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# Pyrene-Based Conjugated Polymer/Bi<sub>2</sub>MoO<sub>6</sub> Z-Scheme Hybrids: Facile Construction and Sustainable Enhanced Photocatalytic Performance in Ciprofloxacin and Cr(VI) Removal under Visible Light Irradiation

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Abstract: The search for appropriate materials with favorable staggered energy band arrangements is important and is a great challenge in order to fabricate Z-scheme photocatalysts with high activity in visible light. In this study, we demonstrated a facile and feasible strategy to construct highly active organic-inorganic Z-scheme hybrids (P-BMO) with linear pyrene-based conjugated polymer (P17-E) and Bi<sub>2</sub>MoO<sub>6</sub>, via an in-situ palladium-catalyzed cross-coupling reaction. The characterization results revealed C-O chemical bond formed at the heterointerface between P17-E and Bi<sub>2</sub>MoO<sub>6</sub> after in-situ polycondensation and endowed the hybrids with observably improved photogenerated carries transfer capabilities. Visible, light-driven photocatalytic removal of ciprofloxacin and Cr(VI) were significantly enhanced after the incorporation of P17-E into  $Bi_2MoO_{6t}$ , whether with the morphology of nanosheets, nanobelts, or microspheres. Moreover, these P-BMO hybrids were also found to exhibit excellent sustainable photocatalytic performance after four runs of photocatalytic evaluation tests, suggesting their high activity and stability. To better eliminate the redox ability enhancement of P-BMO, a reasonable Z-scheme electrons transferring mechanism between P17-E and Bi<sub>2</sub>MoO<sub>6</sub> was proposed and proved by the determination of  $\bullet O_2^-$  and  $\bullet OH$  and Pt nanoparticles photodeposition experiments. This work might provide a viable source and insight into the design of Z-scheme photocatalysts with excellent redox ability for environmental remediation.

Keywords: photocatalysis; Z-scheme; conjugated polymer; Bi<sub>2</sub>MoO<sub>6</sub>

# 1. Introduction

As a trustworthy technique to harvest solar light for environmental remediation, photocatalysis has been widely utilized in the removal of antibiotics and heavy metals by virtue of its sustainable, economical, and environmentally benign properties [1–4]. To acquire suitable photocatalysts with broad photo absorption, fast charge transportation, and efficient surface reactions, several commonly used techniques have been explored, such as sensitization, doping, fabrication of heterojunction, surface engineering, and so on [5–9]. Among them, the fabrication of Z-scheme hybrids, especially the direct Z-scheme photocatalysts, is recognized to be extraordinarily attractive, since it can enormously extend the light absorption region and accelerate the separation of  $e^-/h^+$  pairs [10–12]. Meanwhile, the direct recombination of carriers between two components can also liberate the conduction band



(CB) and valence band (VB) with stronger redox abilities, thus endowing the hybrids with efficient surface reactions [11,13]. For instance, a direct Z-scheme photocatalyst with the  $W_{18}O_{49}/g-C_3N_4$  heterostructure, reported by Zhang et al., was found to possess almost a full-spectrum-driven photocatalytic activity for highly efficient H<sub>2</sub> evolution [14]. Hong et al. explored V<sub>2</sub>O<sub>5</sub>-decorated g-C<sub>3</sub>N<sub>4</sub> as a Z-scheme photocatalyst for efficient environmental purification [15]. Furthermore, Li et al. synthesized Z-scheme Bi<sub>2</sub>MoO<sub>6</sub>/MO (M = Cu, Co<sub>3</sub>/<sub>4</sub>, or Ni) hybrids with enhanced photocatalytic performance toward organic degradation [16]. However, limited by the intrinsic band-gap and corresponding band potentials of conventional semiconductors, it remains a great challenge to seek out appropriate materials with favorable staggered energy band arrangements to fabricate highly active Z-scheme photocatalysts.

Recently, conjugated polymers (CPs), consisting of  $\pi$ -electron conjugated structure, have emerged as a functional organic semiconductor because of their marvelous photoelectrochemical activity and charge carriers mobility [17–19]. In addition to the traditional utilizations in light-driven organic synthesis and organic photovoltaics, CPs have also displayed fantastic performance in photocatalysis, such as poly(diphenylbutadiyne) for pollutants degradation, polybenzothiadiazoles for H<sub>2</sub> evolution, and poly(dibenzo[*b*,*d*]thiophene 5,5-dioxide) for NO oxidation [20–24]. In addition, unlike the conventional semiconductors, theirHighest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) potentials can be fine-tuned through varying the monomers or adjusting the molecular structures [25,26], implying that CPs might be ideal candidates for constructing Z-scheme hybrids, which has been confirmed by our previous studies. [27,28]. However, the heterocycles structure in CPs gave rise to their poor stability during the photocatalytic process. Accordingly, we further explored a new linear pyrene-based conjugated polymer (P17-E) without heteroatom, which exhibited high activity and stability in H<sub>2</sub> evolution [29]. This linear conjugated polymer is expected to be a better substitute in the construction of Z-scheme hybrids with superior stability and activity.

