



Article

Construction of 2D/2D Mesoporous WO₃/CeO₂ Laminated Heterojunctions for Optimized Photocatalytic Performance

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Abstract: Photocatalytic elimination of antibiotics from the environment and drinking water is of great significance for human health. However, the efficiency of photoremoval of antibiotics such as tetracycline is severely limited by the prompt recombination of electron holes and slow charge migration efficacy. Fabrication of low-dimensional heterojunction composites is an efficient method for shortening charge carrier migration distance and enhancing charge transfer efficiency. Herein, 2D/2D mesoporous WO₃/CeO₂ laminated Z-scheme heterojunctions were successfully prepared using a two-step hydrothermal process. The mesoporous structure of the composites was proved by nitrogen sorption isotherms, in which sorption-desorption hysteresis was observed. The intimate contact and charge transfer mechanism between WO₃ nanoplates and CeO₂ nanosheets was investigated using high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy measurements, respectively. Photocatalytic tetracycline degradation efficiency was noticeably promoted by the formation of 2D/2D laminated heterojunctions. The improved photocatalytic activity could be attributed to the formation of Z-scheme laminated heterostructure and 2D morphology favoring spatial charge separation, confirmed by various characterizations. The optimized 5WO₃/CeO₂ (5 wt.% WO₃) composites can degrade more than 99% of tetracycline in 80 min, achieving a peak TC photodegradation efficiency of 0.0482 min^{−1}, which is approximately 3.4 times that of pristine CeO₂. A Z-scheme mechanism is proposed for photocatalytic tetracycline by from WO₃/CeO₂ Z-scheme laminated heterojunctions based on the experimental results.

Keywords: photocatalysis; WO₃ nanoplate; mesoporous CeO₂ nanosheet; Z-scheme; laminated heterojunction



Citation: Wang, W.; Yang, D.; Mou, Y.; Liao, L.; Wang, S.; Guo, L.; Wang, X.; Li, Z.; Zhou, W. Construction of 2D/2D Mesoporous WO₃/CeO₂ Laminated Heterojunctions for Optimized Photocatalytic Performance. *Nanomaterials* **2023**, *13*, 1798. <https://doi.org/10.3390/nano13111798>

Academic Editors: Smagul Karazhanov and Luminița Andronic

Received: 16 May 2023

Revised: 29 May 2023

Accepted: 1 June 2023

Published: 4 June 2023



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1. Introduction

Excessive current use of antibiotics has led to the wide distribution of antibiotic residues in the global environment, even in drinking water, which adversely affects human health [1,2]. Thus, the removal of antibiotics is of great importance for life on earth and the sustainable development of human society. Various technologies such as physical purification, chemical degradation, biological degradation, and catalytic elimination have been developed to remove antibiotics from polluted water [3,4]. Among these methods, photocatalysis is one of the most promising routes for residual antibiotic elimination because it is a solar-driven process that does not consume energy [5]. However, the application of photocatalytic antibiotic removal in natural conditions is hindered by the low efficiency of the photocatalytic process. Therefore, research on improving photocatalytic efficiency is significant for antibiotic removal.

Semiconductor-based photocatalytic technology can create electrons and holes under light illumination, which in turn produce superoxide radicals (O₂[−]) and hydroxyl radicals

($\cdot\text{OH}$) in the presence of water and oxygen [6]. These reactive oxygen radicals and photo-generated holes are capable of oxidizing antibiotics into CO_2 and H_2O [7]. Various types of semiconductors, including TiO_2 -based materials [8], bismuth-based photocatalysts [9], $\text{g-C}_3\text{N}_4$ -based systems [10], heterojunction and surface plasmon resonance enhanced photocatalysts [11], and other materials have been explored for photocatalytic removal of antibiotics [12]. Among these photocatalysts, WO_3 has drawn much attention for visible light pollutant removal because of its narrow band gap [13]. Kim et al. investigated the influence of different inorganic oxidants on the photocatalytic performance of WO_3 for visible light degradation of 4-chlorophenol, demonstrating charge separation enhancement by oxyanions [14]. Nguyen et al. reported that amoxicillin could be degraded by WO_3 under simulated solar irradiation, which followed pseudo-first-order kinetics [15]. In addition, near-infrared light photocatalytic removal of methylene blue was achieved on a longitudinally grown WO_3 nanoparticle surface [16]. However, the photocatalytic activity of WO_3 is severely restricted by the prompt charge recombination and the lack of superoxide radicals because of its low conduction band position [17]. These drawbacks can be overcome by the formation of heterojunctions with metals or other semiconductors with high conduction band levels. The electron–hole pair separation and visible light absorption were much improved by the loading of Ag on WO_3 surfaces, producing excellent sulfanilamide degradation activity [18]. The formation of WO_3 /carbon nanotubes was also reported to effectively suppress the recombination of charge carriers and promote sonophotocatalytic tetracycline removal efficiency [19]. Oxidizing species were proved to be OH and h^+ without O_2^- in that research [19].

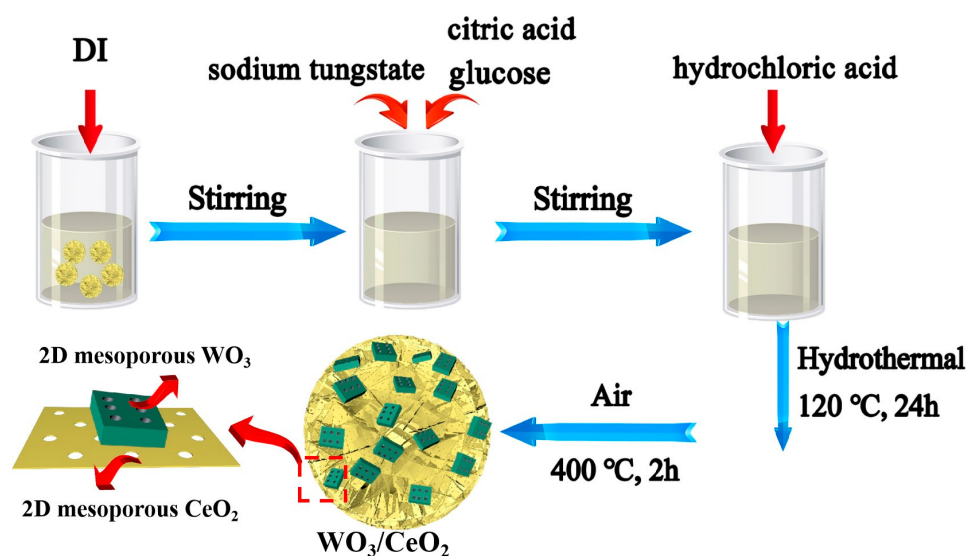
CeO_2 is an attractive candidate for constructing heterojunction photocatalysts with other semiconductors because it is chemically stable, nontoxic, and has proper band positions, where the conduction band is positioned at ca. -0.78 eV (vs. NHE) [19]. Oxygen vacancies were proved to be present on the CeO_2 surface, thereby enhancing charge separation and transfer efficiency [20]. Recently, various heterojunctions such as $\text{SnIn}_4\text{S}_8/\text{CeO}_2$ [21], Ni/CeO_2 [22], CdS/CeO_2 [23], and 3D/0D $\text{Cu}_3\text{SnS}_4/\text{CeO}_2$ heterojunctions [24] have been reported to show significant improvement in photocatalytic performance. Bahadoran et al. reported an S-scheme WO_3/CeO_2 heterojunction with enhanced visible light photocatalytic sulfamerazine degradation performance [25]. Moreover, the photodegradation activity of indigo carmine dye was much improved by the formation of type II WO_3/CeO_2 heterojunction nanoparticles [26].

Because of its wide band gap of ca. 3.2 eV, CeO_2 photocatalysts can only be activated by UV irradiation, but possess decent photocatalytic activity for pollutant degradation with the generation of oxidizing radicals including O_2^- and OH [26]. In contrast, WO_3 has a narrow band gap of 2.4–2.8 eV, thus exhibiting potential applications in visible-light-driven photocatalytic reactions [27,28]. However, the photogenerated electrons and holes on the WO_3 surface demonstrate insufficient redox ability due to its band positions [28]. Therefore, the addition of small amounts of WO_3 to CeO_2 photocatalysts could extend the light response range from ultraviolet to the visible light region without significant deactivation. Although type II heterojunctions have been investigated for indigo carmine dye removal [26], to our knowledge, the construction of 2D/2D mesoporous WO_3/CeO_2 Z-scheme laminated heterojunctions with promoted photocatalytic tetracycline degradation activity has never been reported. We fabricated 2D/2D mesoporous WO_3/CeO_2 Z-scheme laminated heterojunctions via a facile two-step hydrothermal process. The transfer efficiency of the photoinduced charges was significantly enhanced by the low-dimension morphology and the formation of the Z-scheme laminated heterostructure. The improved charge transfer efficiency and suppressed electron hole recombination were confirmed by various characterizations, including electrochemical impedance spectra, transient photocurrent responses, surface photovoltage spectroscopy, and photoluminescence.

