Metal–Organic-Framework-Derived Ball-Flower-like Porous Co₃O₄/Fe₂O₃ Heterostructure with Enhanced Visible-Light-Driven Photocatalytic Activity

Qi Cao 1,*,†, Qingqing Li 2,†, Zhichao Pi 3, Jing Zhang 1, Li-Wei Sun 1, Junzhou Xu 1, Yunyi Cao 4, Junye Cheng 5,* and Ye Bian 1,*

Abstract: A porous ball-flower-like Co₃O₄/Fe₂O₃ heterostructural photocatalyst was synthesized via a facile metal–organic-framework-templated method, and showed an excellent degradation performance in the model molecule rhodamine B under visible light irradiation. This enhanced photocatalytic activity can be attributed to abundant photo-generated holes and hydroxyl radicals, and the combined effects involving a porous structure, strong visible-light absorption, and improved interfacial charge separation. It is notable that the ecotoxicity of the treated reaction solution was also evaluated, confirming that an as-synthesized Co₃O₄/Fe₂O₃ catalyst could afford the sunlight-driven long-term recyclable degradation of dye-contaminated wastewater into non-toxic and colorless wastewater.

Keywords: MOF derivative; cobalt oxide; iron oxide; hierarchical heterostructure; photocatalysis

1. Introduction

Various pollutants in water environments can directly cause serious harm to the lives and health of human beings, animals and plants. Organic dyes, for example rhodamine B (RhB), methylene blue and methyl orange, as one of the most common industrial pollution sources at present, have attracted tremendous attention because of their geno- and ecotoxicity [1–6]. Therefore, the development of water treatment technologies regarding dye degradation has become a top priority. Among various methods, photocatalysis is recognized as one green and efficient alternative for organic pollutant degradation, where its key issue lies in the facile preparation of highly active and stable photocatalysts [7–10].

As one of the most promising multi-functional materials, metal–organic frameworks (MOFs) are often considered to be novel photocatalysts due to their abundant and editable active sites and large surface area. However, some of their defects, such as poor light absorption and metal ion leaching due to an unstable structure, may seriously limit their practical applications [11–13]. In order to solve these problems, in this study, a flower-like cobalt 2,5-thiophenedicarboxylic coordination polymer (Co-TDC) was used as a template to synthesize a novel Co₃O₄/Fe₂O₃ heterostructural photocatalyst with improved light harvesting and photocatalytic performance. The facile preparation, structural versatility,
and superior dye degradation performance of this Co$_3$O$_4$/Fe$_2$O$_3$ heterostructure provides new inspirations for the development of higher-performance photocatalysts towards water environment remediation.

2. Materials and Methods

2.1. Synthesis of Ball-Flower-like Porous Co$_3$O$_4$/Fe$_2$O$_3$ Heterostructure

Briefly, 0.1 g of Co-TDC (Sinopharm Group Co., Ltd., Shanghai, China) and 0.0482 g of FeCl$_3$·6H$_2$O (Sinopharm Group Co., Ltd., Shanghai, China) were added into 5 mL of deionized water. After 30 min of ultrasonic treatment, the mixture was dried at 60 °C for 12 h. Afterwards, the obtained powder was calcined at 550 °C for 2 h. The final Co$_3$O$_4$/Fe$_2$O$_3$ product is denoted as CF in this work for convenience.

2.2. Characterization

The chemical composition and phase structure of samples were analyzed by X-ray powder diffraction (XRD, SmartLab® by Rigaku, Tokyo, Japan). The morphology was recorded using field-emission scanning electron microscopy (SEM, JSM-7800F by JEOL, Japan) and transmission electron microscopy (TEM, JEM-2100F by JEOL, Japan). X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi by Thermo Fisher Scientific, Waltham, MA, USA) was performed to investigate element distribution and valence states. The magnetism and optical properties of samples were studied using vibrating sample magnetometer (VSM, LakeShore7404 by Quantum Design, San Diego, CA, USA) and diffuse-reflection spectroscopy (DRS, Cary-5000 by Agilent, Santa Clara, CA, USA).

