

## Article

# Photocatalytic Degradation of Methyl Orange Dyes Using Green Synthesized $\text{MoS}_2/\text{Co}_3\text{O}_4$ Nanohybrids

Tsung-Mo Tien <sup>\*</sup>, Chao-Hsiang Chen, Chen-Tang Huang and Edward L. Chen <sup>\*</sup>

Coastal Water and Environment Center, College of Hydrosphere Science, National Kaohsiung University of Science and Technology, Kaohsiung City 81157, Taiwan

<sup>\*</sup> Correspondence: tmtien@nku.edu.tw (T.-M.T.); edwardljchen@gmail.com (E.L.C.)

**Abstract:** In this work, a new binary  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids was successfully fabricated and the chemical structures, morphologies, electrochemical and optical characterizations were carried out. In addition, heterojunction nanoparticles present in S-scheme structures act as electron traps and promote light absorption capacity for the degradation of Methyl orange (MO) with visible-light activity.  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids suggested excellent photocatalytic performance compared to bare  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$ , where 95.6% of MO was degraded within 170 min, respectively. The results also showed excellent stability and recyclability over five consecutive cycles, without noticeable changes in the nanocomposite structure. The boosted photocatalytic degradation and redox activities of  $\text{MoS}_2/\text{Co}_3\text{O}_4$  can be attributed to the created S-scheme heterostructure to facilitate the separation of and to delay recombination of photoinduced charge carriers. We believe that this strategy of exploiting nanohybrid photocatalysts has great potential in the field of environmental catalysis and diverse applications.

**Keywords:** photodegradation; nanohybrids;  $\text{MoS}_2/\text{Co}_3\text{O}_4$ ; methyl orange (MO); environment remediation



**Citation:** Tien, T.-M.; Chen, C.-H.; Huang, C.-T.; Chen, E.L. Photocatalytic Degradation of Methyl Orange Dyes Using Green Synthesized  $\text{MoS}_2/\text{Co}_3\text{O}_4$  Nanohybrids. *Catalysts* **2022**, *12*, 1474. <https://doi.org/10.3390/catal12111474>

Academic Editors: Jorge Bedia and Carolina Belver

Received: 25 October 2022

Accepted: 15 November 2022

Published: 18 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

Environmental contamination and energy demand represent a worldwide concern. To overcome these problems, nanomaterials are an alternative to address environmental aspects of wastewater treatment contamination and energy generation by organic compounds [1–3]. The immoderate emptying of waste toxic organic dyes, such as methyl orange (MO), into soils and water pools counteracts environmental protection and safety. Consequently, it is necessary to treat the dyeing wastewater with practical and harmless methods [4,5]. It is well-known that solar light is a favorite choice of clean energy for decomposing pollutants due to its great redox activity and energy density only makes  $\text{H}_2\text{O}$  [6]. The utilization of visible light is a rather effective process as it adopts abundantly available solar light. To date, the photocatalytic system, as a green and direct reach, has been found to be effective in environmental treatment, especially in the removal of organic pollutants. Photocatalytic degradation with visible light activity is employed to excite the semiconductor material creating electron ( $e^-$ ) and hole ( $h^+$ ) pairs for the degradation of organic compounds. To date, different semiconductors have been adopted as photocatalysts in environmental applications [7]. Photocatalytic removal pollutants have attracted sufficient exploration attention and are considered a hopeful system to solve the energy crisis and environmental issues. However, the low absorption of sunlight, high electron–hole recombination, and photo-decay effects are still limiting to the acquisition of an efficient photocatalyst with visible light activity. [8]. Accordingly, it is necessary to fabricate and acquire nano-heterojunction photocatalysts with great solar-to-redox reaction conversion performance.

Recently, heterostructured photocatalysts have attracted researchers' attention due to superior features such as improved electron–hole pair separation performance [9]. The

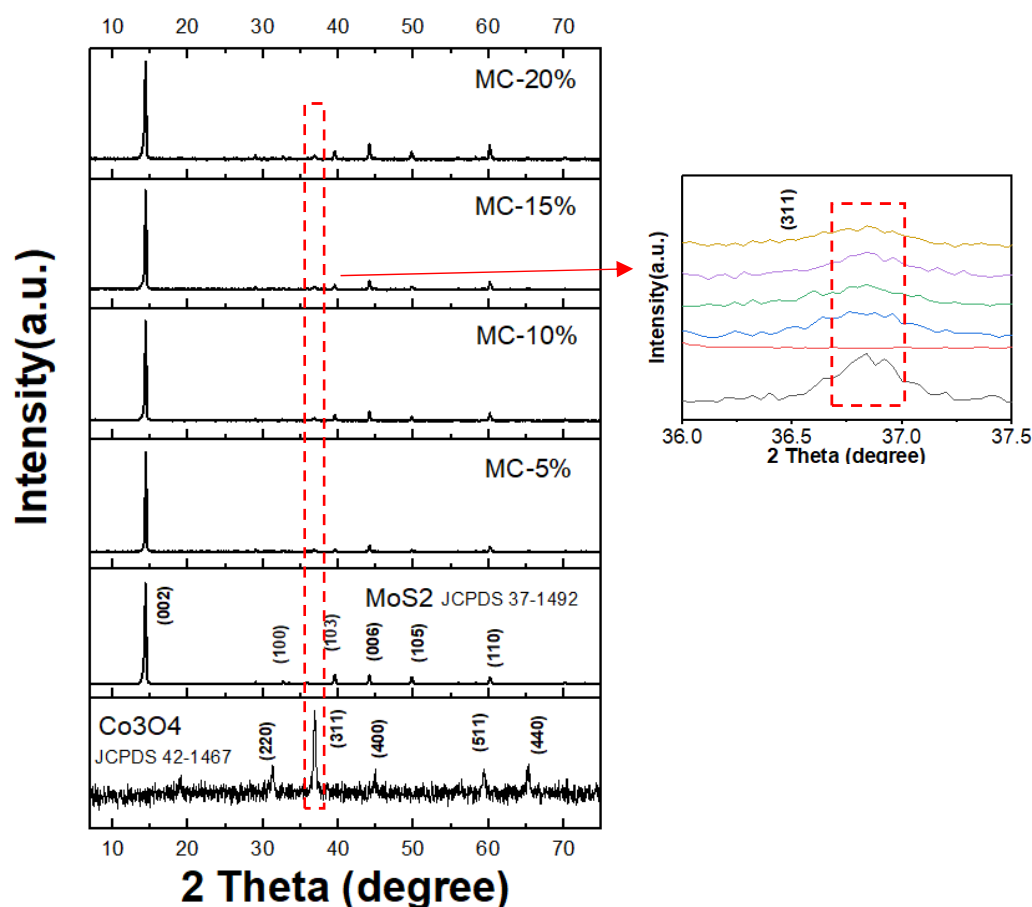
transition-metal dichalcogenides (TMDs) have obtained large attention owing to a series of interesting excellent properties [10]. Between these materials, molybdenum disulfide ( $\text{MoS}_2$ ) has great charge carrier density, high conductivity, and a controllable energy band gap, which is valuable and effective for optimizing environmental remediation and improving photocatalytic water splitting capability with visible light irradiation [11]. As a kind of normal TMDs,  $\text{MoS}_2$  has a bandgap energy of about 1.7–2.7 eV and proper valence conduction band potentials that own great photocatalytic efficiency and can employ an immense section of solar light [12]. Unfortunately, the poor light harvesting ability, inactive removal pollutants performance, and quick recombination rate of photo-excited charge carriers are the natural disadvantages that inhibit the useful utilization of  $\text{MoS}_2$  [13]. In addition,  $\text{Co}_3\text{O}_4$  also exhibits obvious stability under the photocatalytic system. In addition,  $\text{Co}_3\text{O}_4$  possesses the matched band gap potential with  $\text{MoS}_2$  to develop an efficient step-scheme (S-scheme) heterostructure because the valence band (VB) of  $\text{Co}_3\text{O}_4$  is close to the conduction band (CB) of  $\text{MoS}_2$  based on previous works [12]. However, the  $\text{Co}_3\text{O}_4$  catalyst absorbs primarily visible light and possesses a wide band gap energy, which prohibits their photocatalytic efficiency. Among these heterostructures,  $\text{MoS}_2$  and Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) photocatalysts exhibit various superior properties for instance remarkable direct bandgaps, excellent mechanical properties, outstanding optical property as well as distinguished photocatalytic efficiency [14–16]. On the other hand, bare  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$  for direct photocatalytic water splitting or removal of contaminants are quite challenging because of their poor operation and high electron and hole recombination rate [17,18]. In addition, this heterojunction not only improved  $\text{H}^+$  adsorption and promoted migration and transport of  $\text{H}^+$  to the surface reactive sites, but further suppress the stacking or aggregation of materials [19]. To solve this issue, a common method is to develop nano-heterostructure between  $\text{Co}_3\text{O}_4$  and  $\text{MoS}_2$  under visible light irradiation to improve their visible light activity. To overcome these barriers, substantial promotions have been made in the reasonable formation and design of  $\text{MoS}_2/\text{Co}_3\text{O}_4$ -based nanohybrids with well-established interfaces and nanostructures [20]. Constructing heterojunction photocatalysts can assist the charge transfer between the diverse photocatalysts and enhance the separation of charge carriers. Therefore, the introduction of new-form nano-heterojunction photocatalysts with structural variety, band gap energy, and better visible-light utilization is superior in this investigate area [21,22].