For confirmation, visible-light responsive Bi2MoO6 was selected as the model semiconductor to construct hybrid photocatalysts with P17-E, in view of its nontoxicity, intrinsic chemical inertness, suitable bandgap (2.5–2.8 eV), and layered structure (characterized by  $[Bi_2O_2]^{2+}$  slabs interleaved with double layers of perovskite-like  $[MoO_4]^{2-}$  [30,31]. Furthermore, various Bi<sub>2</sub>MoO<sub>6</sub>-based catalysts have been synthesized and applied in environmental remediation and CO2 photoreduction thus far [32–34]. However, constrained by the intrinsic band-gap and charge carriers mobility of  $Bi_2MoO_6$ , the quantum efficiencies of these materials still need to be further strengthened [35,36]. Here, the Z-scheme hybrids (P-2BMO) were first fabricated through the cross-coupling reaction of 1,6-dibromopyrene and 1,4-diethynylbenzene on the surface of Bi<sub>2</sub>MoO<sub>6</sub> nanosheets. Extensive characterizations were employed to investigate the crystallinity, morphology, chemical states, and optical property of the hybrids. Photocatalytic removal of ciprofloxacin and Cr(VI) under visible light irradiation were utilized to evaluate the photocatalytic activity of these novel organic–inorganic hybrids. Moreover, to evaluate the applicability of the method for constructing Z-scheme photocatalysts, 6.7% P-1BMO and 6.7% P-3BMO hybrids were further fabricated using Bi<sub>2</sub>MoO<sub>6</sub> nanobelts and microspheres, respectively. Their photocatalytic activity was also investigated and compared with the pristine P17-E and  $Bi_2MoO_6$ . Finally, based on systematical measurements—including photoelectrochemical tests and determination of reactive species—a reasonable Z-scheme mechanism was proposed and verified by a series of credible techniques, including the nitroblue tetrazolium (NBT) photodegradation, terephthalic acid (TA) photo-luminescence probing technique, and Pt nanoparticles photodeposition experiment [37-39]. This work, using different dimensional Bi<sub>2</sub>MoO<sub>6</sub> as the model materials, provides an available strategy to construct Z-scheme organic-inorganic hybrid photocatalysts with enhanced photocatalytic performance.

## 2. Results and Discussion

## 2.1. Characterization of the Samples

The crystalline and morphologic properties of the hybrids are illustrated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis (Figure 1). As shown in Figure 1a, the as-prepared Bi<sub>2</sub>MoO<sub>6</sub> nanosheets showed distinctive diffraction peaks at  $2\theta = 28.2^{\circ}$ ,  $32.6^{\circ}$ ,  $33.1^{\circ}$ , 36.0°, 46.7°, 47.1°, 55.5°, 56.2°, and 58.4°, which can be indexed to the (131), (002), (060), (151), (202), (062)/(260), (331)/(133), (191), and (262) planes, respectively, of the orthorhombic phase Bi<sub>2</sub>MoO<sub>6</sub> (JCPDS card no. 76-2388) [30]. P17-E is found to be amorphous with broad and low peaks, which is common in conjugated polymers. When compared with the pristine  $Bi_2MoO_6$  nanosheets, no significant change in the XRD patterns of P-2BMO hybrids can be observed, indicating that the incorporation of P17-E made no difference to the crystal structure of 2BMO. TEM images in Figure 1b,c demonstrate that the pristine 2BMO and P17-E are composed of homogeneous nanosheets and agglomerate flakes, respectively. After introducing P17-E to the surface of Bi<sub>2</sub>MoO<sub>6</sub> nanosheets, some nonspecific flakes can be observed in the TEM image of 6.7% P-2BMO (Figure 1d), indicating that intimate contact occurs in the hybrid photocatalyst. In addition, the hybrids are observed to have legible orthorhombic lattice fringes with spaces of 0.274 nm and 0.275 nm (inset in Figure 1d), corresponding to the (002) and (200) planes, respectively, of  $Bi_2MoO_6$ . The coverture layer without lattice fringe can be thought of as the P17-E attached to the Bi<sub>2</sub>MoO<sub>6</sub>.



**Figure 1.** (a) X-ray diffraction (XRD) patterns of Z-scheme hybrids (2BMO), 6.7% P-2BMO, and linear pyrene-based conjugated polymer (P17-E); transmission electron microscopy (TEM) images of (b) 2BMO, (c) P17-E, and (d) 6.7% P-2BMO, inset shows the corresponding high-resolution transmission electron microscopy (HRTEM) images; and (e) Raman spectra of 2BMO, 6.7% P-2BMO, and P17-E.

