **2018**, *224*, 692–704. [\[CrossRef\]](#)
- Huang, C.; Chen, L.; Li, H.; Mu, Y.; Yang, Z. Synthesis and Application of Bi₂WO₆ for the Photocatalytic Degradation of Two Typical Fluoroquinolones under Visible Light Irradiation. *RSC Adv.* **2019**, *9*, 27768–27779. [\[CrossRef\]](#) [\[PubMed\]](#)
- Shi, Q.; Zhang, Y.; Sun, D.; Zhang, S.; Tang, T.; Zhang, X.; Cao, S. Bi₂O₃-Sensitized TiO₂ Hollow Photocatalyst Drives the Efficient Removal of Tetracyclines under Visible Light. *Inorg. Chem.* **2020**, *59*, 18131–18140. [\[CrossRef\]](#)
- Guo, J.; Li, X.; Liang, J.; Yuan, X.; Jiang, L.; Yu, H.; Sun, H.; Zhu, Z.; Ye, S.; Tang, N.; et al. Fabrication and Regulation of Vacancy-Mediated Bismuth Oxyhalide towards Photocatalytic Application: Development Status and Tendency. *Coord. Chem. Rev.* **2021**, *443*, 214033. [\[CrossRef\]](#)
- Zhu, G.; Hojamberdiev, M.; Zhang, S.; Din, S.T.U.; Yang, W. Enhancing Visible-Light-Induced Photocatalytic Activity of BiOI Microspheres for NO Removal by Synchronous Coupling with Bi Metal and Graphene. *Appl. Surf. Sci.* **2019**, *467–468*, 968–978. [\[CrossRef\]](#)
- Xiao, X.; Jiang, J.; Zhang, L. Selective Oxidation of Benzyl Alcohol into Benzaldehyde over Semiconductors under Visible Light: The Case of Bi₁₂O₁₇Cl₂ Nanobelts. *Appl. Catal. B Environ.* **2013**, *142–143*, 487–493. [\[CrossRef\]](#)
- Wang, C.-Y.; Zhang, X.; Qiu, H.-B.; Wang, W.-K.; Huang, G.-X.; Jiang, J.; Yu, H.-Q. Photocatalytic Degradation of Bisphenol A by Oxygen-Rich and Highly Visible-Light Responsive Bi₁₂O₁₇Cl₂ Nanobelts. *Appl. Catal. B Environ.* **2017**, *200*, 659–665. [\[CrossRef\]](#)
- Liu, X.; Xing, Y.; Liu, Z.; Du, C. Enhanced Photocatalytic Activity of Bi₁₂O₁₇Cl₂ Preferentially Oriented Growth along [200] with Various Surfactants. *J. Mater. Sci.* **2018**, *53*, 14217–14230. [\[CrossRef\]](#)
- Fang, K.; Shi, L.; Wang, F.; Yao, L. The Synthesis of 3D Bi₁₂O₁₇Cl₂ Hierarchical Structure with Visible-Light Photocatalytic Activity. *Mater. Lett.* **2020**, *277*, 128352. [\[CrossRef\]](#)
- Zhang, Y.; Di, J.; Zhu, X.; Ji, M.; Chen, C.; Liu, Y.; Li, L.; Wei, T.; Li, H.; Xia, J. Chemical Bonding Interface in Bi₂Sn₂O₇/BiOBr S-Scheme Heterojunction Triggering Efficient N₂ Photofixation. *Appl. Catal. B Environ.* **2023**, *323*, 122148. [\[CrossRef\]](#)
- Guo, M.; He, H.; Cao, J.; Lin, H.; Chen, S. Novel I-Doped Bi₁₂O₁₇Cl₂ Photocatalysts with Enhanced Photocatalytic Activity for Contaminants Removal. *Mater. Res. Bull.* **2019**, *112*, 205–212. [\[CrossRef\]](#)
- Zhang, M.; Bi, C.; Lin, H.; Cao, J.; Chen, S. Construction of Novel Au/Bi₁₂O₁₇Cl₂ Composite with Intensive Visible Light Activity Enhancement for Contaminants Removal. *Mater. Lett.* **2017**, *191*, 132–135. [\[CrossRef\]](#)
- Ma, J.; Shi, L.; Hou, L.; Yao, L.; Lu, C.; Geng, Z. Fabrication of Graphene/Bi₁₂O₁₇Cl₂ as an Effective Visible-Light Photocatalyst. *Mater. Res. Bull.* **2020**, *122*, 110690. [\[CrossRef\]](#)