In the present study, a new  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrid photocatalyst was fabricated by a facile hydrothermal route for powerful photocatalytic activity. The green-hydrothermal technique is energy-saving, cost-effective, environmentally friendly, and a green process compared with other synthesis methods [23,24]. To our knowledge, there is no report on the photocatalytic degradation of  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids with visible light irradiation. A potential S-scheme heterojunction can be constructed between  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$  while Schottky junction developed at the  $\text{MoS}_2/\text{Co}_3\text{O}_4$  interface, respectively, which connected to enhance the charge carriers separation ability. With the optimized amount of  $\text{Co}_3\text{O}_4$  loading in the composite, the  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nano-heterojunction displayed a great removal MO rate of 95.6%, which was approximately 2.1 and 2.3 folds higher than that of bulk  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$  samples, respectively.  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids demonstrated higher photocatalytic efficiency than  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$  on the removal of MO dye with visible light irradiation. This system opened up a new route for the controlled fabrication of  $\text{MoS}_2$ -based heterojunction and also improved their organic compound photodegradation activity. The further the surface reactive positions created by the huger specific surface area, the higher the redox efficiency due to the farther negative conduction capacity, and decreased recombination degree of photogenerated electrons and holes eventually resulted in improved photocatalytic performance.

## 2. Results and Discussion

XRD analysis was further collected to check the crystal phase form and structural composition of the as-fabricated photocatalysts, as exhibited in Figure 1. During the

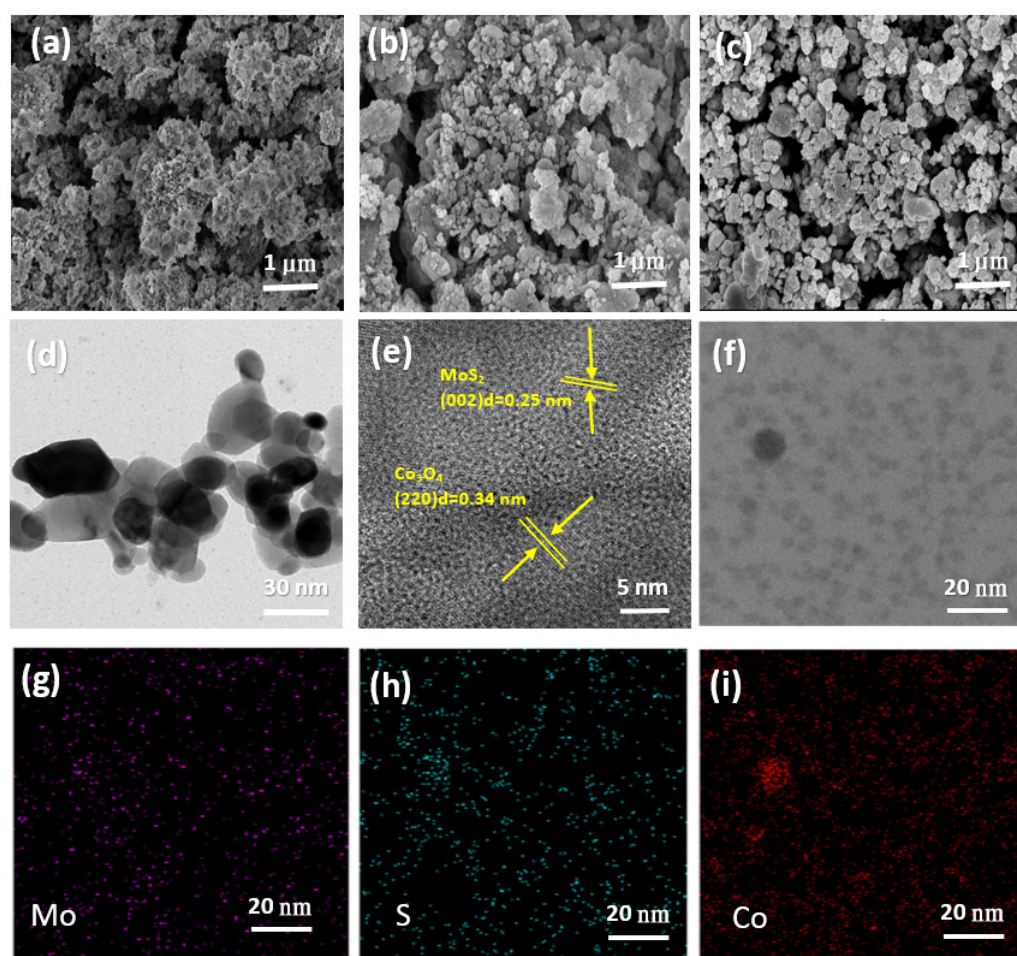
hydrothermal process, the apparent feature peaks of MoS<sub>2</sub> were weaker while several new feature peaks appeared at 31.2°, 36.8°, 44.9° and 59.4° of the MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> photocatalysts, which are related with the (220), (311), (400) and (511) diffraction face of Co<sub>3</sub>O<sub>4</sub> (JCPDS No. 42-1467) [15], respectively. The MoS<sub>2</sub> materials exhibits a series of primary feature peaks at 14.3°, 32.9°, 39.8°, 44.5°, 50.2°, 50.7°, and 60.7°, which assigned to the (002), (100), (103), (006), (105), and (110) crystal planes (JCPDS: 37-1492), respectively, and no other impurity peaks were perceived [11]. Its value indicating that there is no altered signal in the XRD analysis of the MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanocomposites compared to the MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> samples, suggesting that the presented Co<sub>3</sub>O<sub>4</sub> content is fewer, and the dispersion is greater, and there are no other impurity peaks or feature peak shift. In addition, when the reaction solutions concentration of Co<sub>3</sub>O<sub>4</sub> was increased from 5 wt% to 20 wt%, the (311) feature peak intensity of Co<sub>3</sub>O<sub>4</sub> became higher, which indicated an enlarge in the dosage of Co<sub>3</sub>O<sub>4</sub> in the heterojunction. In particular, contrast with the XRD analysis of Co<sub>3</sub>O<sub>4</sub>, the overall diffraction intensities of MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> heterojunctions were altered at 36.8° with (311) diffraction face (see Figure 1 inset). In addition, the feature peaks of MC-X (X = 5 wt%, 10 wt%, 15 wt%, and 20 wt%) are comparable to the feature XRD analysis of MoS<sub>2</sub> without additional impurity peaks, which suggests that the nanohybrids photocatalyst further possess coherent crystal structure [25,26].



**Figure 1.** XRD patterns of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, MC-5%, MC-10%, MC-15%, and MC-20% samples, inset shows the intensity of (311) XRD peak.

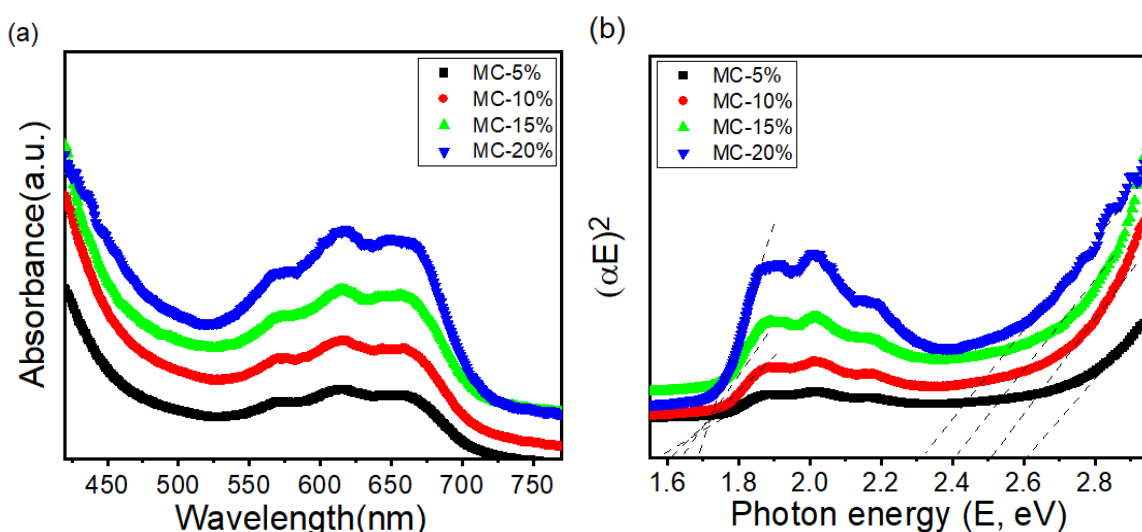
In order to explore the development step of morphologies after hydrothermal process, SEM and TEM were characterized. As exhibited in Figure 2a,b, apparently large-sized bulk MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> can be found, respectively. It is obtained that the microstructure of the photocatalyst is sphere-like and plate-like with approximately 5  $\mu$ m equivalent size.