2.3. Photocatalysis Measurements

The adsorption and photocatalysis processes of as-prepared catalysts were evaluated by the degradation of RhB in an aqueous solution under visible light irradiation at room temperature (ca. 25 °C). A 500 W xenon lamp with a cut-off filter (λ > 420 nm) was used to generate visible light. Amounts of 0.1 g of catalyst powder and 50 mL RhB aqueous solution (initial solution pH ≈ 4) were added to a 100 mL quartz tube and continuously stirred during the degradation experiment. Before irradiation, the reaction solution was magnetically stirred in the dark for 30 min to reach complete adsorption/desorption equilibrium. During the photocatalytic experiment, 5 mL reaction solution was extracted every 10 min, and the concentration of residual RhB was determined by measuring its absorbance at 590 nm on a UV-visible spectrometer (UV-3600i Plus by Shimadzu, Kyoto, Japan). The 5 mL solution was added back into the reaction solution after measurement.

3. Results and Discussion

The chemical composition and crystal structure of CF were analyzed by XRD. As shown in Figure 1a, the characteristic diffraction peaks located at 19.1°, 31.2°, 36.8°, 44.7°, 59.1°, and 65.1° could be attributed to Co$_3$O$_4$ (PDF#42-1467), while the other peaks at 35.6° and 62.9° could be assigned to Fe$_2$O$_3$ (PDF#39-1346), indicating that the as-prepared sample was composed of Co$_3$O$_4$ and Fe$_2$O$_3$. The chemical states of the sample surface were further analyzed by XPS. Considering the sample preparation method, only cobalt element was studied emphatically. In Co 2p spectra (Figure 1b), the asymmetric peaks at around 780.7 eV and 796.8 eV, and shake-up type satellite peaks at 785.8 eV and 802.3 eV of Co-TDC, could be well-indexed to Co$^{2+}$, implying that cobalt in Co-TDC was only in the form of Co (II). On the other hand, for CF, two new peaks could be identified at around 779.4 eV and 794.3 eV, which were both ascribed to Co$^{3+}$ [14–18]. This revealed that Co$^{2+}$ in Co-TDC was partially oxidized to Co$^{3+}$ during calcination, and thus Co$_3$O$_4$ was obtained as a result. Meanwhile, Fe 2p spectrum of CF was also recorded, as shown in Figure S1. It was revealed that Fe$^{3+}$ ions were still dominant, which corresponded to the Fe$_2$O$_3$ phase. However, the minor peak at around 732.2 eV suggests that a little Fe$^{3+}$ was reduced to Fe$^{2+}$ along with the oxidation of Co$^{2+}$ to Co$^{3+}$ [19–23].
When the catalyst was not present in the solution, RhB could hardly undergo self-degradation.

Typically, the contribution of RhB removal by adsorption is lower than 20%, which is in agreement with the XRD result. This could be explained by the following aspects: (i) The highly porous structure of CF provided abundant active sites, as revealed in Figure 2b,c [24–26]; (ii) The p-n heterojunction that formed between Fe2O3 and Co3O4 could promote the separation of photo-generated electron and hole pairs [27–30]. The promoted charge separation, and thus the inhibited charge recombination, was witnessed by the significantly decreased photoluminescence (PL) intensity of CF composites compared to pristine Fe2O3 particles, as displayed in Figure S5 of the Supplementary Materials [31–38]. The variation in the RhB degradation efficiency of CF in different pH conditions is presented in Figure 3b, suggesting that the catalyst could maintain a superior photocatalytic degradation activity in the pH range of 4–10, despite the fact that the degradation rate decreased to a certain extent in a strong acid environment (pH ≤ 2). This may be due to the dissolving of oxides by strong acid, resulting in a loss of active material in the CF catalyst for the degradation of RhB. However, considering that the actual surface water or groundwater is mostly weakly acidic or weakly alkaline, the CF catalyst is still applicable to the oxidative degradation of organic pollutants in natural water bodies.
t stirred in the sed for five cycles, which catalysis systems, CF demonstrated as revealed in Figure 2b,c

- solution to remove the residual organics on the surface. After the reaction, the catalyst in the solution could be easily and quickly separated due to its magnetism, as revealed in Figure 3c. Then, the recycled CF catalyst was rinsed with ethanol solution to remove the residual organics on the surface.

- degradation of organic pollutants in natural water bodies.