24. He, G.; Xing, C.; Xiao, X.; Hu, R.; Zuo, X.; Nan, J. Facile Synthesis of Flower-like Bi₁₂O₁₇Cl₂/β-Bi₂O₃ Composites with Enhanced Visible Light Photocatalytic Performance for the Degradation of 4-Tert-Butylphenol. *Appl. Catal. B Environ.* **2015**, *170*–171, 1–9. [CrossRef]
25. In Situ Assembly of BiOI@Bi₁₂O₁₇Cl₂ P-n Junction: Charge Induced Unique Front-Lateral Surfaces Coupling Heterostructure with High Exposure of BiOI {001} Active Facets for Robust and Nonselective Photocatalysis. *Appl. Catal. B Environ.* **2016**, *199*, 75–86. [CrossRef]
26. Guo, J.; Sun, H.; Yuan, X.; Jiang, L.; Wu, Z.; Yu, H.; Tang, N.; Yu, M.; Yan, M.; Liang, J. Photocatalytic Degradation of Persistent Organic Pollutants by Co-Cl Bond Reinforced CoAl-LDH/Bi₁₂O₁₇Cl₂ Photocatalyst: Mechanism and Application Prospect Evaluation. *Water Res.* **2022**, *219*, 118558. [CrossRef] [PubMed]
27. Liu, T.; Shi, L.; Wang, Z.; Liu, D. Preparation of Ag₂O/Bi₁₂O₁₇Cl₂ p-n Junction Photocatalyst and Its Photocatalytic Performance under Visible and Infrared Light. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *632*, 127811. [CrossRef]
28. Kim, K.-H.; Choi, Y.-H. Surface Oxidation of Cobalt Carbonate and Oxide Nanowires by Electrocatalytic Oxygen Evolution Reaction in Alkaline Solution. *Mater. Res. Express* **2022**, *9*, 034001. [CrossRef]
29. Wang, Y.; Zhu, C.; Zuo, G.; Guo, Y.; Xiao, W.; Dai, Y.; Kong, J.; Xu, X.; Zhou, Y.; Xie, A.; et al. 0D/2D Co₃O₄/TiO₂ Z-Scheme Heterojunction for Boosted Photocatalytic Degradation and Mechanism Investigation. *Appl. Catal. B Environ.* **2020**, *278*, 119298. [CrossRef]
30. Dai, X.; Cui, L.; Yao, L.; Shi, L. Facile Construction of Novel Co₃O₄/Bi₁₂O₁₇Cl₂ Heterojunction Composites with Enhanced Photocatalytic Performance. *J. Solid State Chem.* **2021**, *297*, 122066. [CrossRef]
31. Quan, Y.; Wang, B.; Liu, G.; Li, H.; Xia, J. Carbonized Polymer Dots Modified Ultrathin Bi₁₂O₁₇Cl₂ Nanosheets Z-Scheme Heterojunction for Robust CO₂ Photoreduction. *Chem. Eng. Sci.* **2021**, *232*, 116338. [CrossRef]
32. Wang, L.; Min, X.; Sui, X.; Chen, J.; Wang, Y. Facile Construction of Novel BiOBr/Bi₁₂O₁₇Cl₂ Heterojunction Composites with Enhanced Photocatalytic Performance. *J. Colloid Interface Sci.* **2020**, *560*, 21–33. [CrossRef]
33. Zhu, J.; Fan, J.; Cheng, T.; Cao, M.; Sun, Z.; Zhou, R.; Huang, L.; Wang, D.; Li, Y.; Wu, Y. Bilayer Nanosheets of Unusual Stoichiometric Bismuth Oxychloride for Potassium Ion Storage and CO₂ Reduction. *Nano Energy* **2020**, *75*, 104939. [CrossRef]
34. Xu, Y.; Ma, Y.; Ji, X.; Huang, S.; Xia, J.; Xie, M.; Yan, J.; Xu, H.; Li, H. Conjugated Conducting Polymers PANI Decorated Bi₁₂O₁₇Cl₂ Photocatalyst with Extended Light Response Range and Enhanced Photoactivity. *Appl. Surf. Sci.* **2019**, *464*, 552–561. [CrossRef]
35. Superior Visible Light Hydrogen Evolution of Janus Bilayer Junctions via Atomic-Level Charge Flow Steering | Nature Communications. Available online: <https://www.nature.com/articles/ncomms11480> (accessed on 15 October 2022).