2. Experimental

2.1. Synthesis of Mesoporous CeO₂ Nanosheets, WO₃ Nanoplates, and WO₃/CeO₂ Composites

The 2D CeO₂ nanosheets were synthesized according to our previously reported method [29]. Typically, 10 mmol glucose was added to 80 mL deionized water and magnetically stirred for 30 min. Subsequently, 15 mmol C₃H₅NO and 5 mmol Ce(NO₃)₃·6H₂O were dissolved in the above solution under magnetic stirring for 1 h, and 3 mL NH₃·H₂O (28 wt%) was added drop by drop to the mixture and stirred for 5 h, creating a dark brown gel mixture. The mixture was transferred into a Teflon-lined autoclave and maintained at 180 °C for 72 h. The solid products were collected and washed via centrifugation with water and ethanol after reaction. CeO₂ nanosheets were obtained via thermal treatment at 600 °C for 6 h under a nitrogen atmosphere and subsequent calcination at 400 °C for 4 h under an air atmosphere. The 2D WO₃ nanoplates were fabricated using a slightly modified procedure [30]. In a typical procedure, 0.06 g Na₂WO₄·2H₂O was first added to 30 mL water. Subsequently, 0.013 g C₆H₈O₇·H₂O and 0.04 g C₆H₁₂O₆ were added to the above solution. After 20 min magnetic stirring, 3 mL HCl (6M) was added dropwise to the mixture, and the mixture was transferred to a 50 mL autoclave and heated at 120 °C for 24 h. After the reaction, the product was collected and washed with anhydrous ethanol and deionized water several times by centrifugation. The sample was then heated to 400 °C at a heating rate of 5 °C min^{−1} and maintained for 2 h to obtain mesoporous WO₃ nanoplates. Mesoporous WO₃/CeO₂ heterojunctions were prepared by a two-step hydrothermal method. The synthetic procedure of WO₃/CeO₂ is presented in Scheme 1. First, 0.06 g Na₂WO₄·2H₂O and 2.3 g prepared CeO₂ were added to 30 mL water to form a transparent solution. Subsequently, 0.013 g C₆H₈O₇·H₂O and 0.04 g C₆H₁₂O₆ were added to the above solution. After 20 min magnetic stirring, 3 mL HCl (6M) was added drop by drop to the mixture, and the solution was transferred to a 50 mL autoclave and maintained at 120 °C for 24 h. After the reaction, the product was centrifuged and washed with anhydrous ethanol and deionized water several times to remove surface impurities. The sample was then heated to 400 °C at a heating rate of 5 °C min^{−1} and kept for 2 h to improve the crystallinity. A yellow powder was obtained, denoted as xWO₃/CeO₂ (x%: mass ratio for WO₃). The 3WO₃/CeO₂, 5WO₃/CeO₂, and 7WO₃/CeO₂ heterojunctions were obtained using 1.39 g, 2.3 g, and 3.25 g CeO₂, respectively, during the synthetic procedure.



Scheme 1. Schematic illustration of the synthesis of 2D/2D mesoporous WO₃/CeO₂ laminated heterojunctions.

2.2. Characterizations

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer (Bruker, Karlsruhe, Germany) using Cu K α radiation ($\lambda = 1.5406$ Å, 40 kV, 40 mA).

The step size and scan range were 0.02° , and $5\text{--}80^\circ$, respectively. The UV-vis absorption spectra were obtained using a UV-visible spectrophotometer (Shimadzu UV-2550, Shimadzu, Tokyo, Japan). A PerkinElmer Lambda 950 UV-vis spectrophotometer (PerkinElmer, Waltham, MA, USA) was used to measure the diffuse reflectance spectrum (DRS) in the wavelength range of 200–1800 nm. Materials morphology was analyzed by scanning electron microscopy (SEM) (Hitachi S-4800, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM) (JEOLJEM-2100, Jeol, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos-Axis ULTRA DLD electron spectrometer with an AlK α (1253.6 eV) excitation source. The results were calibrated using the standard C 1s peak (284.6 eV). Nitrogen sorption measurements were performed with a TriStar 3020 ii automatic analyzer. The Brunauer-Emmett-Teller (BET) equation and the adsorption branch of BET isotherms were used to obtain the specific surface area and pore size distribution, respectively. The surface photovoltage spectroscopy (SPS) was tested on a homemade instrument in the wavelength range of 200–600 nm. The photoluminescence spectra (PL) were measured using a PELS 55 instrument with a selected excitation wavelength of 275 nm. The photoelectric characteristics of the samples were analyzed on a Princeton VersaSTAT workstation (Princeton Applied Research, Oak Ridge, TN, USA) with a three-electrode system, using a catalyst as the photoanode, platinum as the cathode, Ag/AgCl as the reference electrode, and 0.5 M Na₂SO₄ solution as the electrolyte, respectively.

2.3. Photocatalytic Activity Measurements

The photocatalytic activity of CeO₂ and WO₃/CeO₂ were measured in the tetracycline (TC) degradation process. First, 100 mg of CeO₂ or WO₃/CeO₂ was added to 100 mL TC solution (10 mg L^{−1}). The suspension was kept in the dark for 20 min and analyzed to evaluate the adsorption properties of the sample. Subsequently, the mixture was illuminated under a 300 W Xe lamp (PerfectLight, Beijing, China) with an AM 1.5G filter. The suspension was sampled every 20 min, 5 times in total. The TC concentration was determined by UV-vis spectroscopy at the wavelength of 357 nm.

3. Results and Discussion

3.1. Morphology and Microstructure

The crystal structures of CeO₂ and WO₃/CeO₂ were analyzed by X-ray diffraction (XRD). Figure 1a and Figure S1 show the XRD profiles of the CeO₂ and WO₃/CeO₂ heterojunction photocatalysts. The characteristic peaks of CeO₂ (JCPDS No. 34-0394) and WO₃ (JCPDS No. 20-1323) can be identified in the samples of CeO₂ and WO₃ [31,32]. The characteristic peaks of WO₃ are not observed in the XRD patterns of 3WO₃/CeO₂ and 5WO₃/CeO₂ because the loading amounts of WO₃ are too low to be detected. The characteristic peaks of both CeO₂ and WO₃ can be identified in the XRD pattern of 7WO₃/CeO₂, indicating the successful formation of WO₃/CeO₂ composites. The subsequent evaluation of photocatalytic TC degradation performance revealed that 5WO₃/CeO₂ (5 wt%) demonstrated the best photocatalytic activity. Thus, 5WO₃/CeO₂ was used for all the characterizations. The light absorption properties of the as-made samples were analyzed by UV-vis spectroscopy, as shown in Figure 1b. CeO₂ exhibited strong absorption in the ultraviolet range (200–400 nm) but limited visible light absorption ability. WO₃ showed strong absorption in the visible light range, thereby enhancing the light absorption ability of the WO₃/CeO₂ heterojunctions. Figure S2 presents the UV-vis diffuse reflection spectra of the samples with different WO₃ contents. The visible light absorption ability of WO₃/CeO₂ increases with the WO₃ content. Figure 1c,d describes the N₂ sorption isotherms and the corresponding BJH pore size distribution plots of CeO₂, WO₃, and WO₃/CeO₂. The BET surface area, average pore size, and total pore volume of the samples are presented in Table S1. Typical type IV hysteresis loops can be observed in all three samples, indicating that mesopores are formed in the synthesized samples, which is consistent with the average pore size data. Materials with mesoporous pores offer enhanced accessibility and superior mass transfer [33,34], thus having the possibility to enhance the photocatalytic redox reac-

tion. The average crystallite diameters (D) of the as-prepared samples were obtained by the Scherrer equation [35]:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