The service life of a catalyst is an important technical indicator for evaluating its potential for practical usage. After the reaction, the catalyst in the solution could be easily and quickly separated due to its magnetism, as revealed in Figure 3c. Then, the recycled CF catalyst was rinsed with ethanol solution to remove the residual organics on the surface.
Afterwards, it could be reused for RhB removal under the same conditions, as presented in Figure 3d. An excellent degradation efficiency of >86% was achieved after the CF catalyst was recycled and reused for five cycles, which maintained about 97% efficiency of the initial cycle (i.e., ~89.1%), confirming the recyclability of CF for long-term dye degradation in practical wastewater treatment.

Figure 4a displays the optical absorption of samples. It is observed that the absorption of Co-TDC is far lower than CF in the visible-light band. The CF catalyst maintains a superior absorption in the range of 550–750 nm, suggesting its capability for a visible-light-driven photocatalytic reaction. In addition, the threshold wavelengths of Co-TDC and CF are determined to be 619 nm and 685 nm, respectively. The corresponding bandgap values of the Co-TDC and CF samples; (Figure 4. (a) Tauc plots, i.e., plots of $(a\nu)^{0.5}$ vs. photon energy ($\nu$), derived from diffuse-reflectance spectra of the Co-TDC and CF samples; (b) Band alignment and photocatalytic mechanism of the CF heterojunction under visible light illumination.)

Figure 4b depicts the photocatalytic mechanism of CF under visible light illumination. The photo-generated electrons in CB cannot reduce O$_2$ to $\cdot$O$_2^-$ because the $E_{CB}$ of Co$_3$O$_4$ and Fe$_2$O$_3$ are more positive than $E$(O$_2^-$/·O$_2^-$) (−0.33 V vs. NHE), while the photo-generated holes are capable of oxidizing OH$^-$ to hydroxyl radicals (·OH) as the $E_{VB}$ of Co$_3$O$_4$ and Fe$_2$O$_3$ are more negative than $E$(·OH/OH$^-$) (1.97 V vs. NHE) [42–44]. In order to further verify this perception, quenching experiments were carried out using tert-butyl alcohol (TBA), ammonium oxalate (AO) and L-ascorbic acid (L-AA) to quench the ·OH, photo-generated holes and $\cdot$O$_2^-$, respectively [45,46]. It can be observed from Figure S6 that the degradation efficiency of RhB clearly decreases in presence of TBA and AO. Therefore, it can be deduced that the main reactive species involved in the photocatalytic reaction are photo-generated holes and hydroxyl radicals (·OH), which consequently degrade RhB molecules to colorless small molecules.
In order to evaluate the ecological toxicity of the RhB solution before and after treatment, *Chlorella vulgaris* (FACHB-8) was used as the model aquatic organism being tested, and the toxicity of the residual RhB after the photocatalytic reaction was assessed according to its growth inhibition rate to *C. vulgaris*. A detailed experimental method for algae density measurement is presented in the Supplementary Materials, which could be referred to as the standard GBT 21805-2008 [47]. As exhibited in Figure 5, the growth of *C. vulgaris* was significantly suppressed in the original RhB solution, and the inhibition rate doubled as time increases. In contrast, *C. vulgaris* could grow normally in the solution after reaction, and the remaining intermediate and final products showed a neglectable influence within 24 h. Even when the incubation time was extended to 96 h, the growth inhibition rate was still about 1%, which is only 15.6% of the original RhB solution. This demonstrates that the CF catalyst can effectively degrade and mineralize RhB molecules to nearly non-toxic products.

![Figure 5. Time-dependent growth inhibition rates of *C. vulgaris* in different solutions.](image)

### 4. Conclusions

In summary, a highly active and stable Co3O4/Fe2O3 heterostructural photocatalyst was prepared by a facile MOF-templated method, with its structure, morphology and optical properties verified by XRD, XPS, SEM and UV-visible DRS methodology. The results indicate that the CF catalyst showed a strong visible-light absorption and high photocatalytic activity towards RhB degradation. By calculating the CB and VB position, it could be inferred that hydroxyl radicals and photo-generated holes were the dominant active species in the reaction. Furthermore, the 96 h growth inhibition rate of *C. vulgaris* by the treated RhB solution was 84.4% lower than the original solution, confirming the potential of the CF photocatalyst for the sunlight-driven long-term degradation of dye molecules into non-toxic and colorless ones.