For better confirmation on the successful introduction of P17-E on  $Bi_2MoO_6$ , Raman spectroscopy was first conducted to investigate the structure of the as-prepared samples (Figure 1e). Peaks at 1362 cm<sup>-1</sup>, 1537 cm<sup>-1</sup>, and 2204 cm<sup>-1</sup> in pure P17-E were identified as ring stretch, C=C stretch, and C=C stretch, respectively [40]. For pristine  $Bi_2MoO_6$  nanosheets, peaks around 805 cm<sup>-1</sup> with two shoulders at 722 and 852 cm<sup>-1</sup> were indexed to the stretching modes of the Mo-O bond and the

 $v_1$  (A1g) vibration for the distorted MoO<sub>6</sub> octahedron, respectively. Peaks between 270 and 360 cm<sup>-1</sup> corresponded to the different bending modes of the MoO<sub>6</sub> octahedral unit [41]. As for the P-2BMO hybrid, all peaks above were observed, while the corresponding Bi<sub>2</sub>MoO<sub>6</sub> Raman peaks' intensity became weaker after the coating of P17-E on its surface, supporting the joint combination of P17-E and Bi<sub>2</sub>MoO<sub>6</sub>. This was further confirmed by Fourier transform infrared (FT-IR) analysis, in which the characteristic peak at 2200 cm<sup>-1</sup>, corresponding to the C $\equiv$ C stretching mode, was found in both pure P17-E and P-2BMO (Figure S1). The X-ray photoelectron spectroscopy (XPS) measurement was subsequently applied to investigate the chemical states and compositions of the hybrids. The typical XPS survey spectra of P17-E, 2BMO, and 6.7% P-2BMO in Figure 2a illustrated the existence of Bi, Mo, O, and C in 6.7% P-2BMO. Their corresponding high-resolution Bi 4f, Mo 3d, O 1s, and C 1s spectra were compared meticulously to gain a deep insight into the interaction between P17-E and Bi<sub>2</sub>MoO<sub>6</sub>. No obvious change could be observed in the Bi 4f and Mo 3d spectra of 2BMO and 6.7% P-2BMO (Figure S2a,b), in which the peaks at 158.7 and 164.0 eV were ascribed to Bi  $4f_{3/2}$  and Bi  $4f_{5/2}$ , respectively, while peaks at 235.1 and 232.0 eV were attributed to Mo  $3d_{3/2}$  and Mo  $3d_{5/2}$ , respectively [42]. For O 1s and C 1s spectra in Figure 2b,c, new peaks at 532.3 eV of O 1s and 288.0 eV of C 1s were observed in 6.7% P-2BMO when compared with the pure Bi<sub>2</sub>MoO<sub>6</sub> and P17-E, accompanied by the minor shift of the BiO peak from 530.78 to 530.76 eV. These new peaks could be ascribed to the formation of CO bond between P17-E and  $Bi_2MoO_6$  [43,44]. This was further verified via the FT-IR spectra (Figure S1a), in which the emerging weak broadband at ~1225 cm<sup>-1</sup> and a shoulder at ~1153 cm<sup>-1</sup>, corresponding to CO stretching vibrations, were detected in the 6.7% P–2BMO hybrid. Based on all of the characterizations above, it can be inferred that the conjugated polymer P17-E is tightly integrated with Bi<sub>2</sub>MoO<sub>6</sub> nanosheets through the formation of CO chemical bond at the heterointerface after in-situ polycondensation, rather than physical mixture, which might be in favor of electrons' migration between P17-E and Bi<sub>2</sub>MoO<sub>6</sub>.



**Figure 2.** X-ray photoelectron spectroscopy (XPS) spectra of 2BMO, 6.7% P-2BMO and P17-E: (**a**) survey spectra, (**b**) O 1s and (**c**) C 1s.

#### 2.2. Photocatalytic Performance of P-2BMO

Ciprofloxacin, as a broad-spectrum antibiotic agent that neither absorbs visible light nor has a sensitization effect, was selected to evaluate the photocatalytic performance of the catalysts [45]. The ciprofloxacin (CIP) photodecomposition efficiency over P-2BMO hybrids with different weight rations was first estimated to investigate the effects of P17-E content on the photocatalytic activity. As shown in Figure 3a, all of the P-2BMO composites exhibit much higher photocatalytic performance than the pristine P17-E and Bi<sub>2</sub>MoO<sub>6</sub> nanosheets, and the corresponding kinetic parameters are calculated and summarized in Figure 3b. Interestingly, the photodegradation efficiency showed an obvious improvement when the P17-E loading level was enhanced from 0 to 6.7%, and then went downhill upon further increase of P17-E proportion. The 6.7% P-2BMO composite, with a real content of approximately 5.9% (Figure S3), possesses the maximum rate constant of 0.034 min<sup>-1</sup>, which is approximately 17 and 5 times as high as that of pure P17-E and Bi<sub>2</sub>MoO<sub>6</sub> nanosheets, respectively. Obviously, the optimal proportion of P17-E for P-2BMO hybrids synthesis was determined to be 6.7%,

since excessive conjugated polymers (more than 6.7%) may impair the formation of the effective heterointerface, hamper the photoinduced carriers transfer, and thus restrain the photocatalytic performance. As expected, in addition to the superior photocatalytic capability, the 6.7% P-2BMO hybrids also exhibited high stability (Figure 3c). No obvious decrease in the photocatalytic activity could be observed even after four recycling runs. Similar to the photoreductive performance of Cr(VI) photoreduction were also carried out to evaluate the photoreductive performance of the samples. As shown in Figure 3d, in comparison with the pristine 2BMO and P17-E, the P-2BMO hybrid exhibits much higher photocatalytic reduction ability in toxic Cr(VI) removal within 50 min. All of these results demonstrated that the incorporation of P17-E into the inorganic semiconductor (Bi<sub>2</sub>MoO<sub>6</sub>) can strengthen both the photodegradation and photoreduction activity of Bi<sub>2</sub>MoO<sub>6</sub>. That is to say, it is feasible to synthesize highly active organic–inorganic composites in the existence of linear conjugated polymer P17-E.