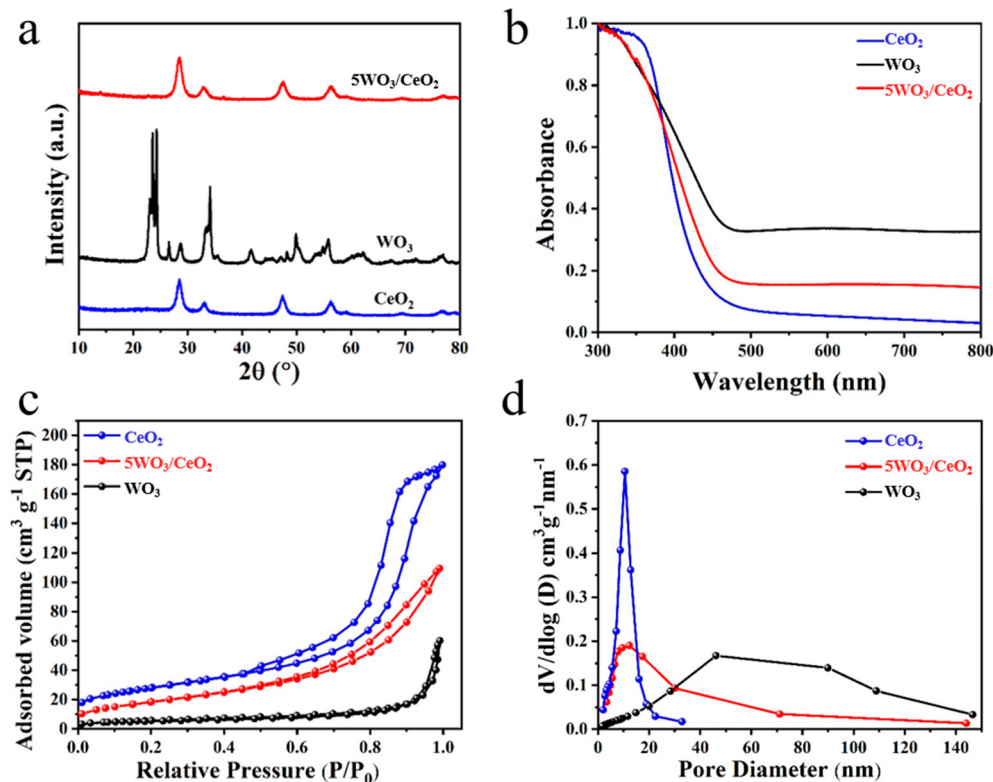


Figure 1. (a) XRD patterns, (b) UV-vis diffuse reflectance spectra, (c) N_2 sorption isotherms, and (d) BJH pore size distribution plots of WO_3 , CeO_2 , and $5\text{WO}_3/\text{CeO}_2$.

λ , β , and θ are the X-ray wavelength, the full width at half maximum of the peak, and the Bragg's diffraction angle of the peak, respectively. The crystallite size, surface area, pore volume, and main pore size are presented in Table 1.

Table 1. Crystallite size, surface area, pore volume, and main pore size of the samples.

Catalyst	D (nm)	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Pore Size (nm)
CeO_2	19.3	100.3	0.21	9.3
WO_3	20.1	22.0	0.20	44.7

The morphology and microscopic structure of WO_3 , CeO_2 , and WO_3/CeO_2 were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as demonstrated in Figure 2. The CeO_2 microspheres (diameter: ca. $4.5 \mu\text{m}$) consist of uniform CeO_2 nanosheets, providing a 2D platform for the formation of laminated heterojunctions. WO_3 nanoplates are uniformly dispersed on the surface of CeO_2 nanosheets after combination with CeO_2 under hydrothermal conditions. Obvious lattice fringes of CeO_2 and WO_3 can be identified by a high-resolution TEM image (Figure 2f), indicating the high crystallinity of the formed WO_3/CeO_2 composites. The spacing of 0.38 nm is ascribed to the (002) plane of WO_3 , while the lattice fringes of 0.317 nm and 0.286 nm are attributed to the (111) plane and (200) plane of CeO_2 , respectively. The microstructure of the WO_3/CeO_2 composites revealed by TEM is in good agreement with the XRD data. In addition, the high-resolution image of WO_3/CeO_2 shows that the lattice fringes of WO_3

and CeO_2 are in close contact with each other, suggesting the successful construction of heterojunction photocatalysts.

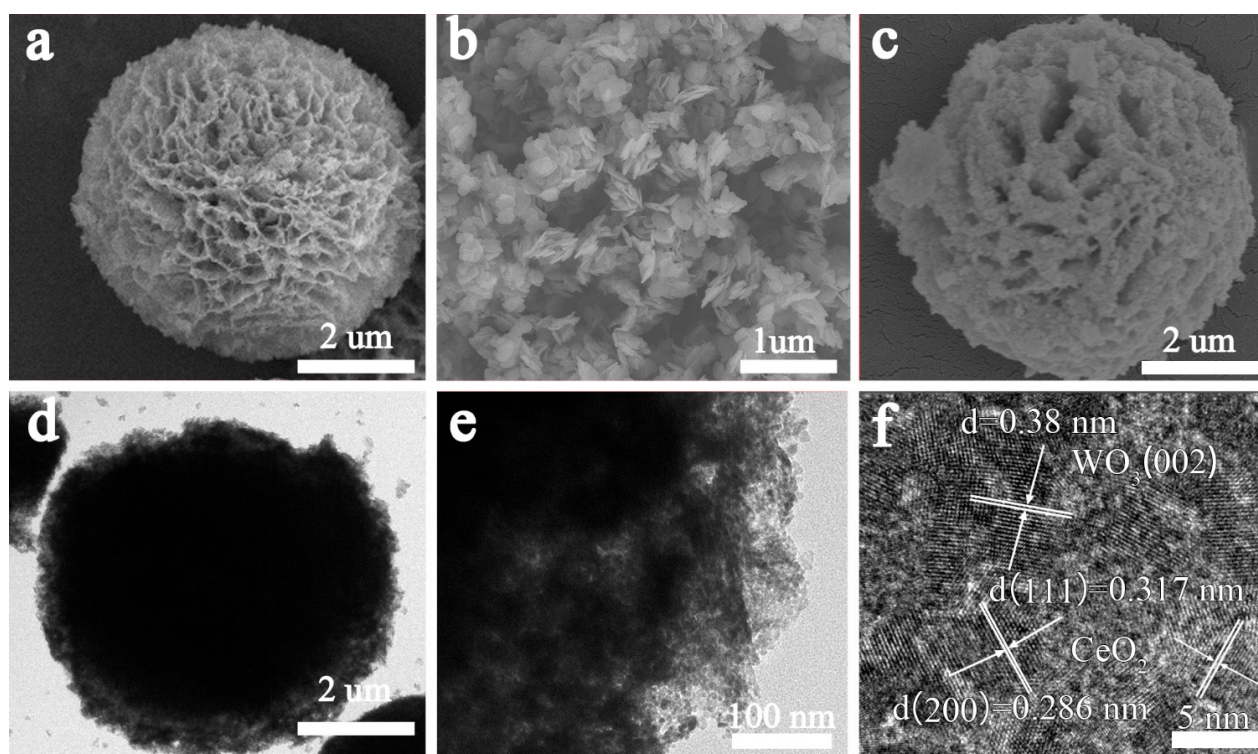


Figure 2. SEM images of CeO_2 (a), WO_3 (b), and WO_3/CeO_2 (c), and TEM images (d,e) and HRTEM image (f) of WO_3/CeO_2 .