**Supplementary Materials:** The followings are available online at [https://www.mdpi.com/article/10.3390/nano12060904/s1](https://www.mdpi.com/article/10.3390/nano12060904/s1), Figure S1: Fe 2p XPS spectrum of as-synthesized CF catalyst, Figure S2: SEM images of pure Co-TDC at different magnifications, Figure S3: SEM images of pure Fe2O3 at different magnifications, Figure S4: Elemental mapping profiles of as-synthesized CF catalyst: (a) O Kα1, (b) Co Kα1, (c) Fe Kα1, Figure S5: PL spectra of CF catalyst comparing with pure Fe2O3 at excitation wavelength of 355 nm, Figure S6: Photocatalytic degradation efficiency of RhB with and without quenching agent, Figure S7: Photocatalytic degradation efficiency of RhB by as-synthesized CF catalyst comparing with commercial Degussa/Evonik P25-TiO2 catalyst, Figure S8: Photocatalytic degradation efficiency of RhB by CF over a prolonged period of time; Experimental biota for toxicity test and algae density measurement.

**Author Contributions:** Conceptualization, Q.C. and Y.B.; Data curation, Q.L., J.Z., L.-W.S. and J.X.; Formal analysis, Q.L. and J.Z.; Funding acquisition, Q.C.; Investigation, Q.L., J.Z. and J.X.; Methodology, Q.C., Q.L., Z.P., J.Z. and L.-W.S.; Project administration, Q.C. and Y.C.; Resources, Q.C., Z.P., L.-W.S. and Y.C.; Supervision, Q.C., L.-W.S., J.C. and Y.B.; Validation, L.-W.S.; Writing—original
draft, Q.L.; Writing—review and editing, Q.C., L.-W.S. and Y.B. 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 (grant number: 52101213) and the Science and Technology Department of Jiangsu Province of China (grant number: BK20210261). The APC was funded by Southeast University of China.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Acknowledgments:** Qi Cao would like to thank the support from the “Zhi-Shan” Scholars Programme of Southeast University of China.

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

### References

1. Han, J.; Yang, D.; Hall, D.R.; Liu, J.; Sun, J.; Gu, W.; Tang, S.; Alharbi, H.A.; Jones, P.D.; Krause, H.M.; et al. Toxicokinetics of Brominated Azo Dyes in the Early Life Stages of Zebrafish (*Danio rerio*) Is Prone to Aromatic Substituent Changes. *Environ. Sci. Technol.* 2020, 54, 4421–4431. [CrossRef] [PubMed]

2. Chen, M.; Jia, Y.; Li, H.; Wu, Z.; Huang, T.; Zhang, H. Enhanced pyrolysis of the pyroelectric BiFeO$_3$/g-C$_3$N$_4$ heterostructure for dye decomposition driven by cold-hot temperature alternation. *J. Adv. Ceram.* 2021, 10, 338–346. [CrossRef]

3. Cao, Q.; Yuan, K.; Liu, Q.; Liang, C.; Wang, M.; Che, R. Gold nanoparticles decorated Ag(Cl,Br) micro-necklaces for efficient and stable SERS detection and visible-light photocatalytic degradation of Sudan, I. *Appl. Catal. B Environ.* 2017, 201, 607–616. [CrossRef]

4. Cao, Q.; Che, R. Tailoring Au–Ag–S composite microstructures in one-pot for both SERS detection and photocatalytic degradation of organic dyes. *Chem. Commun.* 2014, 50, 4931–4933. [CrossRef]

5. Cao, Q.; Che, R.; Chen, N. Scalable synthesis of Cu$_2$S double-superlattice nanoparticle systems with enhanced UV/visible-light-driven photocatalytic activity. *Appl. Catal. B Environ.* 2015, 162, 187–195. [CrossRef]