**Figure 3.** (a) Photodegradation of ciprofloxacin over various photocatalysts under visible light irradiation; (b) corresponding rate constants over different photocatalysts; (c) cycling runs for ciprofloxacin degradation over 6.7% P-2BMO; and (d) photoreduction of Cr(VI) over 2BMO, 6.7% P-2BMO, and P17-E under visible light irradiation.

#### 2.3. Strategy Evaluation

To evaluate the applicability of the strategy for constructing highly active photocatalysts, we further synthesized 6.7% P-1BMO and 6.7% P-3BMO using  $Bi_2MoO_6$  nanobelts and microspheres, respectively. As shown in Figures S4–S8, systematic characterizations, including XRD, TEM, FT-IR, Raman, and thermogravimetric (TG) demonstrated that P17-E was also successfully introduced to the surface of 1BMO and 3BMO via the cross-coupling reaction. Furthermore, their photocatalytic performance was checked and is displayed in Figure S9. Obviously, when compared with P17-E and the pristine  $Bi_2MoO_6$ , the resulting 6.7% P-1BMO and 6.7% P-3BMO hybrids demonstrated

not only improved photooxidative ability in CIP decomposition, but also enhanced photoreductive performance in Cr(VI) removal, indicating the suitability of the proposed method to construct highly active organic–inorganic hybrids of different morphologies. In addition, 6.7% P-2BMO revealed the highest activity among all the hybrids, which can be ascribed to its sheet-like morphology. As shown in Figure 1d and Figure S5, the P17-E in 6.7% P-2BMO dispersed more uniformly, which guaranteed the strong attachment between Bi<sub>2</sub>MoO<sub>6</sub> nanosheets and P17-E, and thus facilitated the transportation of photoinduced charge carriers. In comparison with other photocatalysts displayed in Table S1, P-BMO hybrids can thought of as valuable photocatalytic materials with a broad photocatalytic spectrum, excellent recyclability, and impressive cyclic stability for treating wastewater.

#### 2.4. Insight of the Photocatalytic Mechanism

As is widely known, surface reactions, solar light harvesting, and  $e^-/h^+$  separation speak loudly in photocatalysis. Thus, we conducted the corresponding measurements to figure out the specific reasons for the enhanced photocatalytic activity over P-BMO composites, especially the most active 6.7% P-2BMO. Figure S10 shows the N<sub>2</sub> adsorption–desorption isotherms of the catalysts, in which all curves complied well with typical Type IV isotherm behavior. All of the P-BMO composites exhibited much larger Brunauer–Emmett–Teller (BET) surface areas than the corresponding pristine Bi<sub>2</sub>MoO<sub>6</sub> (Table S2), which could be ascribed to the more dispersive feature of P17-E in the hybrids, just as the TEM images displayed. That is to say, more surface-active sites might be offered after the hybridization of P17-E and BMO. Nevertheless, P-BMO hybrids still possessed much higher CIP degradation rates after surface area normalization, implying that the increased number of surface-active sites was not the major reason for boosting the photocatalytic activity over P-BMO composites.

The Ultraviolet-visible (UV-Vis) absorption spectra were measured and are displayed in Figure 4a. When compared with the three kinds of pristine  $Bi_2MoO_6$ , the corresponding hybrids exhibited much more intense continuous absorption over the Visible-near infrared (Vis-NIR) region, which could be attributed to the existence of the conjugate structure within P17-E. Based on the plots of  $(\alpha h\nu)^{1/2}$ versus photon energy ( $h\nu$ ), the band gap (E<sub>g</sub>) of 1BMO, 2BMO, and 3BMO were calculated to be 2.61, 2.62, and 2.63 eV, respectively (Figure 4b). In addition, their CB and VB positions were further investigated to analyze their photoredox ability. Figure 4c depicts the Mott-Schottky (MS) plots of the samples, from which the flat band potentials of 1BMO, 2BMO, and 3BMO were estimated to be -0.92, -0.87, and -0.85 V, respectively, versus the Ag/AgCl electrode, which were equal to -0.31, -0.26, and -0.24 V, respectively, versus the Normal Hydrogen Electrode (NHE). Since the CB potential of the Negative-type (n-type) semiconductors was more negative than that of the flat band by 0.1 eV, the CB potentials of 1BMO, 2BMO, and 3BMO were calculated to be -0.41, -0.36, and -0.34 V, respectively [46]. Combined with the band gaps, their VB positions were determined to be 2.20, 2.26, and 2.29 V. As for P17-E, its LUMO and HOMO potentials were found to be -0.80 and 1.12 eV in our previous report [29]. For better comparison, the respective data are summarized in Table S3 and displayed in Figure 4d. Obviously, favorable staggered energy band arrangements were obtained between P17-E and Bi<sub>2</sub>MoO<sub>6</sub>. Through the tight C-O connection formed in the interface as previous discussed, the separation and migration of photoinduced  $e^{-}/h^{+}$  might be significantly promoted.