However, the  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$  possess a high grade of collection, which intensely suppress the surface of the active location of the photocatalysts. As displayed in Figure 2c, the  $\text{MoS}_2/\text{Co}_3\text{O}_4$  heterojunction presents a nanomaterial with an irregular surface, which gives it a greater specific surface area. Therefore, this reflection was verified in the specific surface area examination test. It is pronounced that despite the size of MC-X being immensely decreased, the crystals of  $\text{MoS}_2$  still retain great crystallinity, as presented by the (002) major peak observed in the XRD patterns (Figure 1). This nanohybrid of  $\text{MoS}_2/\text{Co}_3\text{O}_4$  serves a sufficient area for the efficient load of  $\text{Co}_3\text{O}_4$ , which can mainly disperse  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids and decrease aggregation. As displayed in Figure 2d, the  $\text{MoS}_2/\text{Co}_3\text{O}_4$ -20% heterojunction displays an aggregated form with a dimension of approximately 4–10 nm. From Figure 2e, the lattice fringe of 0.26 nm could be apparently noticed, which corresponds to the (002) plane of hexagonal  $\text{MoS}_2$ . The fringe spacing of 0.32 nm is assigned to the (311) plane of  $\text{Co}_3\text{O}_4$ . During further testing, it could be found that the  $\text{MoS}_2/\text{Co}_3\text{O}_4$ -20% nanohybrids were eventually constructed. The element mappings exhibit that the Mo, S, and Co elements are consistently distributed in the  $\text{MoS}_2/\text{Co}_3\text{O}_4$ -20% nanohybrids (Figure 2f–i). The construction of the heterostructure of  $\text{MoS}_2/\text{Co}_3\text{O}_4$  is broadly supposed to possess a definite effect on promoting the charge carrier's separation ability of photocatalytic. The consistent distribution of Mo, S, and Co elements can confirm the effective formation of  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids.



**Figure 2.** SEM images (a)  $\text{MoS}_2$  (b)  $\text{Co}_3\text{O}_4$  (c)  $\text{MoS}_2/\text{Co}_3\text{O}_4$ , (d) TEM and (e) HRTEM images of  $\text{MoS}_2/\text{Co}_3\text{O}_4$ , (f–i) Elemental mapping images of  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids with elemental distribution of Mo, S, and Co.

The UV-vis absorption spectra are generally adopted to check the visible light absorption capability of the photocatalyst, and the analysis of the as-prepared MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> heterojunction is exhibited in Figure 3. As can be observed, the two optical band gaps of MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub>-X nanocomposites are 1.56~1.69 eV (*E<sub>g1</sub>*) and 2.31~2.61 eV (*E<sub>g2</sub>*), which are in good agreement with the MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> energy band gap. As MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> photocatalyst is a photo-response sample, it possessed a wide wavelength absorption ability. *E<sub>g1</sub>* is joined to the onset of O(II)-Co(III) excitations [13–15]. The maximum response wavelength of MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> is extended to 550 nm. Then, it presents a narrower band gap (*E<sub>g2</sub>*) of 2.31~2.61 eV after adding Co<sub>3</sub>O<sub>4</sub>, which is favorable to improve visible light application and photoexcited charge carriers. In addition, the UV-vis spectra of the MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids are relatively close. The construction for this case is that the minor added dosage of Co<sub>3</sub>O<sub>4</sub> does not generate an apparent alteration to the light absorption efficiency of the MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids. The MC-20% nanohybrids display better light absorption and the absorption range has a minor red shift in the range of 550–680 nm. It could be assigned to the cooperation between MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>. Hence, the Co<sub>3</sub>O<sub>4</sub> materials may be a significant reason to enlarge the light absorption of the MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids. The band gap energy (*E<sub>g</sub>*) of the corresponding photocatalyst was received via the transformed Kubelka–Munk function [27,28]. As exhibited in Figure 3b, the *E<sub>g2</sub>* (*E<sub>g1</sub>*) values of MC-5%, MC-10%, MC-15%, and MC-20% are about 2.61 (1.56) eV, 2.51 (1.61) eV, 2.45 (1.64) eV, and 2.31 (1.69) eV.



**Figure 3.** (a) UV-vis DRS absorption spectrum and (b) Tauc plots of as-prepared nanocomposites.

Then, X-ray photoelectron spectroscopy (XPS) is validated to recognize surface information of the fabricated samples. Figure 4a displays the survey XPS spectra. As further observed, MC-20% is constructed of Mo, S, Co and O elements, which involve the integral elements of MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids. There are no other impurity peaks emerging in survey spectra, suggesting that there are no other contaminate photocatalysts during hydrothermal route. The high-resolution spectrum of Mo 3d (Figure 4b) could be divided into two peaks, which centered are at ~229.6 eV and ~232.8 eV, referring to Mo 3d 5/2 and Mo 3d 3/2 [10]. Correspondingly, two feature peaks in the high-resolution S 2p XPS spectra of MC-20% centered at nearly 162.6 eV and nearly 163.6 eV (Figure 4c) are referring to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub>, respectively [11]. As shown in Figure 4d, binding energies of ~780.1 eV and ~795.5 eV referring to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> for MC-20% nanohybrids, respectively [14]. The O 1s spectra of MC-20% (Figure 4e) binding energies at 529.8 eV and 531.8 eV, referring to the O<sup>2−</sup> in the Co<sub>3</sub>O<sub>4</sub> and the adsorbed oxygen [15]. These results suggested that the MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids were well fabricated with a strong interaction between MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>. The elements concerned with the formation of

MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids were confirmed by the EDS spectra. Four noticeable peaks were obtained at nearly 0.8 keV, which was owing to the presence of oxygen atom, and other three peaks arising at 0.8 keV and 6.9 keV related to Co, and 2.3 keV, are related to Mo and S as exhibited in Figure 4f. The results confirmed the successful fabrication of MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids. The Brunauer-Emmett-Teller (BET) specific surface areas of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MC-20% are evaluated to be ~35.2, 24.6, and 68.7 m<sup>2</sup> g<sup>−1</sup>, respectively (Table 1). The main aperture size of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MC-20% are ~38.4, 48.5 and 8.9 nm, respectively. The pore volumes of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MC-20% are ~0.193 cm<sup>3</sup> g<sup>−1</sup>, 0.124 cm<sup>3</sup> g<sup>−1</sup> and 0.372 cm<sup>3</sup> g<sup>−1</sup>, respectively. BET of MC-20% was more than 2 times than that of MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>, demonstrating the introduced Co<sub>3</sub>O<sub>4</sub> had a critical influence on raising the specific surface area of MoS<sub>2</sub>.

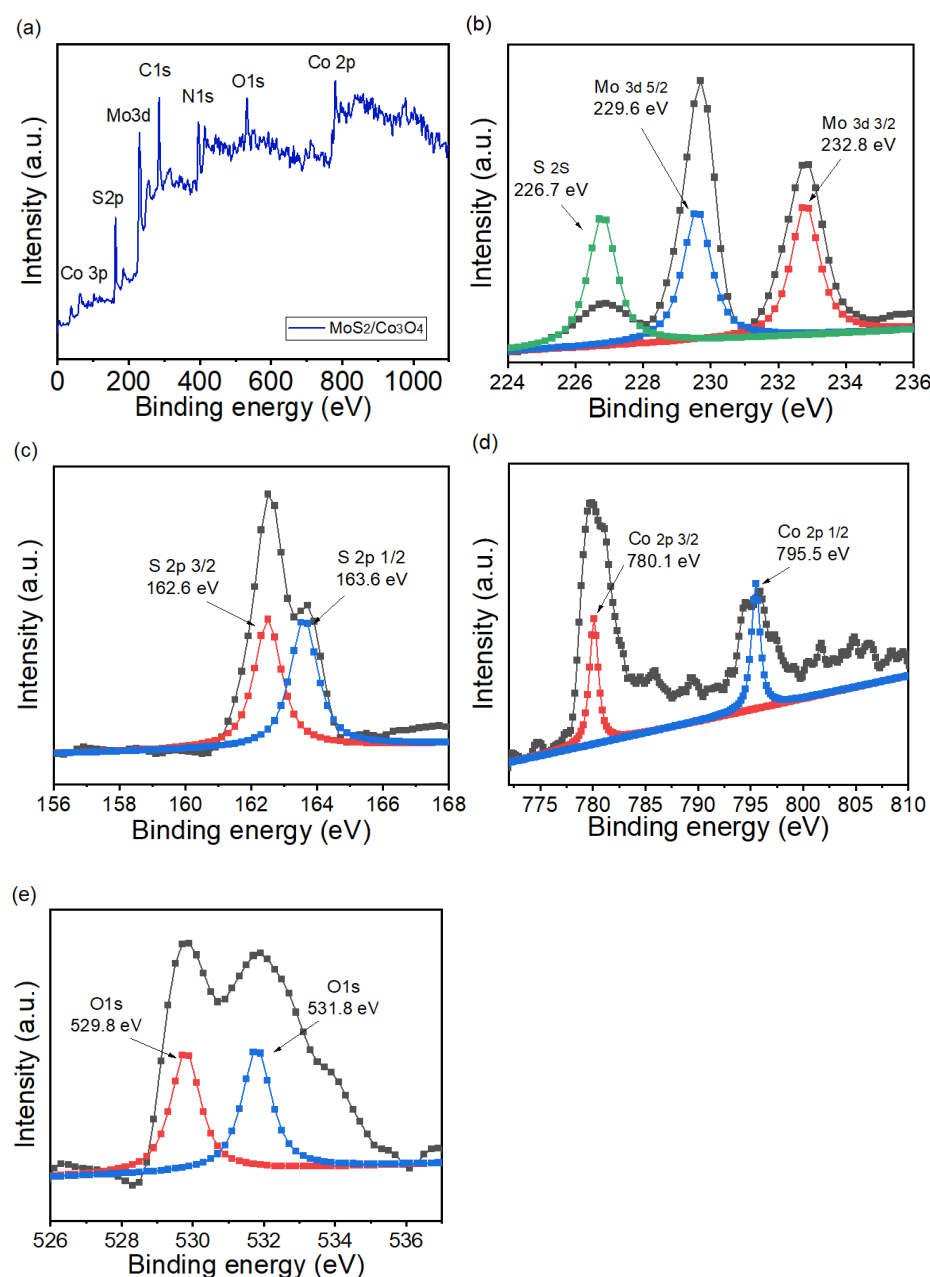
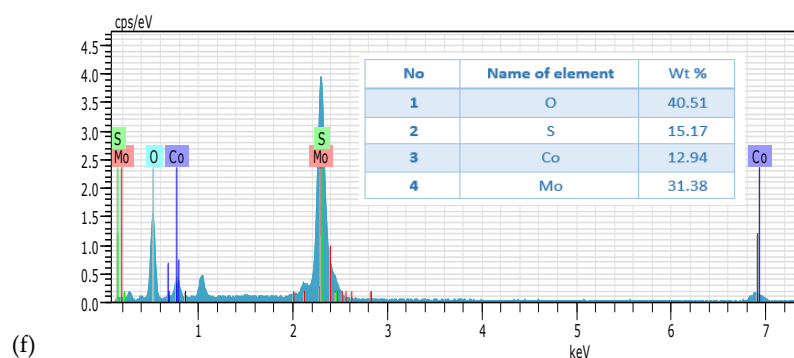


Figure 4. Cont.