6. Dong, J.; Zhang, X.; Dong, X.; Ng, K.H.; Xie, Z.; Chen, I.-W.P.; Ng, Y.H.; Huang, J.; Lai, Y. Coupled porosity and heterojunction engineering: MOF-derived porous Co$_3$O$_4$ embedded on TiO$_2$ nanotube arrays for water remediation. *Chemosphere* 2021, 274, 129799. [CrossRef] [PubMed]

7. Lee, K.M.; Lai, C.W.; Ngai, K.S.; Juan, J.C. Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Res.* 2016, 88, 428–448. [CrossRef]

8. Sadeghzadeh-Attar, A. Photocatalytic degradation evaluation of N–Fe codoped aligned TiO$_2$ nanorods based on the effect of annealing temperature. *J. Adv. Ceram.* 2020, 9, 107–122. [CrossRef]

9. Cao, Q.; Yuan, K.; Liu, Q.; Liang, C.; Wang, X.; Cheng, Y.-F.; Li, Q.; Wang, M.; Che, R. Porous Au–Ag Alloy Particles Inlaid AgCl Membranes As Versatile Plasmonic Catalytic Interfaces with Simultaneous, in Situ SERS Monitoring. *ACS Appl. Mater. Interfaces* 2015, 7, 18491–18500. [CrossRef]

10. Cao, Q.; Che, R. Tailoring Au–Ag–S composite microstructures in one-pot for both SERS detection and photocatalytic degradation of plasticizers DEHA and DEHP. *ACS Appl. Mater. Interfaces* 2014, 6, 7020–7027. [CrossRef]

11. Cheng, J.; Liu, K.; Li, X.; Huang, L.; Liang, J.; Zheng, G.; Han, G. Nickel-metal-organic framework nanobelt based composite membranes for efficient Sr$^{2+}$ removal from aqueous solution. *Environ. Sci. Ecotechnol.* 2020, 3, 100035. [CrossRef]

12. Cheng, J.; Liang, J.; Dong, L.; Chai, J.; Zhao, N.; Ullah, S.; Wang, H.; Zhang, D.; Imtiaz, S.; Shan, G.; et al. Self-assembly of 2D-metal–organic framework/graphene oxide membranes as highly efficient adsorbents for the removal of Cs$^+$ from aqueous solutions. *RSC Adv.* 2018, 8, 40813–40822. [CrossRef]

13. Dong, J.; Zhang, X.; Dong, X.; Ng, K.H.; Xie, Z.; Chen, I.-W.P.; Ng, Y.H.; Huang, J.; Lai, Y. Coupled porosity and heterojunction engineering: MOF-derived porous Co$_3$O$_4$ embedded on TiO$_2$ nanotube arrays for water remediation. *Chemosphere* 2021, 274, 129799. [CrossRef] [PubMed]

14. Cao, Q.; Hao, S.; Wu, Y.; Pei, K.; You, W.; Che, R. Interfacial charge redistribution in interconnected network of Ni$_2$P–Co$_2$P boosting electrocatalytic hydrogen evolution in both acidic and alkaline conditions. *Chem. Eng. J.* 2021, 424, 130444. [CrossRef]

15. Li, R.; Fu, Q.; Zou, X.; Zheng, Z.; Luo, W.; Yan, L. Mn–Co–Ni–O thin films prepared by sputtering with alloy target. *J. Adv. Ceram.* 2020, 9, 64–71. [CrossRef]

16. Zhang, L.; Liu, Y.; Tan, T.T.; Liu, Y.; Zheng, J.; Yang, Y.; Hou, X.; Feng, L.; Suo, G.; Ye, X.; et al. Thermoelectric performance enhancement by manipulation of Sr/Ti doping in two sublayers of Ca$_3$Co$_4$O$_9$. *J. Adv. Ceram.* 2020, 9, 769–781. [CrossRef]

17. Li, H.; Zhang, H.; Thayil, S.; Fang, A.; Sang, X.; Ma, X. Enhanced aging and thermal shock performance of Mn$_{1.96-\alpha}$Co$_{0.21}$Ni$_{0.84}$Sr$_3$O$_4$ NTC ceramics. *J. Adv. Ceram.* 2021, 10, 258–270. [CrossRef]