**Figure 4.** (a) Ultraviolet–visible (UV-Vis) absorption spectra of all the samples; (b) plots of  $(\alpha h\nu)1/2$  versus energy *hv*; (c) Mott–Schottky plots for 1BMO, 2BMO, and 3BMO; and (d) the diagram of band positions for 1BMO, 2BMO, 3BMO, and P17-E.

Hence, the steady-state photoluminescence (PL) measurements, photocurrent measurements and electrochemical impedance spectra (EIS) were performed for further confirmation. As shown in Figure 5a, all three P-BMO composites displayed much weaker fluorescence intensity than the corresponding pristine  $Bi_2MoO_6$ , implying that the construction of effective hybrids could markedly inhibit the recombination of  $e^-/h^+$  pairs. Among all of the composites, 6.7% P-2BMO presented the lowest fluorescence intensity, which was in accord with the results of activity tests. Moreover, all of the hybrids exhibited higher photocurrents and smaller semicircle diameters in comparison with 1BMO, 2BMO, 3BMO, and P17-E, corresponding to the enhanced separation efficiency and mobility of photoinduced carriers (Figure 5b,c, and Figure S11). As such, more active species can participate in the catalytic reaction, including electrons, holes,  $\bullet O_2^-$ , and so on, thus significantly enhancing the photocatalytic activity.



**Figure 5.** (a) Photoluminescence (PL) spectra of all of the samples; (b) photocurrent response spectra; and (c) electrochemical impedance spectra of 2BMO, P17-E, and 6.7% P-BMO.

The trapping experiments were subsequently conducted to figure out the contribution of the active species during the CIP decomposition over different catalysts. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, triethanolamine (TEOA), isopropanol (IPA), superoxide dismutase (SOD), and  $\beta$ -carotene were taken as the scavengers for  $e^-$ ,  $h^+$ , •OH, •O<sub>2</sub><sup>-</sup>, and <sup>1</sup>O<sub>2</sub>, respectively [47]. As displayed in Figure 6, for both 2BMO and 6.7% P-2BMO, the slight decreases in photocatalytic performance with the existence of IPA demonstrated that •OH

was not the main active species in CIP removal, whereas the remarkable inhibition on CIP degradation caused by TEOA implied the crucial effects of holes on CIP removal for both of them. This was the reason for the obvious improvement in the photocatalytic activity of 2BMO after  $K_2Cr_2O_7$  was added to trap electrons, leaving more holes to degrade CIP. Besides, approximately 15.9% and 23.5% CIP decomposition were hampered for 2BMO and 6.7% P-2BMO, respectively, under the presence of SOD, while about 60.3% and 85.3% CIP removal were inhibited for 2BMO and 6.7% P-2BMO, respectively, after the addition of  $\beta$ -carotene.



**Figure 6.** Trapping measurements and the corresponding rate constants for ciprofloxacin photodegradation over 2BMO (**a**,**b**) and 6.7% P-2BMO (**c**,**d**). Triethanolamine (TEOA); isopropanol (IPA); superoxide dismutase (SOD).

These results suggested that  $\bullet O_2^-$  and  ${}^1O_2$  were also important active radicals in CIP degradation. The enhanced inhibition proportions of  $\bullet O_2^-$  and  ${}^1O_2$  for 6.7% P-2BMO implied that the modification of Bi<sub>2</sub>MoO<sub>6</sub> with P17-E might improve the generation of  $\bullet O_2^-$  and  ${}^1O_2$ . Similar results were also observed when comparing either 1BMO with 6.7% P-1BMO or 3BMO with 6.7% P-3BMO (Figures S12 and S13).

Accordingly, the electron spin resonance (ESR) spectra of 2BMO, P17-E, and 6.7% P-2BMO were recorded to confirm this corollary. As expected, the 6.7% P-2BMO hybrid indeed possessed a much higher  $\bullet O_2^{-}$ ,  ${}^1O_2$ , and  $\bullet OH$  generation capability than that of the pristine 2BMO and P17-E after being irradiated in visible light for 12 min (Figure 7). As shown in Figure 7a, signals of 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO)- $\bullet O_2^{-}$  adduct were detected in all samples under visible light irradiation. This is consistent with the previous band position analysis (Figure 4d), because the conduction band potentials of both 2BMO (-0.36 V vs NHE) and P17-E (-0.80 V NHE) were more negative than that of molecule oxygen reduction ( $O_2/\bullet O_2^{-}$ , -0.33 V vs NHE). As the HOMO potential of P17-E (1.12 V) was not positive enough to oxidize H<sub>2</sub>O (H<sub>2</sub>O/ $\bullet$ OH, 2.40 V) or surface hydroxyl (1.99 V), the  $\bullet$ OH generated over P17-E might be derived from the reaction of  $\bullet O_2^{-}$  via  $\bullet O_2^{-} \rightarrow H_2O_2 \rightarrow \bullet$ OH process (Figure 7c) [48–50].