36. Diallo, A.; Beyé, A.C.; Doyle, T.B.; Park, E.; Maaza, M. Green Synthesis of Co₃O₄ Nanoparticles via Aspalathus Linearis: Physical Properties. *Green Chem. Lett. Rev.* **2015**, *8*, 30–36. [CrossRef]
37. Wang, Y.; Wei, X.; Hu, X.; Zhou, W.; Zhao, Y. Effect of Formic Acid Treatment on the Structure and Catalytic Activity of Co₃O₄ for N₂O Decomposition. *Catal. Lett.* **2019**, *149*, 1026–1036. [CrossRef]
38. Lopes Matias, J.A.; Sabino da Silva, E.B.; Raimundo, R.A.; Ribeiro da Silva, D.; Oliveira, J.B.L.; Morales, M.A. (Bi₁₃Co₁₁)Co₂O₄₀-Co₃O₄ Composites: Synthesis, Structural and Magnetic Properties. *J. Alloy. Compd.* **2021**, *852*, 156991. [CrossRef]
39. Gu, Y.; Guo, B.; Yi, Z.; Wu, X.; Zhang, J.; Yang, H. Synthesis of a Self-Assembled Dual Morphologies Ag-NPs/SrMoO₄ Photocatalyst with LSPR Effect for the Degradation of Methylene Blue Dye. *ChemistrySelect* **2022**, *7*, e202201274. [CrossRef]
40. Urgunde, A.B.; Kamboj, V.; Kannattil, H.P.; Gupta, R. Layer-by-Layer Coating of Cobalt-Based Ink for Large-Scale Fabrication of OER Electrocatalyst. *Energy Technol.* **2019**, *7*, 1900603. [CrossRef]
41. Din, S.T.U.; Lee, H.; Yang, W. Z-Scheme Heterojunction of 3-Dimensional Hierarchical Bi₃O₄Cl/Bi₅O₇I for a Significant Enhancement in the Photocatalytic Degradation of Organic Pollutants (RhB and BPA). *Nanomaterials* **2022**, *12*, 767. [CrossRef]
42. Li, R.; Hu, B.; Yu, T.; Chen, H.; Wang, Y.; Song, S. Insights into Correlation among Surface-Structure-Activity of Cobalt-Derived Pre-Catalyst for Oxygen Evolution Reaction. *Adv. Sci.* **2020**, *7*, 1902830. [CrossRef]
43. Yu, L.; Lei, T.; Nan, B.; Kang, J.; Jiang, Y.; He, Y.; Liu, C.T. Mo Doped Porous Ni-Cu Alloy as Cathode for Hydrogen Evolution Reaction in Alkaline Solution. *RSC Adv.* **2015**, *5*, 82078–82086. [CrossRef]
44. Yang, Y.; Zhao, S.; Bi, F.; Chen, J.; Wang, Y.; Cui, L.; Xu, J.; Zhang, X. Highly Efficient Photothermal Catalysis of Toluene over Co₃O₄/TiO₂ p-n Heterojunction: The Crucial Roles of Interface Defects and Band Structure. *Appl. Catal. B Environ.* **2022**, *315*, 121550. [CrossRef]
45. Rational Design of Carbon-Doped Carbon Nitride/Bi₁₂O₁₇Cl₂ Composites: A Promising Candidate Photocatalyst for Boosting Visible-Light-Driven Photocatalytic Degradation of Tetracycline | ACS Sustainable Chemistry & Engineering. Available online: <https://pubs.acs.org/doi/full/10.1021/acssuschemeng.8b00782> (accessed on 2 November 2022).
46. Guerrero-Araque, D.; Acevedo-Peña, P.; Ramírez-Ortega, D.; Lartundo-Rojas, L.; Gómez, R. SnO₂-TiO₂ Structures and the Effect of CuO, CoO Metal Oxide on Photocatalytic Hydrogen Production. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 1531–1539. [CrossRef]
47. Patel, M.; Park, W.-H.; Ray, A.; Kim, J.; Lee, J.-H. Photoelectrocatalytic Sea Water Splitting Using Kirkendall Diffusion Grown Functional Co₃O₄ Film. *Sol. Energy Mater. Sol. Cells* **2017**, *171*, 267–274. [CrossRef]
48. Zhu, G.; Hojamberdiev, M.; Zhang, W.; Taj Ud Din, S.; Joong Kim, Y.; Lee, J.; Yang, W. Enhanced Photocatalytic Activity of Fe-Doped Bi₄O₅Br₂ Nanosheets Decorated with Au Nanoparticles for Pollutants Removal. *Appl. Surf. Sci.* **2020**, *526*, 146760. [CrossRef]
49. Xiong, J.; Cheng, G.; Li, G.; Qin, F.; Chen, R. Well-Crystallized Square-like 2D BiOCl Nanoplates: Mannitol-Assisted Hydrothermal Synthesis and Improved Visible-Light-Driven Photocatalytic Performance. *RSC Adv.* **2011**, *1*, 1542–1553. [CrossRef]

50. Kato, D.; Tomita, O.; Nelson, R.; Kirsanova, M.A.; Dronskowski, R.; Suzuki, H.; Zhong, C.; Tassel, C.; Ishida, K.; Matsuzaki, Y.; et al. Bi₁₂O₁₇Cl₂ with a Sextuple Bi—O Layer Composed of Rock-Salt and Fluorite Units and Its Structural Conversion through Fluorination to Enhance Photocatalytic Activity. Available online: <https://onlinelibrary.wiley.com/doi/10.1002/adfm.202204112> (accessed on 6 October 2022).