18. Liu, L.; Huang, X.; Wei, Z.; Duan, X.; Zhong, B.; Xia, L.; Zhang, T.; Wang, H.; Jia, D.; Zhou, Y.; et al. Solvents adjusted pure phase CoCO$_3$ as anodes for high cycle stability. *J. Adv. Ceram.* 2021, 10, 509–519. [CrossRef]
19. Song, B.; Yuan, K.; Wei, Y.; Chen, D.; Meng, F.; Cao, Q.; Song, M.; Liu, H. In-furnace control of arsenic vapor emissions using Fe\textsubscript{2}O\textsubscript{3} microspheres with good sintering resistance. *Environ. Sci. Technol.* 2021, 55, 8613–8621. [CrossRef]

20. Ye, F.; Dai, H.; Peng, K.; Li, T.; Chen, J.; Chen, Z.; Li, N. Effect of Mn doping on the microstructure and magnetic properties of CuFe\textsubscript{2}O\textsubscript{4} ceramics. *J. Adv. Ceram.* 2020, 9, 444–453. [CrossRef]

21. Lassoued, A.; Lassoued, M.S.; Dkhil, B.; Ammar, S.; Gadri, A. Synthesis, photoluminescence and magnetic properties of iron oxalate nanodendrite array with enhanced photoelectrochemical properties. *Nano Energy* 2017, 41, 543–551. [CrossRef]

22. Chen, C.; Yu, J.; Yuan, K.; Zhong, M.; Delaunay, J.-J. Facile and Large-Area Preparation of Porous Ag\textsubscript{3}PO\textsubscript{4} Nanosheets for Efficient Photoelectrochemical Oxidation of Neutral Water Solutions. *J. Mater. Chem. A* 2017, 5, 14697–14706. [CrossRef]

23. Zhang, D.; Liu, T.; Cheng, J.; Cao, Q.; Zheng, G.; Liang, S.; Wang, H.; Cao, M.S. Lightweight and high-performance microwave absorber based on 2D WS\textsubscript{2}–RGO heterostructures. *Nano Micro Lett.* 2019, 11, 38. [CrossRef] [PubMed]

24. Cao, C.; Yu, J.; Cao, Q.; Zheng, G.; Liang, S.; Wang, H.; Cao, M.S. Oxygen-deficient WO\textsubscript{3}–TiO\textsubscript{2} core-shell nanosheets for efficient photoelectrochemical oxidation of neutral water solutions. *J. Mater. Chem. A* 2017, 5, 20051–20055. [CrossRef]

25. Yu, K.; Cao, Q.; Li, X.; Chen, H.-Y.; Deng, Y.; Wang, Y.-Y.; Liao, W.; Li, H.-L.; Zhang, D.W. Synthesis of WO\textsubscript{3}–RGO heterostructures. *Nano Micro Lett.* 2021, 10, 20051–20055. [CrossRef]

26. Zhang, D.; Liu, T.; Cheng, J.; Cao, Q.; Zheng, G.; Liang, S.; Wang, H.; Cao, M.S. Lightweight and high-performance microwave absorber based on 2D WS\textsubscript{2}–RGO heterostructures. *Nano Micro Lett.* 2019, 11, 38. [CrossRef] [PubMed]

27. Lassoued, A.; Lassoued, M.S.; Dkhil, B.; Ammar, S.; Gadri, A. Synthesis, photoluminescence and magnetic properties of iron oxalate (α-Fe\textsubscript{2}O\textsubscript{3}) nanoparticles through precipitation or hydrothermal methods. *Phys. E Low Dimens. Syst. Nanostructures* 2018, 101, 212–219. [CrossRef]

28. Zhang, D.; Li, T.; Cheng, J.; Cao, Q.; Zheng, G.; Liang, S.; Wang, H.; Cao, M.S. Lightweight and high-performance microwave absorber based on 2D WS\textsubscript{2}–RGO heterostructures. *Nano Micro Lett.* 2019, 11, 38. [CrossRef] [PubMed]

29. Cao, C.; Yu, J.; Cao, Q.; Delaunay, J.-J.; Che, R. Unusual effects of vacuum annealing on large-area Ag\textsubscript{3}PO\textsubscript{4} microcrystalline film photoanode boosting cocatalyst- and scavenger-free water splitting. *J. Mater. Chem. A* 2021, 7, 929–939. [CrossRef]