For better confirmation, quantitative determination of  $\bullet O_2^-$  and  $\bullet OH$  over 2BMO, P17-E, and 6.7% P-2BMO were thus conducted through the NBT photodegradation and TA photoluminescence (PL) tests under visible light irradiation (Figure 8, Figures S14, and S15). As displayed in Figure 8a,  $\bullet O_2^-$  accumulation was found for all samples under the visible light irradiation. Among them, the 6.7% P-2BMO possessed the highest  $\bullet O_2^-$  concentration (28.2 µmol/L) in three hours, which is similar to the ESR results. During the whole  $\bullet OH$  determination tests, N<sub>2</sub> was bubbled in the solution to exclude

the  $\bullet O_2^- \rightarrow H_2O_2 \rightarrow \bullet OH$  path. As can be seen in Figure 8b, an obvious  $\bullet OH$  generation was found for 2BMO in visible light without the involvement of  $O_2$ , confirming that 2BMO can directly oxidize surface hydroxyl to •OH. As for P17-E, almost no •OH was accumulated in three hours under visible light irradiation after O2 was excluded by N2, which was in line with expectations, thereby verifying that the •OH detected by the ESR results from the transformation of  $\bullet O_2^-$ . Intriguingly, the 6.7% P-2BMO can also oxidize the surface hydroxyl and generate more •OH in comparison with 2BMO. That is to say, the P-BMO hybrids conserved the stronger oxidizing ability of BMO and the higher reducing ability of P17-E as well, thus we deduce that the electron transfer mode of P-BMO is Z-scheme, rather than the conventional type II (Figure 8c). This was further confirmed by Pt photodeposition experiments. From the high-resolution transmission electron microscopy (HRTEM) images of Pt nanoparticles (NPs) decorated 6.7% P-2BMO (Figure 8d-f), most of the Pt NPs with clear characteristic lattice fringes corresponding to the Pt (111) plane were observed on the surface of P17-E, rather than Bi2MoO6 nanosheets. As Pt NPs are inclined to deposit and accumulate around electron-rich sites because of the electrophilic nature of Pt<sup>4+</sup> species [39], it could be inferred that the electrons were transported from the CB of 2BMO to the HOMO of P17-E through the Z-scheme mechanism, and thus reduced the Pt (IV) to Pt NPs on the surface of P17-E. Combining the above results, the Z-scheme mechanism was proved to be reasonable, validating the availability of the proposed strategy to construct Z-scheme organic-inorganic hybrids with enhanced photocatalytic performance.



**Figure 7.** Electron spin resonance (ESR) spectra of 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO)- $\bullet O_2^-$  (**a**), 2,2,6,6-tetramethylpiperidine (TEMP)- $^1O_2$  (**b**), and DMPO- $\bullet$ OH (**c**).



**Figure 8.** Quantitative determination of  $\bullet O_2^-$  (**a**) and  $\bullet OH$  (**b**) generation for 2BMO, 6.7% P-2BMO, and P17-E; (**c**) proposed photocatalytic mechanism of P-BMO according to Z-scheme electron transfer mode; (**d**–**f**) TEM and corresponding HRTEM images of 6.7% P-2BMO hybrid after in-situ photodeposition of Pt from H<sub>2</sub>PtCl<sub>6</sub>.

#### 3. Materials and Methods

## 3.1. Materials

Bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O), oleylamine, nitric acid, ammonia, ethylene glycol, *N*, *N*-Dimethylformamide (DMF), triethylamine (TEA), methanol (MeOH), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), and copper(I) iodide (CuI) were purchased from Sinopharm Chemical Reagent Corp. (China, Shanghai). Bis(triphenylphosphine)palladium(II) chloride (Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>) was obtained from Energy Chemical. 1,6-Dibromopyrene and 1,4-diethynylbenzene were supplied by Shanghai Bepharm Corporation (Shanghai, China). All of the reagents were analytically pure level and used as received without further purification. Deionized water was used throughout the synthesis.

#### 3.2. Preparation of Photocatalysts

The pristine conjugated polymer P17-E was synthesized via the Sonogashira–Hagihara crosscoupling reaction following our previous report [29]. The Bi<sub>2</sub>MoO<sub>6</sub> nanosheets (2BMO) were synthesized via a facile hydrothermal process. Typically, 2 mmol Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O was dissolved in 20 mL nitric acid solution (2 M). Then, 10 mL Na<sub>2</sub>MoO<sub>4</sub> solution (0.1 M) was added to the above solution under vigorous magnetic stirring. Following this, the pH value of the system was adjusted to seven, with concentrated ammonia. The obtained light-yellow suspension was transferred into a Teflon-lined stainless steel autoclave, and heated at 180 °C for 24 h. Finally, the resultant precipitates were collected, washed with deionized water and ethanol, and dried at 80 °C overnight.