Figure 3 presents the XPS spectra of CeO_2 and WO_3/CeO_2 composites. All the binding energy positions in the XPS measurements were calibrated using C 1s as the reference at 284.8 eV. The full XPS survey spectra of CeO_2 and WO_3/CeO_2 composites are illustrated in Figure 3a, while the analysis of the high-resolution XPS spectra for W, Ce, and O are presented in Figure 3b–d. The presence of W, O, and Ce elements in the XPS survey spectrum of WO_3/CeO_2 provides evidence that the WO_3/CeO_2 composites were successfully constructed without impurities. The binding energy at 35.7 and 37.8 eV can be ascribed to W $4f_{7/2}$ and W $4f_{5/2}$, confirming the presence of W^{6+} in the WO_3/CeO_2 composites [36]. Upon the formation of the WO_3/CeO_2 composites, the above two peaks of W 4f shifted to lower energy levels, indicating electron transfer occurs because of the energy level difference. Thus, the electron density on the surface of WO_3 in the composites increased. As shown in Figure 3c, two kinds of spin-orbit interaction, including Ce $3d_{3/2}$ (XPS peaks are denoted as u or u-derivatives) and Ce $3d_{5/2}$ (XPS peaks are denoted as v or v-derivatives), can be clearly observed in the high-resolution Ce 3d XPS spectra. The peaks located at 901.1 eV (u), 903.7 eV (u'), 907.3 eV (u''), and 916.7 eV (u''') can be attributed to Ce $3d_{3/2}$, while the binding energies at 882.5 eV (v), 884.8 eV (v'), 888.8 eV (v''), and 898.2 eV (v''') are assigned to Ce $3d_{5/2}$. The O 1s peaks at 529.4 and 531.3 eV originate from lattice oxygen (O_L : W–O, Ce–O) and chemisorbed oxygen (O_C), respectively, in WO_3 and CeO_2 , confirming the firm adhesion between WO_3 and CeO_2 in the heterojunction composites [25,29]. Moreover, the Ce 3d, and O 1s main peaks of the WO_3/CeO_2 composites demonstrate migration after the construction of composites, suggesting the change of chemical environment and the existence of strong interaction between WO_3 and CeO_2 .

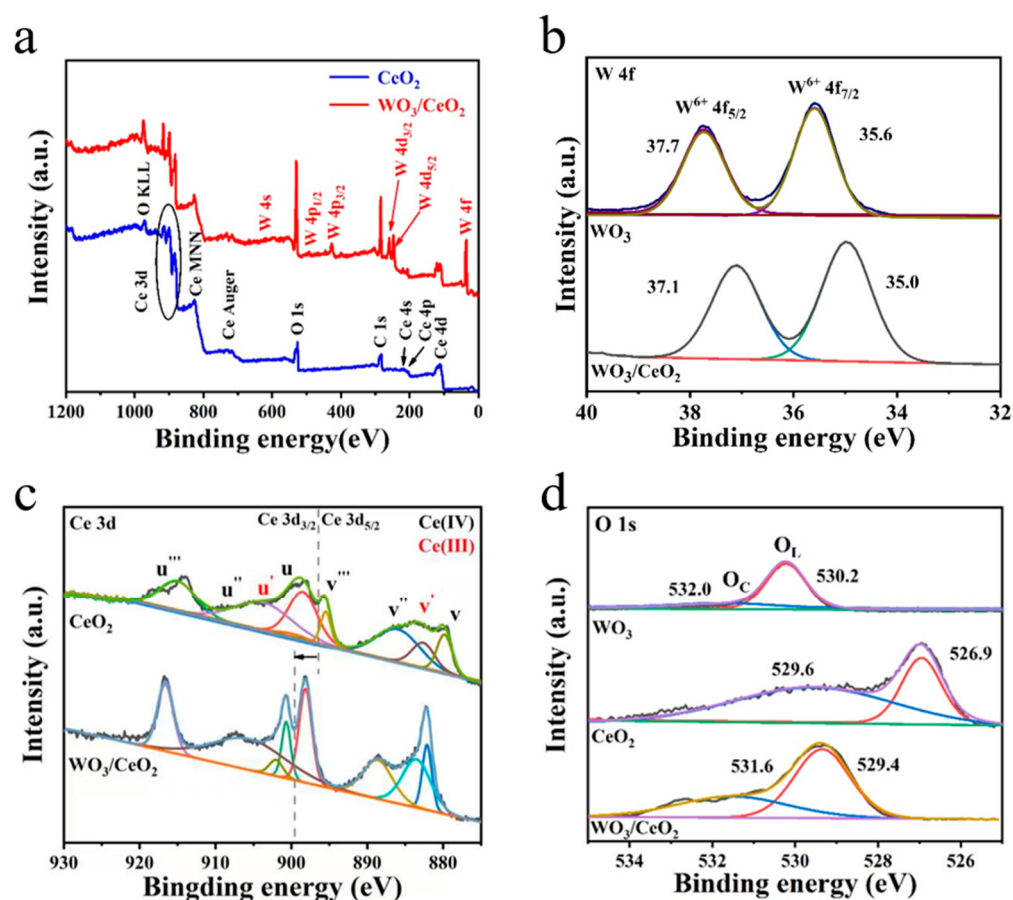


Figure 3. The XPS spectra of WO_3 , CeO_2 and WO_3/CeO_2 : (a) survey spectra, (b) W 4f, (c) Ce 3d, (d) O 1s.

The energy band gaps (E_g) for WO_3 and CeO_2 were obtained by using the Kubella-Munk formula ($\alpha h\nu = A(h\nu - E_g)^{n/2}$), where A , α , h , and n , are the constant, the absorption coefficient close to the absorption edge, the Planck constant, and the coefficient of the semiconductor, respectively. The value of coefficient n of CeO_2 and WO_3 is 4, since both semiconductors have indirect band gaps [37,38]. The E_g values of the as-synthesized CeO_2 and WO_3 samples were determined to be 2.62 eV and 2.58 eV, respectively, by the Kubella-Munk formula plots derived from the UV-Vis spectra, as presented in Figure 4a,c. The valence band (VB) maximum positions of the materials were normally measured by the valence band XPS spectra [39]. As displayed in Figure 4b,d, the surface valence band edges of CeO_2 and WO_3 were estimated to be 2.1 eV and 2.67 eV, respectively, by drawing the tangent line [40]. Based on the empirical equation $E_{CB} = E_{VB} - E_g$ (E_{CB} , E_{VB} , and E_g are the conduction band, valence band positions, and the band gap of semiconductors, respectively), and the results of the obtained band gaps and valence band maximum positions, the conduction band (CB) minimum positions of CeO_2 and WO_3 are calculated to be -0.52 eV and 0.09 eV, respectively. The energy scale is normally demonstrated in volts using the normal hydrogen electrode (NHE) as a reference [41]. The Fermi levels of WO_3 and CeO_2 were reported to be 0.57 and -0.353 eV, respectively [42,43]. It should be noted that the band bending direction in the interface of composites could be significantly influenced by the Fermi level of the two semiconductors [43]. The charge transfer process of WO_3/CeO_2 heterojunction is assumed to be a Z-scheme mechanism, which is proved and analyzed below. Therefore, the band edge of CeO_2 with a high Fermi level is bent upward while the band edge of WO_3 with a low Fermi level is bent downward, because the electrons migrate from the high Fermi level to the low Fermi level [43]. A built-in electric field in the heterojunction interface could be formed because of the curved band edges and charge

transfer equilibrium between CeO_2 and WO_3 [44]. Thus, the WO_3/CeO_2 heterojunction is probably fabricated with a staggered band alignment, as shown in Figure 4e.