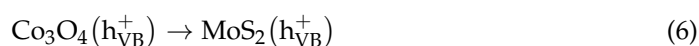
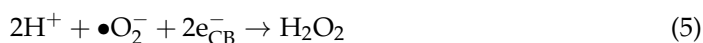
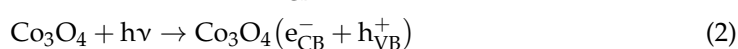
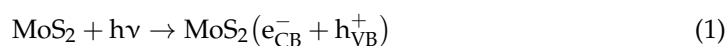
**Figure 4.** The surface chemical station analysis of MC-20%, (a) Survey spectra, High resolution XPS spectra of (b) Mo 3d spectra, (c) S 2p spectra, (d) Co 2p spectra, and (e) O 1s spectra, (f) EDS analysis of MC-20% nanohybrids.

**Table 1.** The physical adsorption parameters of the photocatalysts of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MC-20% were measured three times.

| Samples                        | Specific Surface Area (m <sup>2</sup> /g, BET) <sup>a</sup> | Total Pore Volume (cm <sup>3</sup> /g, BET) <sup>b</sup> | Average Pore Diameter (nm, BJH) <sup>b</sup> |
|--------------------------------|-------------------------------------------------------------|----------------------------------------------------------|----------------------------------------------|
| MoS <sub>2</sub>               | 35.2 ± 5                                                    | 0.193 ± 0.02                                             | 38.4 ± 5                                     |
| Co <sub>3</sub> O <sub>4</sub> | 24.6 ± 5                                                    | 0.124 ± 0.02                                             | 48.5 ± 5                                     |
| MC-20%                         | 68.7 ± 5                                                    | 0.372 ± 0.02                                             | 8.9 ± 3                                      |

<sup>a</sup> Received from BET analysis. <sup>b</sup> Relative pressure (P/P<sub>0</sub>) was 0.99.

Figure 5a exhibits the decay in absorbance peak intensity of 447 nm with extending irradiation time. It displays that the absorbance ability of MO was continuously removed with visible light activity in the presence of the as-fabricated photocatalysts. In addition, the absorbance of MO decreased significantly with the increase of irradiation time by using MC-20% nanohybrids as primarily photocatalyst under solar irradiation was recorded by UV-vis absorption spectroscopy, which proved the destruction of MO molecules. The photocatalytic activity of MO by as-fabricated MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> and MC-X materials was evaluated with and without visible light activities (Figure 5b). The control experiments displayed the capability values for the self-photocatalytic of MO pollutants under same light condition. This result suggests that the degradation of MO pollutants is owing to the photodegradation activity in the as-fabricated samples. On the other hand, the individual MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> samples could degrade about 45.8 and 41.4% of MO under 140 min of visible light radiation. The photodegradation capability of the photocatalysts followed the sequence: MC-20% nanohybrids > MC-15% nanohybrids > MC-10% nanohybrids > MC-5% nanohybrids > MoS<sub>2</sub> > Co<sub>3</sub>O<sub>4</sub>. This poor photodegradation performance could be assigned to the high recombination of electrons and holes in the bulk component [29]. Noticeably, MC-20% nanohybrids described excellent photodegradation performance of MO pollutants (~95.6%) than bare MoS<sub>2</sub> or Co<sub>3</sub>O<sub>4</sub>, which was about 2.3 folds than bare Co<sub>3</sub>O<sub>4</sub>. The major process of photocatalytic reaction for the composite magnetic photocatalyst MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> based on the basic principles and studies reported in the literature can be summarized as follows:



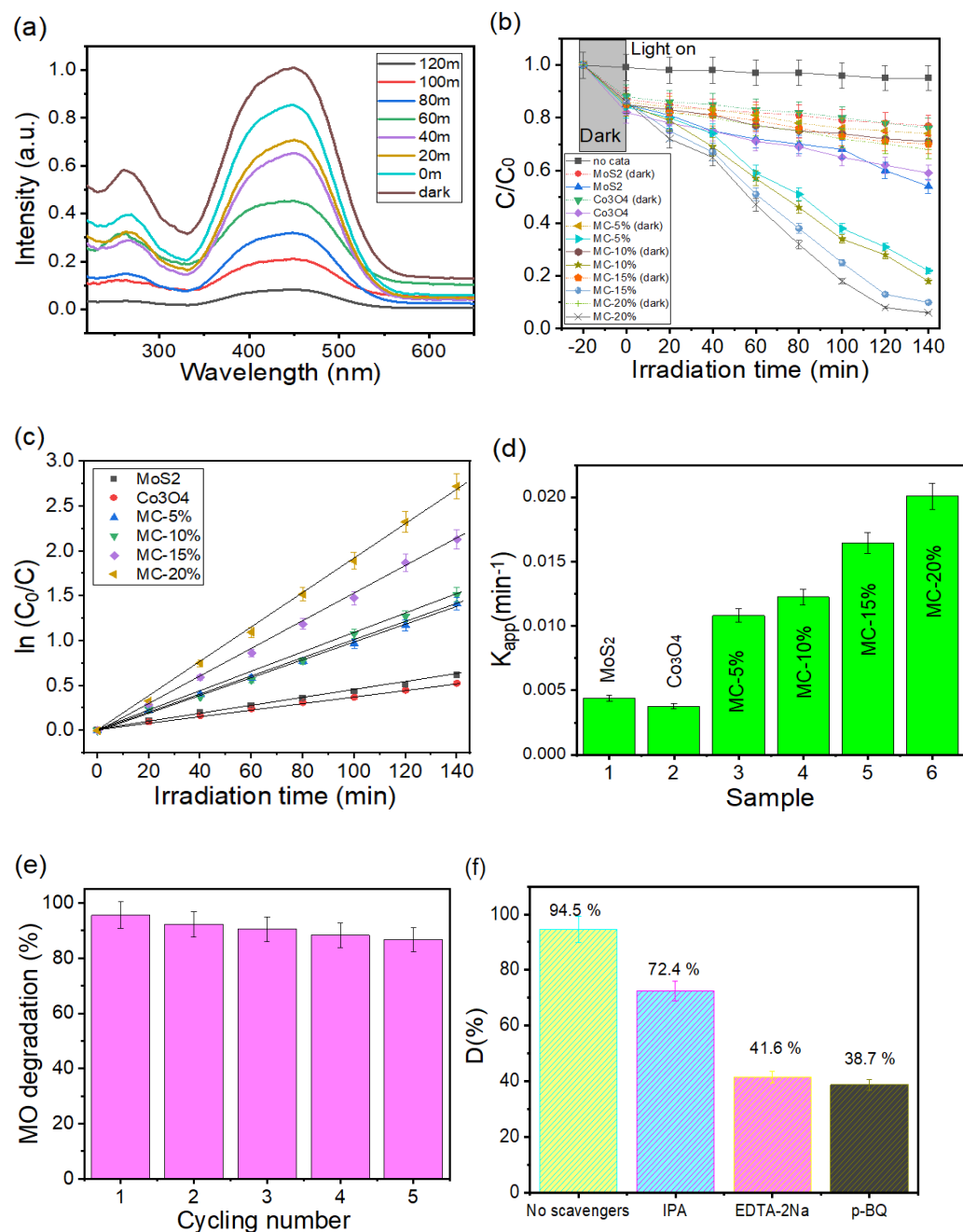
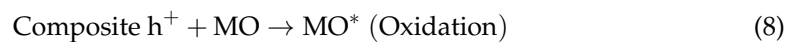
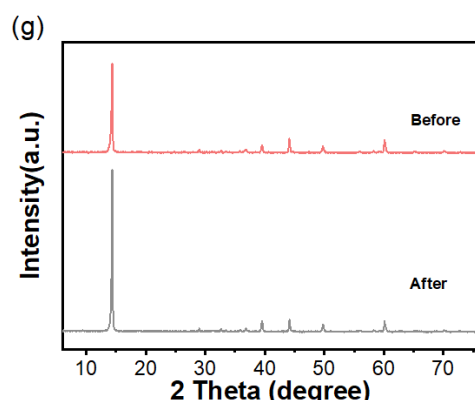


Figure 5. Cont.