30. Cao, Q.; Cheng, Y.-F.; Bi, H.; Zhao, X.; Yuan, K.; Liu, Q.; Li, Q.; Wang, M.; Che, R. Crystal defect-mediated band-gap engineering: A new strategy for tuning the optical properties of Ag\textsubscript{2}Se quantum dots toward enhanced hydrogen evolution performance. *J. Mater. Chem. A* 2015, 3, 20051–20055. [CrossRef]

31. Liu, N.; Mei, L.; Bin, J.; Zhang, Z.; Peng, Z. Effect of anionic group [SiO\textsubscript{4}]\textsuperscript{4–}/[PO\textsubscript{4}]\textsuperscript{3–} on the luminescence properties of Dy\textsuperscript{3+}-doped tungstate structural compounds. *J. Adv. Ceram.* 2021, 10, 843–851. [CrossRef]

32. Shao, Y.; Feng, K.; Guo, J.; Zhang, R.; He, S.; Wei, X.; Lin, Y.; Ye, Z.; Chen, K. Electronic structure and enhanced photoelectrocatalytic performance of Ru\textsubscript{2}Zn\textsubscript{1-x}/O/Ti electrodes. *J. Adv. Ceram.* 2021, 10, 1025–1041. [CrossRef]

33. Zhong, M.; Feng, Q.; Yuan, C.; Liu, X.; Zhu, B.; Meng, L.; Zhou, C.; Xu, J.; Wang, J.; Rao, G. Photocurrent density and electrical properties of Bi\textsubscript{0.5}Na\textsubscript{0.5}TiO\textsubscript{3}–Ba\textsubscript{3}Na\textsubscript{0.5}Nb\textsubscript{2}O\textsubscript{5} ceramics. *J. Adv. Ceram.* 2021, 10, 1119–1128. [CrossRef]

34. Siahroudi, M.G.; Daryakenari, A.A.; Molamahaleh, Y.B.; Cao, Q.; Daryakenari, M.A.; Delaunay, J.-J.; Siavoshi, H.; Molaei, F. Ethylene glycol assisted solvothermal synthesis of NGr–Co\textsubscript{3}O\textsubscript{4} nanostructures for ethanol electrooxidation. *Int. J. Hydrogen Energy* 2020, 45, 30357–30366. [CrossRef]
43. Yu, J.; Wang, J.; Long, X.; Chen, L.; Cao, Q.; Wang, J.; Qiu, C.; Lim, J.; Yang, S. Formation of FeOOH Nanosheets Induces Substitutional Doping of CeO$_{2-x}$ with High-Valence Ni for Efficient Water Oxidation. *Adv. Energy Mater.* 2021, 11, 2002731. [CrossRef]

44. Li, Z.; Dong, T.; Zhang, Y.; Wu, L.; Li, J.; Wang, X.; Fu, X. Studies on In(OH)$_y$S$_z$ solid solutions: Syntheses, characterizations, electronic structure, and visible-light-driven photocatalytic activities. *J. Phys. Chem. C* 2007, 111, 4727–4733. [CrossRef]

45. Zhao, Y.; Song, M.; Cao, Q.; Sun, P.; Chen, Y.; Meng, F. The superoxide radicals’ production via persulfate activated with CuFe$_2$O$_4$@Biochar composites to promote the redox pairs cycling for efficient degradation of o-nitrochlorobenzene in soil. *J. Hazard. Mater.* 2020, 400, 122887. [CrossRef] [PubMed]

46. Meng, F.; Song, M.; Song, B.; Wei, Y.; Cao, Q.; Cao, Y. Enhanced degradation of Rhodamine B via α-Fe$_2$O$_3$ microspheres induced persulfate to generate reactive oxidizing species. *Chemosphere* 2020, 243, 125322. [CrossRef]

47. Pei, Z.-T.; Xu, R.-R.; Liu, H.-Y.; Wang, W.-Q.; Zhang, M.; Zhang, L.-L.; Zhang, J.; Wang, W.-Q.; Yu, R.; Sun, L.-W. Development and application of a novel whole sediment toxicity test using immobilized sediment and *Chlorella vulgaris*. *Ecotoxicol. Environ. Saf.* 2020, 189, 109979. [CrossRef]