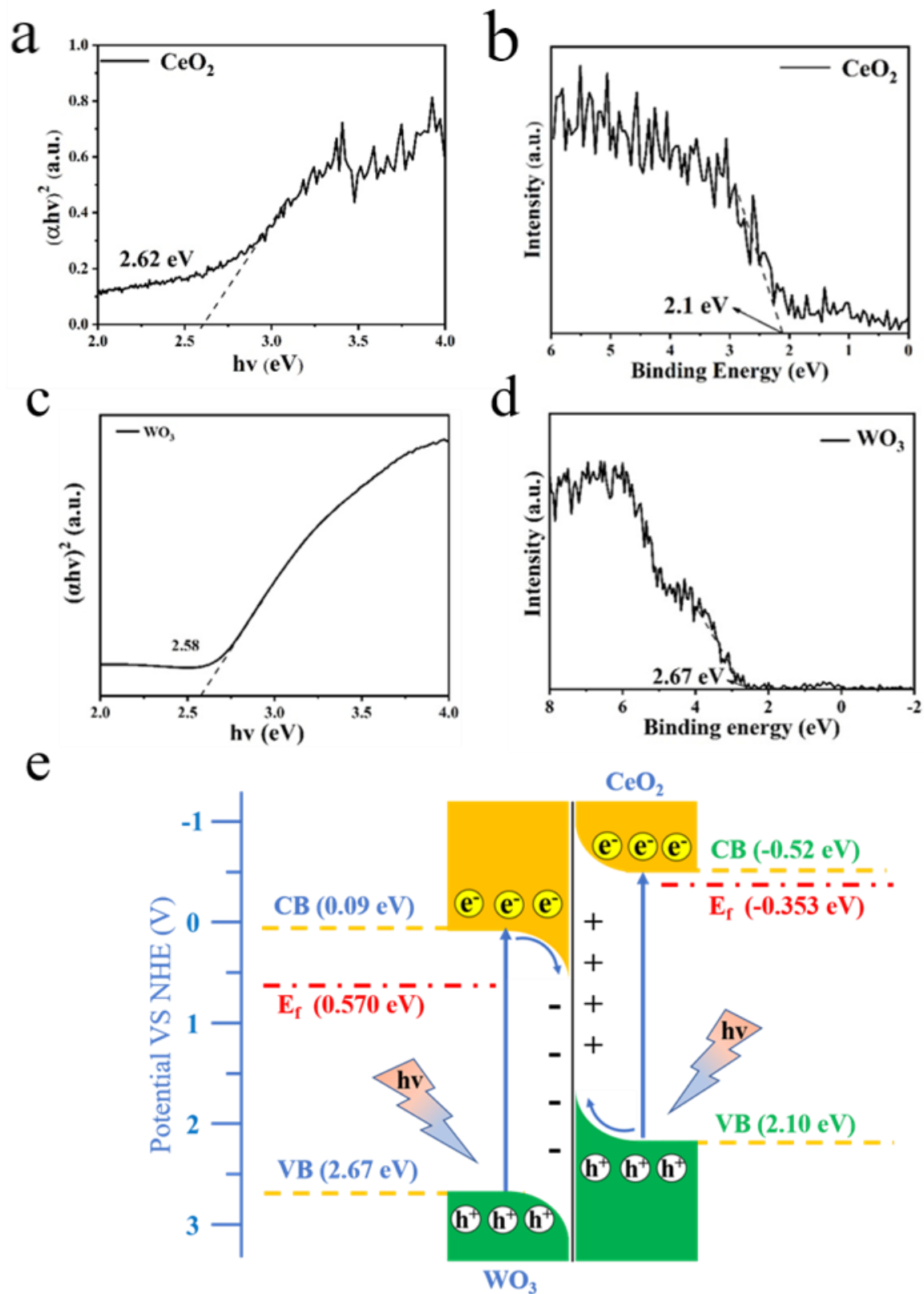


Figure 4. Band gap energies (a,c) and valence band XPS spectra (b,d) and band alignments (e) of WO_3 and CeO_2 , respectively.

3.2. Photocatalytic Activity

The photocatalytic activity of different samples in the tetracycline degradation process was evaluated under AM 1.5G illumination. Photocatalytic TC removal efficiency in the presence of the heterojunction photocatalysts with different amounts of WO_3 was measured. As shown in Figure 5a, the photocatalytic TC degradation efficiency of CeO_2 was much improved after the construction of the heterostructure with WO_3 . The photocatalytic efficiency for TC degradation increases with the amount of WO_3 . Under light illumination, $5\text{WO}_3/\text{CeO}_2$ (5 wt.% WO_3) heterojunctions exhibit the highest photocatalytic efficiency, at 99.1% within 80 min for TC removal. The enhanced photocatalytic efficiency of the heterojunctions compared to pristine WO_3 or CeO_2 is mainly attributed to the formation of the laminated heterostructure and the mesoporous structure. The heterojunction interface could inhibit the photogenerated charge recombination rate, thereby facilitating the charge transfer and the generation of oxidizing radicals. The mesoporous structure presented a relatively high absorption capacity for tetracycline. Moreover, a 2D structure could shorten the distance of charge transfer in the heterojunction interface. However, $7\text{WO}_3/\text{CeO}_2$ (7 wt.% WO_3) composites showed a decreased TC removal efficiency (97.9% within 80 min) under identical reaction conditions. Despite the enhanced charge separation and transfer efficiency at the interface of the heterojunctions, excess amounts of WO_3 would result in the coverage of active sites of CeO_2 , thus decreasing the photocatalytic activity. Therefore, $5\text{WO}_3/\text{CeO}_2$ composites present the proper tradeoff between enhanced charge separation efficiency and active site coverage. The photocatalytic TC removal efficiency of individual WO_3 has been measured to be 64.9% within 80 min, which is much lower than that of CeO_2 . As shown in Figure 5b, the photocatalytic TC degradation rate of CeO_2 decreased quickly with reaction time because of the prompt photoinduced electron–hole combination, reaching a final removal efficiency of 83.9%. Owing to the reduced electron–hole recombination rate, $5\text{WO}_3/\text{CeO}_2$ composites demonstrated accelerated TC removal efficiency compared to pristine CeO_2 . As illustrated in Figure 5c, the photocatalytic TC degradation rates were well-matched with a pseudo-first-order kinetic model. The kinetic constant (K) of $5\text{WO}_3/\text{CeO}_2$ heterojunctions for TC photodegradation achieved 0.0482 min^{-1} , which was approximately 3.4 times that of pristine CeO_2 . To verify the outcome of the TC degradation performance, the total organic carbon (TOC) concentration after the reaction in the presence of WO_3/CeO_2 was measured using a carbon analyzer (TOC 5000A Shimadzu), as illustrated in Table S2. The TOC concentration after the reaction photocatalyzed by $5\text{WO}_3/\text{CeO}_2$ heterojunctions was determined to be 1.6 mg L^{-1} , which is in agreement with the UV-Vis spectroscopy measurements.

The reusability of the optimized photocatalysts ($5\text{WO}_3/\text{CeO}_2$) was evaluated in 10 cycling tests, and the TC photoremoval efficiency is presented in Figure 5d. The heterojunction composites exhibited stable TC elimination efficiency under light illumination, which was almost 100% maintained after ten consecutive cycling measurements, suggesting that the as-synthesized composites possess relatively high photocatalytic stability in the TC elimination process. Table 2 presents the photocatalytic tetracycline degradation performance of 2D/2D mesoporous WO_3/CeO_2 compared with reported CeO_2 -based materials. It can be clearly seen that the as-synthesized WO_3/CeO_2 laminated heterojunctions exhibit superior photocatalytic TC removal activity compared to other photocatalysts. Moreover, the cycling tests of photocatalytic TC degradation in this study were performed 10 times without apparent photocatalyst deactivation, while only 4 or 5 cycling tests were conducted in the previous studies.

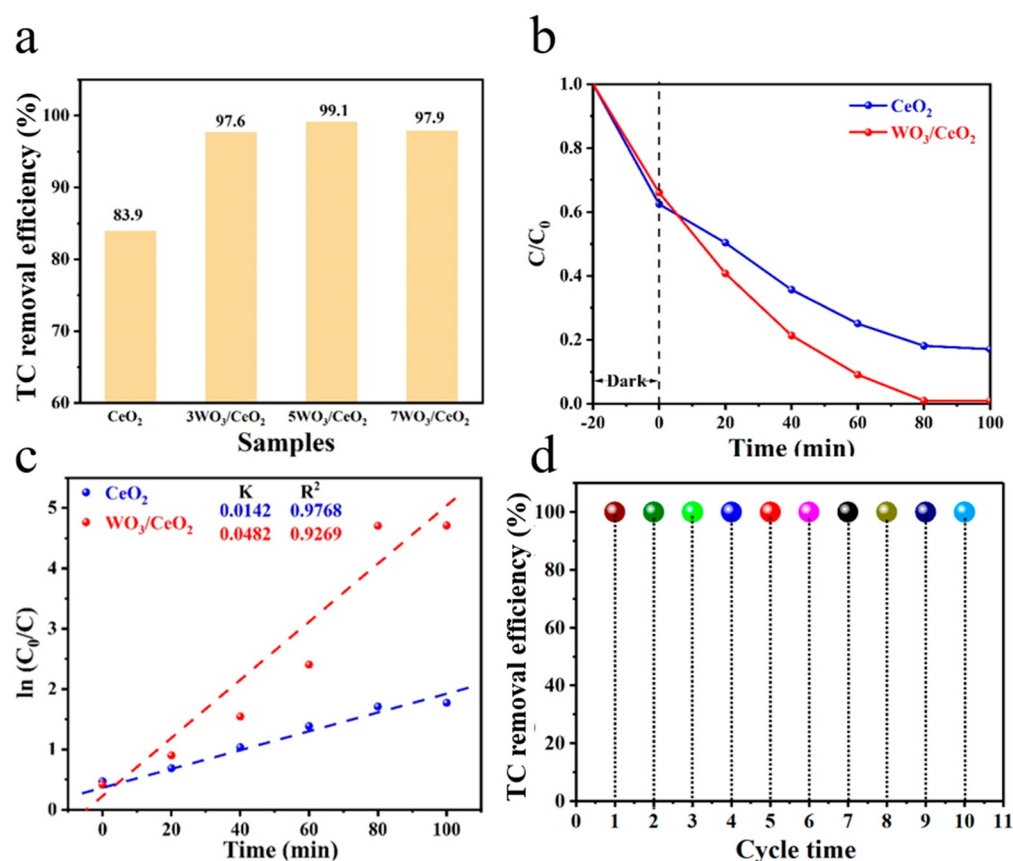


Figure 5. (a) TC removal efficiency of the samples with different WO₃ contents, (b) photocatalytic TC degradation performance, (c) linear transformation $\ln(C_0/C)$ of the kinetic curves of photocatalytic TC degradation for CeO₂ and WO₃/CeO₂, and (d) removal efficiency in cycling tests of photocatalytic TC degradation under AM 1.5G.