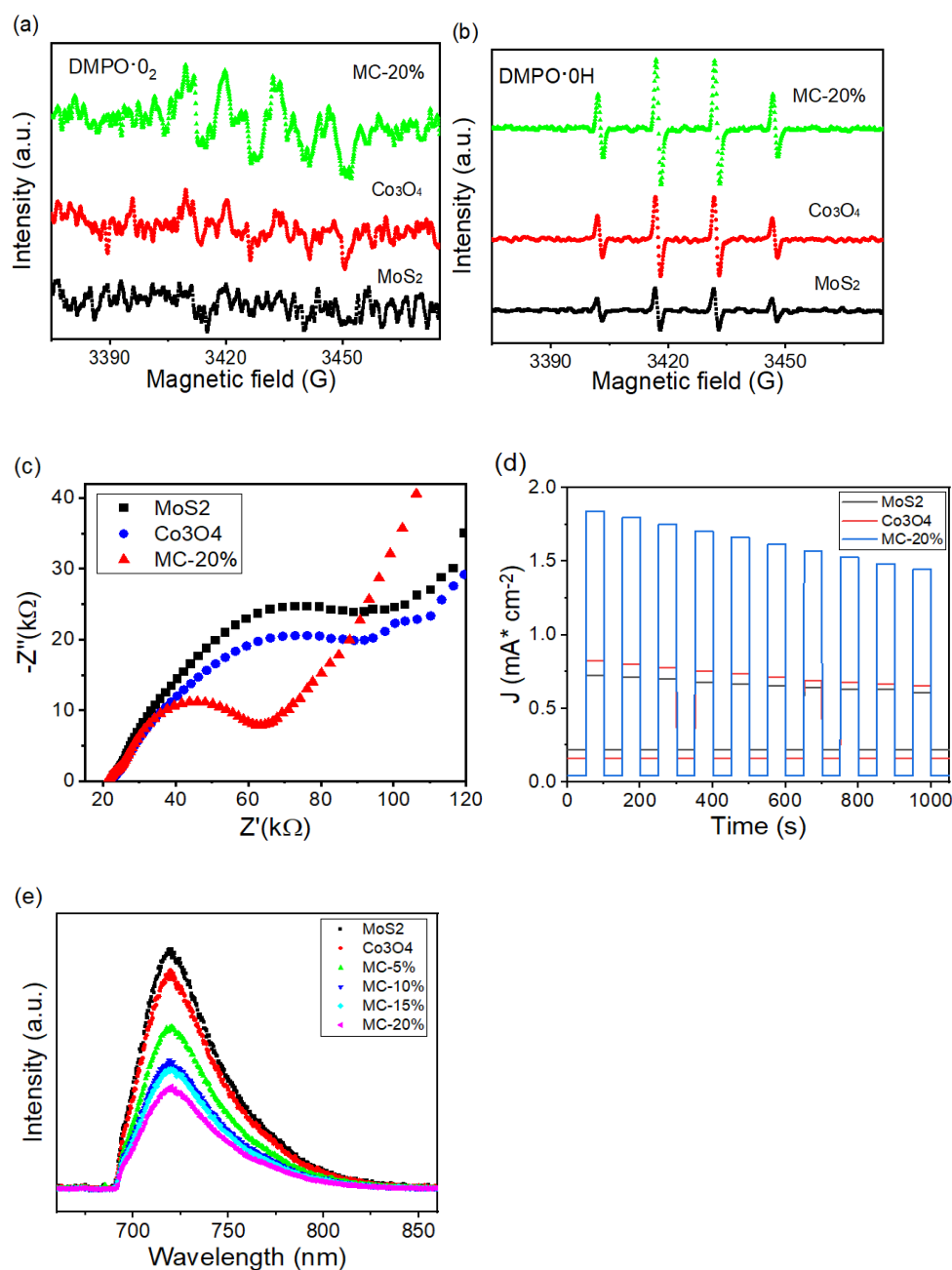
**Figure 5.** Photocatalytic study of MO degradation, (a) time-dependent UV–Vis absorption spectra, (b) conversion of MO over various photocatalysts, (c) pseudo–first-order kinetics study of the degradation, (d) degradation rate constant of as–fabricated samples, (e) recycling and (f) radical scavenging activity during the decomposition of MO over MC–20% under visible light, (g) Comparison of XRD analysis of MC–20% samples before and after photocatalytic.

In addition, the photocatalytic reaction kinetics of an MO removal test was calculated to a pseudo first order equation model in order to check the photocatalytic activity. The linear relationship between  $\ln(C_0/C)$  vs. irradiation time ( $t$ ) is exhibited in Figure 5c and the removal rate constant ( $K_{app}$ ) is displayed in Figure 5d. The MC-20% nanohybrids were measured with a higher  $K_{app}$  value compared to the other synthesized samples. For effective utility purposes, the stability and reusability of MC nanohybrids were estimated by cycling runs. After every test, the sample was centrifuged, washed and dried before operating the next run. As shown in Figure 5e, the photodegradation capability of the MC-20% sample was 95.6%, 92.3%, 90.5%, 88.3%, and 86.8% for first, second, third, fourth, and fifth test, respectively. The noticed reduction of the photocatalytic activity of MC-20% can be referred to an adsorbed MO and its evolution products on the surface of MC-20% nanohybrids, thus prohibiting the active sites and visible light from approaching the photocatalyst [30]. The exploration of the photodegradation mechanism of the nanohybrids acted as a critical factor in the effective utilization of the heterojunction photocatalyst. Accordingly, the free radical trapping tests were performed, in which p-BQ (1,4-benzoquinone), IPA (2-propanol) and EDTA-2Na were adopted as scavenging free radical ( $\bullet O_2^-$ ,  $\bullet OH$  and  $h^+$ ) agents [31]. It could be observed from the analysis results in Figure 5f that when various scavenging free radical agents were further joined, the photocatalytic efficiency of the MC-20% sample was influenced to altering degrees. The MC-20% sample was highly responsive to p-BQ and EDTA-2Na, implying that  $\bullet O_2^-$  and  $h^+$  were the major active species during the photodegradation activity, and  $\bullet OH$  only acted as an assisting active species. Consequently, these results demonstrate that the formation of  $MoS_2/Co_3O_4$  with a proper ratio (20 wt%) is able to receive the better photocatalytic efficiency of  $MoS_2/Co_3O_4$  in the nano-heterostructure. The stability and repeatability of the sample are important indexes to evaluate the performance of photocatalysts. XRD analysis was performed after the fourth recycling experiment. Taking MC-20% photocatalyst as an example, its activity did not change significantly after five cycles, which can still degrade 86.8% of MO (Figure 5g). This result clearly suggests the stability of the fabricated  $MoS_2/Co_3O_4$  NC photocatalyst. In addition, Table 2 displays the photocatalytic performance of relevant heterojunction in previous reports [31–36]. By contrast, it is observed that the  $MoS_2/Co_3O_4$  nanomaterial we prepared has remarkable benefits for organic compounds of high concentration in the photocatalytic process.

**Table 2.** Comparison of photocatalytic activity of some photocatalysts for removal MO dye under visible light irradiation.

| Catalysts                                           | Pollutants Volume | Concentration            | Lamp      | Mass of Catalysts | Time (min) | Degradation Rate % | Reference    |
|-----------------------------------------------------|-------------------|--------------------------|-----------|-------------------|------------|--------------------|--------------|
| ZnO-TiO <sub>2</sub> /SO <sub>4</sub> <sup>2−</sup> | 25 mL             | 20 mg L <sup>−1</sup>    | halide    | 20 mg             | 72         | 90                 | [31]         |
| CoO <sub>x</sub> /g-C <sub>3</sub> N <sub>4</sub>   | 35 mL             | 10 mg L <sup>−1</sup>    | Xenon     | 35 mg             | 180        | 92                 | [32]         |
| ZnPcs                                               | 3 mL              | 3.3 × 10 <sup>−5</sup> M | White LED | 10 mg             | 720        | 93                 | [33]         |
| SbSI MRs                                            | 50 mL             | 30 mg L <sup>−1</sup>    | halide    | 25 mg             | 10         | 78                 | [34]         |
| Sn-ZnO/GO                                           | 1000 mL           | 50 mg L <sup>−1</sup>    | Xenon     | 100 mg            | 120        | 87                 | [35]         |
| CdS                                                 | 150 mL            | 10 mg L <sup>−1</sup>    | Xenon     | 500 mg            | 180        | 94                 | [36]         |
| MoS <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub>    | 50 mL             | 20 mg L <sup>−1</sup>    | halide    | 10 mg             | 170        | 96                 | Present work |