51. Chen, Y.; Liu, G.; Dong, L.; Liu, X.; Liu, M.; Wang, X.; Gao, C.; Wang, G.; Teng, Z.; Yang, W.; et al. A Microwave-Assisted Solvothermal Method to Synthesize BiOCl Microflowers with Oxygen Vacancies and Their Enhanced Photocatalytic Performance. *J. Alloy. Compd.* **2023**, *930*, 167331. [[CrossRef](#)]
52. Chang, F.; Wang, X.; Luo, J.; Wang, J.; Xie, Y.; Deng, B.; Hu, X. Ag/Bi₁₂O₁₇Cl₂ Composite: A Case Study of Visible-Light-Driven Plasmonic Photocatalyst. *Mol. Catal.* **2017**, *427*, 45–53. [[CrossRef](#)]
53. Chang, F.; Lei, B.; Zhang, X.; Xu, Q.; Chen, H.; Deng, B.; Hu, X. The Reinforced Photocatalytic Performance of Binary-Phased Composites Bi-Bi₁₂O₁₇Cl₂ Fabricated by a Facile Chemical Reduction Protocol. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *572*, 290–298. [[CrossRef](#)]
54. Meng, X.; Shi, L.; Yao, L.; Zhang, Y.; Cui, L. Fe (III) Clusters Modified Bi₁₂O₁₇Cl₂ Nanosheets Photocatalyst for Boosting Photocatalytic Performance through Interfacial Charge Transfer Effect. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *594*, 124658. [[CrossRef](#)]
55. Shi, L.; Si, W.; Wang, F.; Qi, W. Construction of 2D/2D Layered g-C₃N₄/Bi₁₂O₁₇Cl₂ Hybrid Material with Matched Energy Band Structure and Its Improved Photocatalytic Performance. *RSC Adv.* **2018**, *8*, 24500–24508. [[CrossRef](#)]
56. Ma, L.; Ai, X.; Chen, Y.; Liu, P.; Lin, C.; Lu, K.; Jiang, W.; Wu, J.; Song, X. Improved Photocatalytic Activity via N-Type ZnO/p-Type NiO Heterojunctions. *Nanomaterials* **2022**, *12*, 3665. [[CrossRef](#)] [[PubMed](#)]
57. Baranowska, D.; Kędzierski, T.; Aleksandrak, M.; Mijowska, E.; Zielińska, B. Influence of Hydrogenation on Morphology, Chemical Structure and Photocatalytic Efficiency of Graphitic Carbon Nitride. *Int. J. Mol. Sci.* **2021**, *22*, 13096. [[CrossRef](#)] [[PubMed](#)]
58. Zhang, L.; Zhang, J.; Xia, Y.; Xun, M.; Chen, H.; Liu, X.; Yin, X. Metal-Free Carbon Quantum Dots Implant Graphitic Carbon Nitride: Enhanced Photocatalytic Dye Wastewater Purification with Simultaneous Hydrogen Production. *Int. J. Mol. Sci.* **2020**, *21*, 1052. [[CrossRef](#)] [[PubMed](#)]
59. Gao, Y.; Liu, F.; Chi, X.; Tian, Y.; Zhu, Z.; Guan, R.; Song, J. A Mesoporous Nanofibrous BiVO₄-Ni/AgVO₃ Z-Scheme Heterojunction Photocatalyst with Enhanced Photocatalytic Reduction of Cr⁶⁺ and Degradation of RhB under Visible Light. *Appl. Surf. Sci.* **2022**, *603*, 154416. [[CrossRef](#)]
60. An, W.; Wang, H.; Yang, T.; Xu, J.; Wang, Y.; Liu, D.; Hu, J.; Cui, W.; Liang, Y. Enriched Photocatalysis-Fenton Synergistic Degradation of Organic Pollutants and Coking Wastewater via Surface Oxygen Vacancies over Fe-BiOBr Composites. *Chem. Eng. J.* **2023**, *451*, 138653. [[CrossRef](#)]
61. de Sousa Filho, I.A.; Arana, L.R.; Doungmo, G.; Grisolia, C.K.; Terrashke, H.; Weber, I.T. SrSnO₃/g-C₃N₄ and Sunlight: Photocatalytic Activity and Toxicity of Degradation Byproducts. *J. Environ. Chem. Eng.* **2020**, *8*, 103633. [[CrossRef](#)]