Table 2. Comparison of photocatalytic tetracycline degradation efficiency of 2D/2D mesoporous WO₃/CeO₂ with reported values.

Photocatalyst	Time (min)	Removal Efficiency (%)	Number of Cycling Test	Ref.
BiOCl@CeO ₂	120	90	4	[45]
CeO ₂ /carbonate doped Bi ₂ O ₂ CO ₃	90	79.5	4	[46]
ZnO/CeO ₂ @Haloysite nanotubes	90	94	4	[47]
SnO/CeO ₂	140	99	5	[48]
AgI/CeO ₂	60	94.34	not studied	[49]
AgBr/CeO ₂	120	77.8	not studied	[50]
CeO ₂ /Ti ₃ C ₂ -MXene	60	80.2	4	[51]
Ag ₂ O/AgBr-CeO ₂	60	93.68	4	[52]
2D/2D mesoporous WO ₃ /CeO ₂	80	99.1	10	this study

To get insights into the photocatalytic process of TC removal, photoelectrochemical measurements were conducted and presented in Figure 6 to study the separation and transfer efficiency of photoinduced charge carriers on the photocatalyst surface. Figure 6a shows the electrochemical impedance spectra (EIS) measurements of the as-prepared samples, which were conducted at the open-circuit potential of the as-made photocatalysts. The diameter of the obtained semicircle of WO₃/CeO₂ composites is clearly smaller than that of the pristine CeO₂, indicating that composites with heterostructures have lower charge transfer resistance. The transient photocurrent responses of CeO₂ and WO₃/CeO₂

were measured under intermittent light illumination, as illustrated in Figure 6b. The photocurrent density of WO_3/CeO_2 was much higher than that of CeO_2 , indicating that the WO_3/CeO_2 laminated heterojunction composites exhibited slower charge recombination rate and stronger electron–hole separation ability. In addition, repeatable photocurrent responses in every illumination cycle can be observed, showing the excellent stability of the constructed heterojunctions. Figure 6c presents the surface photovoltage spectroscopy (SPV) data of the samples. The SPV measurements of WO_3/CeO_2 demonstrate much-increased surface voltage under light irradiation compared to CeO_2 , showing the accelerated charge transfer efficiency on the heterojunction surface [53]. The suppressed-charge recombination rate was also examined using PL emission measurements, as shown in Figure 6d. The PL spectra of WO_3/CeO_2 show clear photoluminescence quenching compared to pure CeO_2 at an excitation wavelength of 365 nm. This result demonstrates that the efficient suppression of photogenerated electron–hole recombination was achieved via the formation of heterojunction interfaces in WO_3/CeO_2 composites. All the above measurements provided solid evidence for the enhanced charge separation and transfer efficiency and suppressed electron–hole recombination, which improves photocatalytic activity for TC degradation.

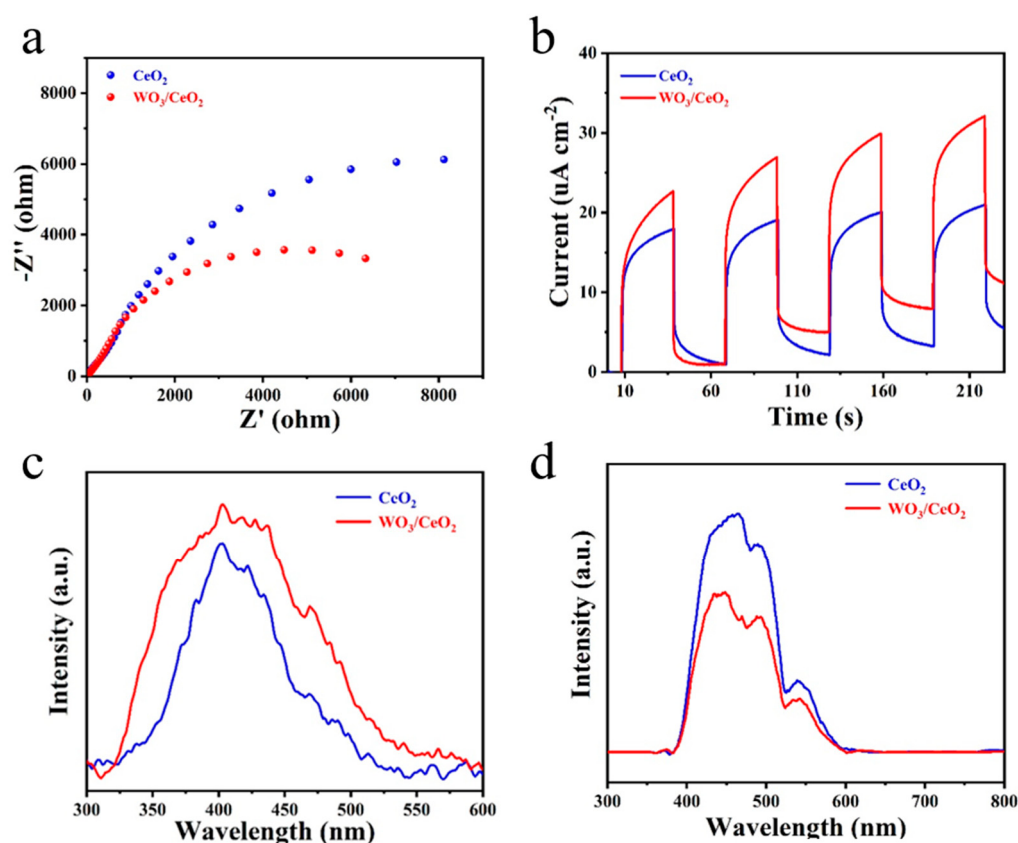


Figure 6. EIS Nyquist plots (a), transient photocurrent responses (b), surface photovoltage spectroscopy (c), and PL spectra (d) of CeO_2 and WO_3/CeO_2 .

All obtained results for TC photodegradation and heterojunction characterizations led to the proposed mechanism for photocatalytic TC elimination on the WO_3/CeO_2 surface, as illustrated in Figure 7. As previously mentioned, the band alignment of WO_3/CeO_2 is assumed to be staggered according to the measured and calculated band positions. The electrons are excited under light irradiation and migrated from the valence band to the conduction band, thereby leaving holes with positive charges in the valence band. If type II heterojunctions were formed in the as-synthesized WO_3/CeO_2 composites, the excited electrons would transfer from the conduction band of CeO_2 to that of WO_3 . The photogenerated holes migrate from the valence band of WO_3 to that of CeO_2 . However,

the photoinduced electrons in the conduction band of WO_3 could not reduce oxygen into superoxide radicals because of the more positive CB position of WO_3 (0.50 eV vs. NHE) compared to the $\text{O}_2/\cdot\text{O}_2^-$ potential (−0.33 V vs. NHE) [54]. Likewise, the photogenerated holes in the VB of both WO_3 (2.62 eV vs. NHE) and CeO_2 (2.1 eV vs. NHE) could not oxidize H_2O to form $\cdot\text{OH}$, due to the more negative VB potential of the two materials compared to the $\text{H}_2\text{O}/\cdot\text{OH}$ potential (2.72 V vs. NHE) [54]. In that scenario, O_2^- and $\cdot\text{OH}$ cannot be generated in the TC degradation process. Thus, the typical type II heterojunction mechanism was impractical in the WO_3/CeO_2 composites. Accordingly, the Z-scheme charge transfer mechanism was applied to the WO_3/CeO_2 heterojunction, as shown in Figure 7. Electrons moved from WO_3 (CB) to CeO_2 (VB). The electrons accumulated in the CB of CeO_2 easily oxidize O_2 into O_2^- . Photogenerated holes in WO_3 (VB) and $\cdot\text{O}_2^-$ would degrade TC simultaneously under light irradiation. Both CeO_2 and WO_3 are two-dimensional (2D) materials, as illustrated in Figure 2, as 2D photocatalysts have significant advantages in charge-transfer kinetics [55]. Thanks to the 2D morphology and the formation of the Z-scheme laminated heterojunction, the spatial charge separation and transfer efficiency are much enhanced under light illumination. Surface-adsorbed oxygen can capture photoinduced electrons to form superoxide radicals (O_2^-). Tetracycline is eventually oxidized into CO_2 and water by the photoinduced radicals and holes on WO_3/CeO_2 surface. However, this mechanism is merely an assumption based on the $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ formation mechanism. The detection of reactive species such as $\cdot\text{O}_2^-$ and the TC oxidation products will be performed in further research.