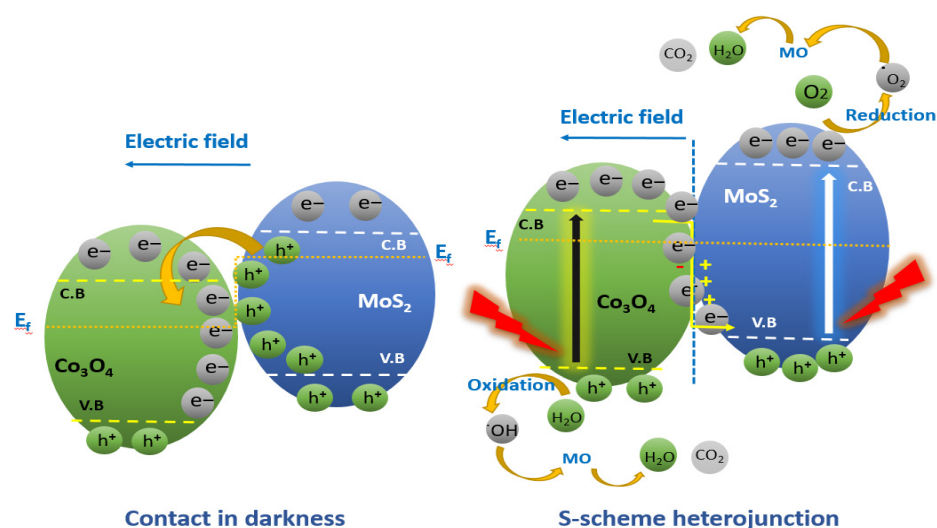
For confirm the presented S-scheme heterojunction, electron spin resonance (ESR) is adopted to recognize the free radicals produced in the system of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> and MC-20% nanohybrids. Applying DMPO as a spin capture agent, DMPO-•O<sub>2</sub><sup>−</sup> and DMPO-•OH are observed with light conditions. It could be found in Figure 6a that the MC-20% photocatalyst displays the higher feature signal of DMPO-•O<sub>2</sub><sup>−</sup>, while the feature signal of DMPO-•O<sub>2</sub><sup>−</sup> of MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> is nearly undetectable. It exhibits that the construction of heterojunction is more favorable to the production of •O<sub>2</sub><sup>−</sup>, which could be referred to the rapid migration and separation of photoexcited charge carriers in heterojunction catalysts [36]. Furthermore, the DMPO-•OH feature signal peaks of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> and MC-20% could be found in Figure 6b, of which MC-20% possess the highest signal peak. Hence, it could be resulted that MC-20% nanohybrids can generate more •O<sub>2</sub><sup>−</sup> and •OH. The coincidence of •O<sub>2</sub><sup>−</sup> and •OH radicals further verify that the charge carrier separation mechanism is S-scheme. The charge transfer routes are analyzed by photoelectrochemical measurements. Electrochemical impedance spectroscopy (EIS) with visible light activity is exhibited in Figure 6c, and the smaller semi-circular curve in Nyquist plots expresses the lesser charge carrier transport resistance. Apparently, the lowest charge carrier transport resistance in MC-20% imply the greatest efficient charge carrier transport routes [37], which corresponds with the outstanding PHE capability of MC-20% nanohybrids. As exhibited in Figure 6d, all the MC-20% nanohybrids electrodes exhibit a great transient photocurrent response than that bare MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> behaves at the highest intensity, implying the great efficient charge separation. Room-temperate PL spectra are carried out to check the charge carrier dynamics behavior. As displayed in Figure 6e, the apparently reduced PL intensity of MC-20% also proves the prohibited electrons and holes recombination, which is in good approval with the above results. Furthermore, the performance of the charge carrier is further explored under photocatalytic redox reactions. The efficient separation of photo-induced charge carriers is a required situation for enhancing the capability of photodegradation [38]. It is also found that the poorer the peak PL intensity, the lower the possibility of electron and hole pairs recombination rate, which is more favorable to the development of the pollutant removal reaction. This is owing to the evidence that the formation of nano-heterojunction improves the quick separation and transport of photo-excited charge carriers, hence, greatly suppressing the recombination rate of photo-induced charge carriers and enhancing the performance of charge carrier separation.



**Figure 6.** DMPO spin-trapping ESR spectra for (a)  $\bullet\text{O}_2^-$  and (b)  $\bullet\text{OH}$  with visible light for MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> and MC-20%, (c) Electrochemical impedance spectra (EIS) of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution with visible light activity, and (d) Transient photocurrent densities of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> electrodes in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution with visible light, (e) PL spectra under the excitation wavelength of 580 nm of MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, MC-5%, MC-10%, MC-15% and MC-20%.

Based on the above data analysis and results, a photocatalytic activity mechanism of MO removal on MC nanohybrids is recommended, as exhibited in Scheme 1. Following the introduction of Co<sub>3</sub>O<sub>4</sub> materials on the surface of MoS<sub>2</sub>, a firm heterostructure is organized. During exposure to visible light, photocatalysis activity has various efficiencies to the incident visible light in varied wavelength ranges. In this work, MC nanohybrids can absorb a broad range of incident visible light with the same conditions, thus generating more photoexcited charge carriers. More significantly, the system of photocatalytic reaction of nanohybrids design is higher than that of single-component design, implying in an improved interaction among reactant and photocatalyst. Ultimately, the excellent hydrogen

evolution and pollutants removal promote the nanohybrids to have a higher charge carrier separation behavior [39,40]. In the meantime, a built electric field from  $\text{Co}_3\text{O}_4$  to  $\text{MoS}_2$  induces the downward band curving of  $\text{MoS}_2$  and upward band curving of  $\text{Co}_3\text{O}_4$  at the heterojunction interface, respectively. During visible light irradiation, both  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$  could be photo-induced to produce electrons and holes. The electric field, curved band edges and the coulomb interaction notably drive the CB electrons of  $\text{MoS}_2$  to rebuild with the VB holes of  $\text{Co}_3\text{O}_4$ , leading to the practical conservation of the high-oxidative holes in the VB of  $\text{MoS}_2$  and high-reductive electrons in the CB of  $\text{Co}_3\text{O}_4$ , which significantly promotes the photo-response efficiency of  $\text{MoS}_2/\text{Co}_3\text{O}_4$ . This facile S-scheme system can efficiently weaken the recombination rate of photoinduced charge carriers in the heterojunction and improve the recombination of limited photo-generated electron and hole pairs, hence increasing the excellent redox activity of the photocatalyst. Finally, the enhanced photodegradation efficiency could be attributed to the increased visible light absorption ability, more reactive sites and powerful transfer of photo response charge carriers. In addition, the interface influence is larger than the efficiency of the photogenerated hole and electron to recombine. The electrons of the conduction band of  $\text{MoS}_2$  contribute to the pollutant removal reduction reaction. Then, the holes of  $\text{Co}_3\text{O}_4$  are oxidized in the valence band by the photocatalytic process. This novel S-scheme nanocomposite possesses better redox ability [19,26,27], which apparently enhances the capability of photocatalytic pollutants removal. The CB and VB of MC with visible light activity, are induced to create photoexcited electrons and holes, respectively. On the other hand, the photo-response charge carriers in  $\text{MoS}_2$  and  $\text{Co}_3\text{O}_4$  will recombine rapidly, implying a weakening in photocatalytic capability. Although, owing to the presence of  $\text{Co}_3\text{O}_4$  cocatalyst, photoexcited electrons will rapidly migrate to  $\text{MoS}_2$ , and also further water reduction so hydrogen evolution will appear. Furthermore, the presence of  $\text{MoS}_2$  can weaken over-potential and serve more active sites for photocatalytic and can further enlarge the visible light absorption of  $\text{Co}_3\text{O}_4$ .

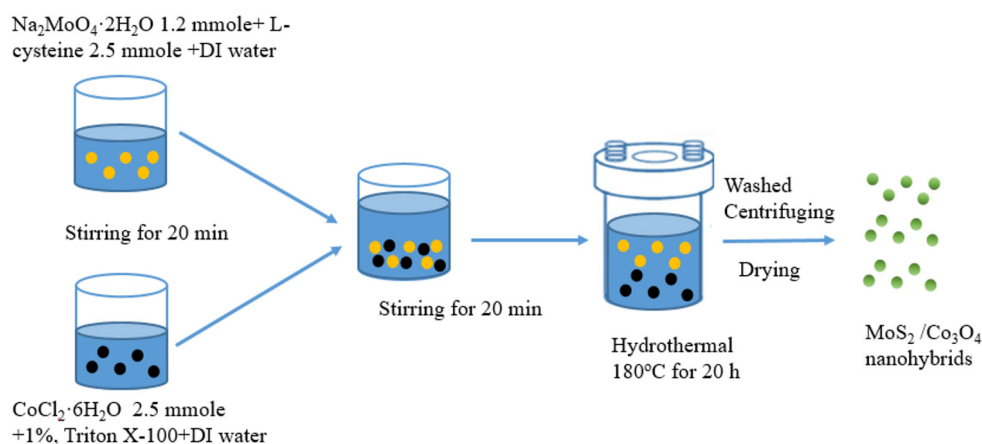


**Scheme 1.** The possible photocatalytic mechanism of nanohybrids.

### 3. Materials and Methods

Sodium molybdenum oxide dehydrates ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) ( $\geq 99.5\%$ ), L-cysteine ( $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ ), Cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 98\%$ ), Methyl orange (MO,  $\geq 85\%$ ), Triton X-100, Potassium hydroxide (KOH,  $\geq 85\%$ ), 1-Methyl-2-pyrrolidone (NMP,  $\geq 99\%$ ), absolute ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\geq 95\%$ ), and acetone ( $\text{CH}_3\text{COCH}_3$ ,  $\geq 99.5\%$ ) were used from Sigma-Aldrich (St. Louis, MO, USA). Deionized water was utilized to produce solutions to be examined. All the chemicals were adopted directly without purification.

Typically, 1.2 mmol of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  and 2.5 mmol the L-cysteine was used to 40 mL of deionized (DI) water to develop a homogeneous solution via stirring and ultrasonic treatment for 30 min.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (2.5 mmol) was added in 40 mL distilled water and a certain amount of surfactant (1%, *w/w*, Triton X-100) was added subsequently. Subsequently, the homogeneous solution was transformed into a Teflon-lined stainless-steel autoclave (100 mL) and reacted at 180 °C for 20 h. After cooling down to room temperature naturally, the pristine dark precipitate was obtained by centrifugation, washed three times with deionized water, NMP, absolute ethanol and acetone, and dried at 70 °C in a vacuum oven overnight. A series of  $\text{MoS}_2/\text{Co}_3\text{O}_4$  photocatalysts was provided by increasing various doses of  $\text{Co}_3\text{O}_4$  (5 wt%~20 wt%); the individual samples are denoted as MC-X (X = 5 wt%, 10 wt%, 15 wt%, and 20 wt%). Finally, the nanocomposite is prepared via the hydrothermal method, as shown in Scheme 2.