The P-2BMO hybrids were fabricated by in-situ polycondensation of P17-E in the presence of  $Bi_2MoO_6$  nanosheets. As schematically illustrated in Scheme S1, a schlenk tube was charged with  $Bi_2MoO_6$ , 1,6-Dibromopyrene, 1,4-diethynylbenzene, Pd(PPh\_3)\_2Cl\_2, CuI, and 10 mL mixed solvent (DMF/TEA = 1/1). The resulting mixture was then stirred at 80 °C for 24 h under Ar atmosphere. Following this, the obtained brown precipitate was filtered off, washed in the Soxhlet extractor containing the mixed solvent of DCM/MeOH for about 48 h, and dried at 60 °C overnight. Moreover, in order to determine the optimum P17-E amount in the hybrids, a series of P-2BMO with different weight ratios were synthesized and labeled as 3.3%, 6.7%, 10%, and 16.7% P-2BMO (x% means the mass ratio of P17-E to  $Bi_2MoO_6$  nanosheets on condition that the precursors were converted completely).

#### 3.3. Characterizations

X-ray diffraction (XRD) patterns were recorded through an X-ray diffractometer equipped with Cu K $\alpha$  radiation (D8 advance Bruker Inc., Karlsruhe, Germany). Raman spectra were acquired on a DXR Raman Microscope (Thermo Fisher, Massachusetts, USA). Fourier transform infrared (FT-IR) spectra were measured on a Nicolet iS50 FT-IR spectrometer (Thermo Fisher, Massachusetts, USA). Transmission electron microscopy (TEM) images were recorded on JEM-2010 (JEOL, Tokyo, Japan). High-resolution transmission electron microscopy (HRTEM) imaging was carried out on a Tecnai G2 F20 S-TWIN microscope (FEI, Oregon State, USA) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) tests were operated on an ESCALAB 250Xi system (Thermo Fisher, Massachusetts, USA), and all binding energies were referenced to the C 1s peak at 284.4 eV of the surface adventitious carbon. Diffuse reflection spectra (DRS) were acquired using a PerkinElmer lambda 650s UV-Vis spectrometer. The photoluminescence (PL) measurements were conducted on a PerkinElmer LS55 fluorescence spectrometer using 325 nm as the excitation wavelength. Brunauer-Emmett-Teller (BET) specific surface area was estimated on nitrogen adsorption-desorption apparatus (ASAP 2040, Micrometrics Inc., Shanghai, China) with all samples degassed at 100 °C for 12 h prior to measurements. Thermogravimetric (TG) analysis was performed in air atmosphere through a thermal gravimetric analyzer (TG209, NETZSCH Inc., Free State of Bavaria Germany) with the temperature increased from 30 to 800 °C and a heating rate of 10 °C  $\cdot$ min<sup>-1</sup>.

#### 3.4. Measurement of Photocatalytic Activity

The visible-light photocatalytic performance of the prepared catalysts was systematically evaluated by the photoremoval of ciprofloxacin (CIP) and toxic Cr(IV). A 300 W Xe lamp (PLS SXE300, Beijing Perfectlight Inc., Beijing, China) served as the simulated solar light source with a light filter ( $\lambda \ge 420$  nm) to eliminate UV light. For CIP photodegradation, 20 mg of the photocatalyst was dispersed in an aqueous solution of CIP (50 mL, 20 ppm). Prior to irradiation, the suspension was continuously stirred in the dark for 1 h to establish adsorption–desorption equilibrium. During the illumination, approximately 3 mL aliquots were sampled from the reactor at 15 min intervals over 60 min, followed by filtration to remove the solid. The concentration of CIP was determined by High Performance Liquid Chromatography (HPLC) equipped with an Agilent TC-C18 column and a UV Detector at 275 nm. The stability of the photocatalysts was evaluated through the recycling experiments. After each reaction, the photocatalyst was collected by centrifugation, washed, dried, and then used for the next run.

Similar to the CIP photodegradation, the photoreduction of toxic Cr(IV) was carried out as follows: 50 mg photocatalyst was suspended in an aqueous solution of Cr(IV) (50 mL, 20 ppm) and 0.01 M·HCl. After the adsorption equilibrium in the dark, approximately 4 mL aliquots were collected and centrifuged at given intervals during the irradiation. The concentration of Cr(IV) was evaluated via the standard diphenylcarbazide (DPC) method with a Shimadzu UV-Vis spectrophotometer.

## 3.5. Detection of Reactive Species

For the trapping experiments, various scavengers were added into the ciprofloxacin aqueous solution to capture the corresponding active species. Briefly, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, triethanolamine (TEOA), isopropanol (IPA), superoxide dismutase (SOD), and natural  $\beta$ -carotene served as electron, hole,  $\bullet$ OH,  $\bullet$ O<sub>2</sub><sup>-</sup>, and <sup>1</sup>O<sub>2</sub> scavengers, respectively. Electron paramagnetic resonance spectroscopy with 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO)-methanol, DMPO, and 2,2,6,6-tetramethylpiperidine (TEMP) as trapping agents, the spin-reactive species were used to detect the  $\bullet$ O<sub>2</sub><sup>-</sup>,  $\bullet$ OH, and <sup>1</sup>O<sub>2</sub>, respectively. The amount of  $\bullet$ O<sub>2</sub><sup>-</sup> was quantitatively analyzed by measuring the wastage of nitroblue tetrazolium (NBT, 2 × 10<sup>-5</sup> mol · L<sup>-1</sup>) on a UV-Vis spectrophotometer at 259 nm, while the generation of  $\bullet$ OH was quantified by detecting the concentration of 2-OH-terephthalic acid, generated from the reaction of terephthalic acid (TA, 5 × 10<sup>-4</sup> mol L<sup>-1</sup> in a 2 × 10<sup>-3</sup> mol L<sup>-1</sup> NaOH solution) with  $\bullet$ OH, using a fluorescence spectrophotometer with the excitation wavelength at 312 nm.