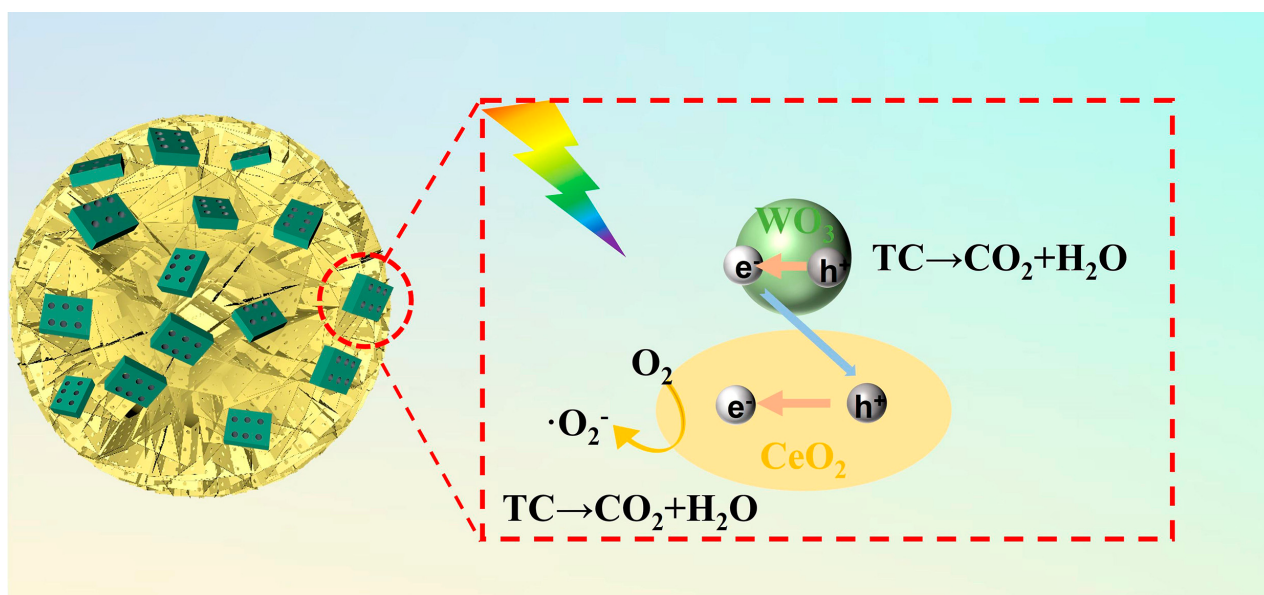


Figure 7. Proposed Z-scheme mechanism for photocatalytic TC degradation on WO_3/CeO_2 surface.

4. Conclusions

In summary, 2D/2D mesoporous WO_3/CeO_2 photocatalysts were constructed via a facile two-step hydrothermal process. The heterojunction structure was confirmed by high-resolution transmission electron microscopy (HRTEM). The light absorption ability of the composites was improved because of the presence of WO_3 . Based on the measured and calculated band positions and the Fermi level positions, the band alignment of WO_3/CeO_2 was assumed to be a staggered Z-scheme heterojunction. The charge separation and migration efficiency were much enhanced in the mesoporous WO_3/CeO_2 heterojunction interface, as confirmed by electrochemical impedance spectra, transient photocurrent responses, and surface photovoltage spectroscopy. The suppression of photogenerated charge recombination was proved by photoluminescence. Thanks to the much enhanced charge migration and separation efficiency, the optimized $5\text{WO}_3/\text{CeO}_2$ (5 wt.% WO_3)

Z-scheme laminated heterojunction photocatalysts demonstrated tetracycline photodegradation efficiency of 99.1% within 80 min, achieving a peak TC photodegradation efficiency of 0.0482 min^{-1} , which is approximately 3.4 times that of pristine CeO_2 . Under light irradiation, the fabricated photocatalysts maintained high TC removal efficiency for 10 cycles. The 2D/2D heterostructure proposed here provides the possibility of rare-earth-metal-based composites for efficient, stable, and reusable water purification.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/nano13111798/s1>, Figure S1: XRD patterns of samples with different WO_3 contents, Figure S2: UV-vis diffuse reflectance spectra of samples with different WO_3 contents, Figure S3: Scanning electron microscope of samples with different WO_3 contents. (a) $3\text{WO}_3/\text{CeO}_2$, (b) $5\text{WO}_3/\text{CeO}_2$ and (c) $7\text{WO}_3/\text{CeO}_2$, Table S1: The structure parameters of WO_3 , CeO_2 and WO_3/CeO_2 , Table S2: The total organic carbon (TOC) concentration before and after photocatalytic TC degradation.

Author Contributions: Writing—original draft preparation, W.W.; methodology, Y.M.; validation, Y.M.; formal analysis, L.G. and X.W.; investigation, D.Y. and L.G.; resources, S.W.; data curation, W.W., D.Y., S.W. and X.W.; writing—review and editing, L.L., Z.L. and W.Z.; supervision, Z.L. and W.Z.; project administration, Z.L. and W.Z.; funding acquisition, W.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (52172206, 22205124), the Shandong Province Natural Science Foundation (ZR2022QD062), the Development plan of the Youth Innovation Team in Colleges and Universities of Shandong Province, and College Student Innovation and Entrepreneurship Training Program of Shandong Province (S202010431118).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data will be made available on request.

Acknowledgments: We gratefully acknowledge the support of the National Natural Science Foundation of China (52172206, 22205124), the Shandong Province Natural Science Foundation (ZR2022QD062), the Development plan of the Youth Innovation Team in Colleges and Universities of Shandong Province, and College Student Innovation and Entrepreneurship Training Program of Shandong Province (S202010431118).

Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this article.

References

1. Wang, J.; Zhuan, R.; Chu, L. The occurrence, distribution and degradation of antibiotics by ionizing radiation: An overview. *Sci. Total Environ.* **2019**, *646*, 1385–1397. [CrossRef] [PubMed]
2. Zainab, S.M.; Junaid, M.; Xu, N.; Malik, R.N. Antibiotics and antibiotic resistant genes (ARGs) in groundwater: A global review on dissemination, sources, interactions, environmental and human health risks. *Water Res.* **2020**, *187*, 116455. [CrossRef] [PubMed]
3. Phoon, B.L.; Ong, C.C.; Saheed, M.S.M.; Show, P.L.; Chang, J.S.; Ling, T.C.; Lam, S.S.; Juan, J.C. Conventional and emerging technologies for removal of antibiotics from wastewater. *J. Hazard. Mater.* **2020**, *400*, 122961. [CrossRef]
4. Oberoi, A.S.; Jia, Y.; Zhang, H.; Khanal, S.K.; Lu, H. Insights into the Fate and Removal of Antibiotics in Engineered Biological Treatment Systems: A Critical Review. *Environ. Sci. Technol.* **2019**, *53*, 7234–7264. [CrossRef] [PubMed]
5. Saadati, F.; Keramati, N.; Ghazi, M.M. Influence of parameters on the photocatalytic degradation of tetracycline in wastewater: A review. *Crit. Rev. Environ. Sci. Technol.* **2016**, *46*, 757–782. [CrossRef]
6. Nosaka, Y.; Nosaka, A.Y. Generation and Detection of Reactive Oxygen Species in Photocatalysis. *Chem. Rev.* **2017**, *117*, 11302–11336. [CrossRef]
7. Calvete, M.J.F.; Piccirillo, G.; Vinagreiro, C.S.; Pereira, M.M. Hybrid materials for heterogeneous photocatalytic degradation of antibiotics. *Coord. Chem. Rev.* **2019**, *395*, 63–85. [CrossRef]
8. Bayan, E.M.; Pustovaya, L.E.; Volkova, M.G. Recent advances in TiO_2 -based materials for photocatalytic degradation of antibiotics in aqueous systems. *Environ. Technol. Innov.* **2021**, *24*, 101822. [CrossRef]
9. Qin, K.; Zhao, Q.; Yu, H.; Xia, X.; Li, J.; He, S.; Wei, L.; An, T. review of bismuth-based photocatalysts for antibiotic degradation: Insight into the photocatalytic degradation performance, pathways and relevant mechanisms. *Environ. Res.* **2021**, *199*, 111360. [CrossRef]
10. Suyana, P.; Ganguly, P.; Nair, B.N.; Pillai, S.C.; Hareesh, U.S. Structural and compositional tuning in $\text{g-C}_3\text{N}_4$ based systems for photocatalytic antibiotic degradation. *Chem. Eng. J. Adv.* **2021**, *8*, 100148. [CrossRef]