**Scheme 2.** Schematic illustration of the formation route of the  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanohybrids.

X-ray diffraction patterns (XRD) were determined by a Bruker D8 Advanced diffractometer (Billerica, MA, USA) at 5–75° with a scanning step of 20°/min at room temperature. Hitachi UV-4100 UV–visible spectrophotometer and Edinburgh Analytical Instruments F-7000 (Tokyo, Japan) were adopted to check the UV–vis diffusive reflectance spectra and photoluminescence (PL) spectra with an excitation wavelength of 620 nm. The microstructure and morphology of different samples also were tested by employing scanning electron microscopy (SEM) micrographs (ZEISS AURIGA, Oberkochen, Germany) and transmission electron microscopy (TEM) experiment (JEOL JEM-2100F, Tokyo, Japan). Electron paramagnetic resonance (EPR) spectra were observed on a Bruker A300 (Munich, Germany) at room temperature under atmospheric conditions. A CH Instruments electrochemical workstation with a standard three-electrode system was recorded to carry out electrochemical measurements in 0.2 M  $\text{Na}_2\text{SO}_4$  solution. Furthermore, the saturated Pt electrode and  $\text{Hg}/\text{Hg}_2\text{Cl}_2$  electrode were used as the counter electrode and reference electrode, respectively. The working electrode was used according to the next procedure: the as-prepared photocatalysts (20 mg) were dispersed in 10 mL of DI water to obtain a homogeneous suspension with a consecutive ultrasonic process. The chemical states and surface species were tested by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Waltham, MA, USA).

Photodegradation of MO pollutants over various MC-X photocatalysts was performed at room temperature with visible light activity. A 350 W Xe lamp was employed as the visible-light source. A total of 20 mg of samples were added in 100 mL MO aqueous solution (20 mg  $\text{L}^{-1}$ ). The above reaction solution was further stirred under the dark for 20 min to organize absorption-desorption equilibrium between photocatalysts and MO compounds. Under light activity, a definite quantity of reaction solution was carried out from the combination solution at contributed intervals, followed by centrifugation to eliminate all the materials. The concentration alters of MO pollutants were obtained via UV-vis spectroscopy under photocatalytic activity.

#### 4. Conclusions

In this study, MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids were fabricated adopting a facile hydrothermal process. The prepared nanohybrids exhibited better capability for the degradation of MO dye from aqueous solution. The maximum MO photodegradation performance approached by the nanohybrids was 95.6%, and the reaction rate constants was 0.021. The MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids with 20 wt% loading of Co<sub>3</sub>O<sub>4</sub> on MoS<sub>2</sub> nanoparticles, displays excellent photocatalytic response for MO dye removal as compared to the bare photocatalysts and other nano-heterojunctions. The 20 wt% MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids were the optimal photocatalysts through photoreduction and photodegradation activity greater than that of bare MoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>. The result demonstrates that the formation of MoS<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrids is conducive to the production of excellent photo response carriers and the enhancement of visible light absorption. In addition, the fabrication of nanohybrids effectively inhibits the recombination rate of photo response electrons and holes in the photocatalytic activity. Thereby, this research paves way for the facile formation of nanohybrids system for diverse environmental fields.

**Author Contributions:** Writing—original draft, Methodology, T.-M.T.; Writing—review and editing, E.L.C.; Data curation, Formal analysis, C.-H.C.; Funding acquisition, T.-M.T.; Validation, C.-T.H.; Resources, T.-M.T.; Formal analysis, data collection, E.L.C.; Supervision, Investigation E.L.C.; Supervision, Project administration. T.-M.T. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** Not available.

**Acknowledgments:** The MOST and the NKUST are gratefully acknowledged for their general support. The authors gratefully acknowledge the use of HRTEM equipment belonging to the Instrument Center of National Cheng Kung University.

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

#### References

- Gaim, Y.T.; Yimanuh, S.M.; Kidanu, Z.G.; Ashebir, M.E. Enhanced Photocatalytic Degradation of Amoxicillin with Mn-Doped Cu<sub>2</sub>O under Sunlight Irradiation. *J. Compos. Sci.* **2022**, *6*, 317. [\[CrossRef\]](#)
- Alam, M.W.; Azam, H.; Khalid, N.R.; Naeem, S.; Hussain, M.K.; BaQais, A.; Farhan, M.; Souayeh, B.; Zaidi, N.; Khan, K. Enhanced Photocatalytic Performance of Ag<sub>3</sub>PO<sub>4</sub>/Mn-ZnO Nanocomposite for the Degradation of Tetracycline Hydrochloride. *Crystals* **2022**, *12*, 1156. [\[CrossRef\]](#)
- Wang, X.; Zhou, J.; Zhao, S.; Chen, X.; Yu, Y. Synergistic effect of adsorption and visible-light photocatalysis for organic pollutant removal over BiVO<sub>4</sub>/carbon sphere nanocomposites. *Appl. Surf. Sci.* **2018**, *453*, 394. [\[CrossRef\]](#)
- Das, T.K.; Remanan, S.; Ghosh, S.; Ghosh, S.K.; Das, N.C. Efficient synthesis of catalytic active silver nanoparticles illuminated cerium oxide nanotube: A mussel inspired approach. *Environ. Nanotechnol. Monit. Manag.* **2021**, *15*, 100411. [\[CrossRef\]](#)
- Remanan, S.; Padmavathy, N.; Rabiya, R.; Ghosh, S.; Das, T.K.; Bose, S.; Sen, R.; Das, N.C. Converting Polymer Trash into Treasure: An Approach to Prepare MoS<sub>2</sub> Nanosheets Decorated PVDF Sponge for Oil/Water Separation and Antibacterial Applications. *Ind. Eng. Chem. Res.* **2020**, *59*, 20141. [\[CrossRef\]](#)
- Hojamberdiev, M.; Kadirova, Z.C.; Gonçalves, R.V.; Yubuta, K.; Matsushita, N.; Teshima, K.; Hasegawa, M.; Okada, K. Reduced graphene oxide-modified Bi<sub>2</sub>WO<sub>6</sub>/BiOI composite for the effective photocatalytic removal of organic pollutants and molecular modeling of adsorption. *J. Mol. Liq.* **2018**, *268*, 715. [\[CrossRef\]](#)
- Chen, L.J.; Chuang, Y.J.; Chen, C. Surface passivation assisted lasing emission in the quantum dots doped cholesteric liquid crystal resonating cavity with polymer template. *RSC Adv.* **2014**, *4*, 18600. [\[CrossRef\]](#)
- Alnassar, M.A.; Alshehri, A.; Narasimharao, K. Visible Light Active Magnesium Silicate–Graphitic Carbon Nitride Nanocomposites for Methylene Blue Degradation and Pb<sup>2+</sup> Adsorption. *Catalysts* **2022**, *12*, 1256. [\[CrossRef\]](#)
- Yadav, A.A.; Hunge, Y.M.; Kang, S.W. Visible Light-Responsive CeO<sub>2</sub>/MoS<sub>2</sub> Composite for Photocatalytic Hydrogen Production. *Catalysts* **2022**, *12*, 1185. [\[CrossRef\]](#)
- Chen, L.J.; Tsai, M.L.; Chuang, Y.; Chen, C.W.; Dong, C.D. Construction of carbon nanotubes bridged MoS<sub>2</sub>/ZnO Z-scheme nanohybrid towards enhanced visible light driven photocatalytic water disinfection and antibacterial activity. *Carbon* **2022**, *196*, 877. [\[CrossRef\]](#)
- Pant, B.; Park, M.; Park, S.J. MoS<sub>2</sub>/CdS/TiO<sub>2</sub> ternary composite incorporated into carbon nanofibers for the removal of organic pollutants from water. *Inorg. Chem. Commun.* **2019**, *102*, 113–119. [\[CrossRef\]](#)