## 3.6. Photoelectrochemical Measurements

All of the photoelectrochemical experiments, including the CV test, photocurrent, electrochemical impedance spectra (EIS), and Mott–Schottky (MS) measurements, were performed on the CHI 660D electrochemical work station (Chenhua Instrument, Shanghai, China). A platinum foil and Ag/AgCl (saturated KCl) were utilized as the counter electrode and reference electrode, respectively. For the CV test, the glassy carbon electrode was applied as the working electrode with 0.1 M TBAPF<sub>6</sub> in acetonitrile as the electrolyte. For the other measurements, the working electrodes were prepared as in our previous paper [27]. In addition, 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte in the photocurrent and MS measurements, while the electrolyte in the EIS test was the mixture solution of 0.1 M KCl and 0.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]. A 300 W Xe lamp (PLS SXE300, Beijing Perfectlight Inc., Beijing, China) was utilized as the light source during the photocurrent measurement.

## 4. Conclusions

In summary, the original organic–inorganic Z-scheme hybrids (P-BMO) were designed and synthesized via the in situ cross-coupling reaction. The incorporation of P17-E into the inorganic semiconductor ( $Bi_2MoO_6$ ) was proven to be a feasible strategy to enhance both the photooxidation and photoreduction activity of  $Bi_2MoO_6$ . The characterization results demonstrated that the enhanced

performance could be attributed to the wider visible light absorption, higher  $e^-/h^+$  separation, and larger surface area. In line with the results of photoelectrochemical measurements and trapping tests, the reasonable Z-scheme mechanism was proposed and verified via the determination of reactive species ( $\bullet O_2^-$  and  $\bullet OH$ ) and Pt nanoparticles photodeposition experiments. This work, using different dimensional Bi<sub>2</sub>MoO<sub>6</sub> as the model materials, provides a suitable strategy to construct Z-scheme organic–inorganic hybrid photocatalysts with enhanced photocatalytic performance.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/5/185/s1, Scheme S1: In situ generation of P17-E on the surface of different dimensional Bi<sub>2</sub>MoO<sub>6</sub>; Figure S1: FT-IR spectra of 2BMO, 6.7% P-2BMO and P17-E; Figure S2: (a) XPS spectra of Bi 4f (b) and Mo 3d; Figure S3: TG analysis of 2BMO, 6.7% P-2BMO and P17-E; Figure S4: XRD patterns of 1BMO, 3BMO, 6.7% P-1BMO, 6.7% P-3BMO and P17-E; Figure S5: TEM images of 1BMO (a), 6.7% P-1BMO (b), 3BMO (c) and 6.7% P-3BMO (d), inset shows the corresponding HRTEM images; Figure S6: FT-IR spectra of 1BMO, 3BMO, 6.7% P-1BMO, 6.7% P-3BMO and P17-E; Figure S7: Raman spectra of 1BMO, 3BMO, 6.7% P-1BMO, 6.7% P-3BMO and P17-E; Figure S8: TG analysis of 1BMO, 3BMO, 6.7% P-1BMO, 6.7% P-3BMO and P17-E; Figure S9: Photodegradation of ciprofloxacin (a) and photoreduction of Cr(VI) (b) over 1BMO, 3BMO, 6.7% P-1BMO, 6.7% P-3BMO and P17-E; Figure S10: N<sub>2</sub>-adsorption-desorption isotherms of all the samples; Figure S11: photocurrent response spectra (a) and electrochemical impedance spectra (b) of all the samples; Figure S12: Trapping measurements and the corresponding rate constants for ciprofloxacin photodegradation over1BMO (a,b) and 6.7% P-1BMO (c,d); Figure S13: Trapping measurements and the corresponding rate constants for ciprofloxacin photodegradation over 3BMO (a,b) and 6.7% P-3BMO (c,d); Figure S14: Spectra of NBT transformation generated by 2BMO (a), P17-E (b) and 6.7% P-2BMO (c) under visible light irradiation. Table S1: Comparison of the photodegradation activity; Table S2: BET surface areas of all the samples; Table S3: The analysis of band positions for 1BMO, 2BMO and 3BMO.

**Author Contributions:** In this paper, Xing Ding and Hao Chen designed the experiments; Xianglong Yang and Yonggang Xiang conducted the experiments; Xuepeng Wang and Shu Li. analyzed the data; Xianglong Yang and Xing Ding wrote the paper.

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