12. Chen, Z.; Li, X.; Wu, Y.; Zheng, J.; Peng, P.; Zhang, X.; Duan, A.; Wang, D.; Yang, Q. S-scheme  $\text{Cs}_2\text{AgBiBr}_6/\text{Ag}_3\text{PO}_4$  heterojunction with efficient photocatalysis performance for  $\text{H}_2$  production and organic pollutant degradation under visible light. *Sep. Purif. Technol.* **2022**, *295*, 121250. [\[CrossRef\]](#)
13. Zia, A.; Naveed, A.B.; Javaid, A.; Ehsan, M.F.; Mahmood, A. Facile Synthesis of  $\text{ZnSe}/\text{Co}_3\text{O}_4$  Heterostructure Nanocomposites for the Photocatalytic Degradation of Congo Red Dye. *Catalysts* **2022**, *12*, 1184. [\[CrossRef\]](#)
14. Wang, L.; Wang, L.; Shi, Y.; Zhu, J.; Zhao, B.; Zhang, Z.; Ding, G.; Zhang, H. Fabrication of  $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3\text{-Ti}$  catalytic membrane for efficient degradation of organic pollutants in water by peroxymonosulfate activation. *J. Colloid Interface Sci.* **2022**, *607*, 451. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Chen, L.J.; Chen, C.W.; Huang, C.P.; Chuang, Y.; Nguyen, T.B.; Dong, C.D. A visible-light sensitive  $\text{MoS}_2$  nanohybrid for the photocatalytic degradation of tetracycline, oxytetracycline, and chlortetracycline. *J. Colloid Interface Sci.* **2022**, *616*, 67. [\[CrossRef\]](#)
16. Zhu, C.; Zhang, L.; Jiang, B.; Zheng, J.; Hu, P.; Li, S.; Wu, M.; Wu, W. Fabrication of Z-scheme  $\text{Ag}_3\text{PO}_4/\text{MoS}_2$  composites with enhanced photocatalytic activity and stability for organic pollutant degradation. *Appl. Surf. Sci.* **2016**, *377*, 99–108. [\[CrossRef\]](#)
17. Kumar, S.; Maivizhikannan, V.; Drews, J.; Krishnan, V. Fabrication of nanoheterostructures of boron doped  $\text{ZnO-MoS}_2$  with enhanced photostability and photocatalytic activity for environmental remediation applications. *Vacuum* **2019**, *163*, 88–98. [\[CrossRef\]](#)
18. Zhong, Y.; Wang, F.; Liang, C.; Guan, Z.; Lu, B.; He, X.; Yang, W.  $\text{ZnO@MoS}_2$  Core-Shell Heterostructures Enabling Improved Photocatalytic Performance. *Appl. Sci.* **2022**, *12*, 4996. [\[CrossRef\]](#)
19. Dharman, R.K.; Shejale, K.P.; Kim, S.Y. Efficient sonocatalytic degradation of heavy metal and organic pollutants using  $\text{CuS}/\text{MoS}_2$  nanocomposites. *Chemosphere* **2022**, *305*, 135415. [\[CrossRef\]](#)
20. Chen, L.J.; Chuang, Y.J. Directly electrospinning growth of single crystal  $\text{Cu}_2\text{ZnSnS}_4$  nanowires film for high performance thin film solar cell". *J. Power Sources* **2013**, *241*, 259. [\[CrossRef\]](#)
21. Chen, L.J.; Chuang, Y.J. Diethylenetriamine assisted synthesis and characterization of stannite quaternary semiconductor  $\text{Cu}_2\text{ZnSnSe}_4$  nanorods by self-assembly. *J. Cryst. Growth* **2013**, *376*, 11. [\[CrossRef\]](#)
22. Zhao, L.; Yu, T.; Yang, B.; Guo, H.; Liu, L.; Zhang, J.; Gao, C.; Yang, T.; Wang, M.; Zhang, Y. Wastewater Purification and All-Solid Z-Scheme Heterojunction  $\text{ZnO-C}/\text{MnO}_2$  Preparation: Properties and Mechanism. *Catalysts* **2022**, *12*, 1250. [\[CrossRef\]](#)
23. Chen, L.J.; Lee, C.R.; Chuang, Y.J.; Wu, Z.H.; Chen, C. Synthesis and Optical Properties of Lead-Free Cesium Tin Halide Perovskite Quantum Rods with High-Performance Solar Cell Application. *J. Phys. Chem. Lett.* **2016**, *7*, 5028. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Chen, L.J. Synthesis and optical properties of lead-free cesium germanium halide perovskite quantum rods. *RSC Adv.* **2018**, *18*, 18396–18399. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Zhao, H.; Zhang, J.; Zheng, H. Facile preparation of dual Z-scheme  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{Ag}_6\text{Si}_2\text{O}_7$  photocatalyst for highly efficient visible-light photocatalytic degradation of organic pollutants. *Appl. Surf. Sci.* **2020**, *527*, 146901. [\[CrossRef\]](#)
26. Wang, J.; Zhang, Q.; Deng, F.; Luo, X.; Dionysiou, D.D. Rapid toxicity elimination of organic pollutants by the photocatalysis of environment-friendly and magnetically recoverable step-scheme  $\text{SnFe}_2\text{O}_4/\text{ZnFe}_2\text{O}_4$  nano-heterojunctions. *Chem. Eng. J.* **2020**, *379*, 122264. [\[CrossRef\]](#)
27. Lu, M.; Javed, M.; Javed, K.; Tan, S.; Iqbal, S.; Liu, G.; Khalid, W.B.; Qamar, M.A.; Alrbyawi, H.; Pashameah, R.A.; et al. Construction of a Well-Defined S-Scheme Heterojunction Based on  $\text{Bi-ZnFe}_2\text{O}_4/\text{S-g-C}_3\text{N}_4$  Nanocomposite Photocatalyst to Support Photocatalytic Pollutant Degradation Driven by Sunlight. *Catalysts* **2022**, *12*, 1175. [\[CrossRef\]](#)
28. Shehzad, N.; Zafar, M.; Ashfaq, M.; Razzaq, A.; Akhter, P.; Ahmad, N.; Hafeez, A.; Azam, K.; Hussain, M.; Kim, W.Y. Development of  $\text{AgFeO}_2/\text{rGO}/\text{TiO}_2$  Ternary Composite Photocatalysts for Enhanced Photocatalytic Dye Decolorization. *Crystals* **2020**, *10*, 923. [\[CrossRef\]](#)
29. Tien, T.M.; Chung, Y.J.; Huang, C.T.; Chen, E.L. WSSe Nanocomposites for Enhanced Photocatalytic Hydrogen Evolution and Methylene Blue Removal under Visible-Light Irradiation. *Materials* **2022**, *15*, 5616. [\[CrossRef\]](#)
30. Tien, T.M.; Chung, Y.J.; Huang, C.T.; Chen, E.L. Fabrication of  $\text{WS}_2/\text{WSe}_2$  Z-Scheme Nano-Heterostructure for Efficient Photocatalytic Hydrogen Production and Removal of Congo Red under Visible Light. *Catalysts* **2022**, *12*, 852. [\[CrossRef\]](#)
31. You, J.; Zhang, L.; He, L.; Zhang, B. Photocatalytic degradation of methyl orange on  $\text{ZnO-TiO}_2/\text{SO}_4^{2-}$  heterojunction composites. *Opt. Mater.* **2022**, *131*, 112737. [\[CrossRef\]](#)
32. Chen, L.; Zhang, M.; Wu, J.; Zheng, X.; Liao, S.; Ou, B.; Tian, L. In situ embedment of  $\text{CoO}_x$  on  $\text{g-C}_3\text{N}_4$  as Z scheme heterojunction for efficient photocatalytic degradation of methyl orange and phenol under visible light. *J. Alloys Compd.* **2022**, *927*, 167047. [\[CrossRef\]](#)
33. Sindelo, A.; Britton, J.; Lanterna, A.E.; Scaiano, J.C.; Nyokong, T. Decoration of glass wool with zinc (II) phthalocyanine for the photocatalytic transformation of methyl orange. *J. Photochem. Photobiol. A Chem.* **2022**, *432*, 114127. [\[CrossRef\]](#)
34. Wang, R.; Wang, Y.; Zhang, N.; Lin, S.; He, Y.; Yan, Y.; Hu, K.; Sun, H.; Liu, X. Synergetic piezo-photocatalytic effect in SbSI for highly efficient degradation of methyl orange. *Ceram. Int.* **2022**, *48*, 31818–31826. [\[CrossRef\]](#)
35. Oyewo, O.A.; Ramaila, S.; Mavuru, L.; Onwudiwe, D.C. Enhanced photocatalytic degradation of methyl orange using  $\text{Sn-ZnO}/\text{GO}$  nanocomposite. *J. Photochem. Photobiol.* **2022**, *11*, 100131. [\[CrossRef\]](#)
36. Guan, J.; Long, Z.; Li, Q.; Han, J.; Du, H.; Wang, P.; Zhang, G. Citric acid modulated preparation of CdS photocatalyst for efficient removal of Cr (VI) and methyl orange. *Opt. Mater.* **2021**, *121*, 111604. [\[CrossRef\]](#)
37. Uma, K.; Muniranthinam, E.; Chong, S.; Yang, T.C.K.; Lin, J.H. Fabrication of Hybrid Catalyst  $\text{ZnO Nanorod}/\alpha\text{-Fe}_2\text{O}_3$  Composites for Hydrogen Evolution Reaction. *Crystals* **2020**, *10*, 356. [\[CrossRef\]](#)

38. Zhang, N.; Peng, S.; Liu, Z.; Li, Y.; Huang, J.; Li, J.; Wan, H.; Zhou, S.; Gao, Z.; Chen, T. Ag NPs decorated on the magnetic  $\text{Fe}_3\text{O}_4$ @PDA as efficient catalyst for organic pollutants removal and as effective antimicrobial agent for microbial inhibition. *J. Alloys Compd.* **2022**, *928*, 167257. [[CrossRef](#)]
39. Vadivel, S.; Fujii, M.; Rajendran, S. Novel S-scheme 2D/2D  $\text{Bi}_4\text{O}_5\text{Br}_2$  nanoplatelets/g- $\text{C}_3\text{N}_5$  heterojunctions with enhanced photocatalytic activity towards organic pollutants removal. *Environ. Res.* **2022**, *213*, 113736. [[CrossRef](#)]
40. Chen, L.J.; Chuang, Y.J. Quaternary Semiconductor Derived and formation mechanism by non-vacuum Route from Solvothermal Nanostructures for High-Performance application. *Mater. Lett.* **2013**, *91*, 372. [[CrossRef](#)]