11. Li, D.; Shi, W. Recent developments in visible-light photocatalytic degradation of antibiotics. *Chin. J. Catal.* **2016**, *37*, 792–799. [\[CrossRef\]](#)
12. Chen, Y.; Yang, J.; Zeng, L.; Zhu, M. Recent progress on the removal of antibiotic pollutants using photocatalytic oxidation process. *Crit. Rev. Environ. Sci. Technol.* **2021**, *52*, 1401–1448. [\[CrossRef\]](#)
13. Dutta, V.; Sharma, S.; Raizada, P.; Thakur, V.K.; Khan, A.A.P.; Saini, V.; Asiri, A.M.; Singh, P. An overview on WO₃ based photocatalyst for environmental remediation. *J. Environ. Chem. Eng.* **2021**, *9*, 105018. [\[CrossRef\]](#)
14. Kim, H.; Yoo, H.-Y.; Hong, S.; Lee, S.; Lee, S.; Park, B.-S.; Park, H.; Lee, C.; Lee, J. Effects of inorganic oxidants on kinetics and mechanisms of WO₃-mediated photocatalytic degradation. *Appl. Catal. B Environ.* **2015**, *162*, 515–523. [\[CrossRef\]](#)
15. Nguyen, T.T.; Nam, S.-N.; Son, J.; Oh, J. Tungsten Trioxide (WO₃)-assisted Photocatalytic Degradation of Amoxicillin by Simulated Solar Irradiation. *Sci. Rep.* **2019**, *9*, 9349. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Yin, X.; Liu, L.; Ai, F. Enhanced Photocatalytic Degradation of Methylene Blue by WO₃ Nanoparticles Under NIR Light Irradiation. *Front. Chem.* **2021**, *9*, 683765. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Liu, X.; Jin, A.; Jia, Y.; Xia, T.; Deng, C.; Zhu, M.; Chen, C.; Chen, X. Synergy of adsorption and visible-light photocatalytic degradation of methylene blue by a bifunctional Z-scheme heterojunction of WO₃/g-C₃N₄. *Appl. Surf. Sci.* **2017**, *405*, 359–371. [\[CrossRef\]](#)
18. Zhu, W.; Liu, J.; Yu, S.; Zhou, Y.; Yan, X. Ag loaded WO₃ nanoplates for efficient photocatalytic degradation of sulfanilamide and their bactericidal effect under visible light irradiation. *J. Hazard. Mater.* **2016**, *318*, 407–416. [\[CrossRef\]](#)
19. Isari, A.A.; Mehregan, M.; Mehregan, S.; Hayati, F.; Kalantary, R.R.; Kakavandi, B. Sono-photocatalytic degradation of tetracycline and pharmaceutical wastewater using WO₃/CNT heterojunction nanocomposite under US and visible light irradiations: A novel hybrid system. *J. Hazard. Mater.* **2020**, *390*, 122050. [\[CrossRef\]](#)
20. Xiao, Y.; Tan, S.; Wang, D.; Wu, J.; Jia, T.; Liu, Q.; Qi, Y.; Qi, X.; He, P.; Zhou, M. CeO₂/BiOIO₃ heterojunction with oxygen vacancies and Ce⁴⁺/Ce³⁺ redox centers synergistically enhanced photocatalytic removal heavy metal. *Appl. Surf. Sci.* **2020**, *530*, 147116. [\[CrossRef\]](#)
21. Shen, C.-H.; Chen, Y.; Xu, X.-J.; Li, X.-Y.; Wen, X.-J.; Liu, Z.-T.; Xing, R.; Guo, H.; Fei, Z.-H. Efficient photocatalytic H₂ evolution and Cr(VI) reduction under visible light using a novel Z-scheme SnIn₄S₈/CeO₂ heterojunction photocatalysts. *J. Hazard. Mater.* **2021**, *416*, 126217. [\[CrossRef\]](#)
22. Li, T.; Yin, J.; Sun, D.; Zhang, M.; Pang, H.; Xu, L.; Zhang, Y.; Yang, J.; Tang, Y.; Xue, J. Manipulation of Mott–Schottky Ni/CeO₂ Heterojunctions into N-Doped Carbon Nanofibers for High-Efficiency Electrochemical Water Splitting. *Small* **2022**, *18*, 2106592. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Wan, Y.; Wang, H.; Liu, J.; Liu, X.; Song, X.; Zhou, W.; Zhang, J.; Huo, P. Enhanced degradation of polyethylene terephthalate plastics by CdS/CeO₂ heterojunction photocatalyst activated peroxydisulfate. *J. Hazard. Mater.* **2023**, *452*, 131375. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Wang, Y.; Zhao, X.; Wei, Q.; He, P.; Cheng, Z.; Wu, J.; Qi, Y.; Sun, Y.; Song, J.; Yang, W. 3D/0D Cu₃SnS₄/CeO₂ Heterojunction Photocatalyst with Dual Redox Pairs Synergistically Promotes the Photocatalytic Reduction of CO₂. *Energy Fuels* **2022**, *36*, 7763–7774. [\[CrossRef\]](#)
25. Bahadoran, A.; Ramakrishna, S.; Masudy-Panah, S.; De Lile, J.R.; Sadeghi, B.; Li, J.; Gu, J.; Liu, Q. Novel S-scheme WO₃/CeO₂ heterojunction with enhanced photocatalytic degradation of sulfamerazine under visible light irradiation. *Appl. Surf. Sci.* **2021**, *568*, 150957. [\[CrossRef\]](#)
26. Channei, D.; Chansaenpak, K.; Phanichphant, S.; Jannoey, P.; Khanitchaidecha, W.; Nakaruk, A. Synthesis and Characterization of WO₃/CeO₂ Heterostructured Nanoparticles for Photodegradation of Indigo Carmine Dye. *ACS Omega* **2021**, *6*, 19771–19777. [\[CrossRef\]](#)
27. Shandilya, P.; Sambyal, S.; Sharma, R.; Mandyal, P.; Fang, B. Properties, optimized morphologies, and advanced strategies for photocatalytic applications of WO₃ based photocatalysts. *J. Hazard. Mater.* **2022**, *428*, 128218. [\[CrossRef\]](#)
28. Niu, X.; Du, Y.; He, J.; Li, X.; Wen, G. Hydrothermal Synthesis of Co-Exposed-Faceted WO₃ Nanocrystals with Enhanced Photocatalytic Performance. *Nanomaterials* **2022**, *12*, 2879. [\[CrossRef\]](#)
29. Yang, D.; Xu, Y.; Pan, K.; Yu, C.; Wu, J.; Li, M.; Yang, F.; Qu, Y.; Zhou, W. Engineering surface oxygen vacancy of mesoporous CeO₂ nanosheets assembled microspheres for boosting solar-driven photocatalytic performance. *Chin. Chem. Lett.* **2022**, *33*, 378–384. [\[CrossRef\]](#)
30. Liu, C.; Mao, S.; Wang, H.; Wu, Y.; Wang, F.; Xia, M.; Chen, Q. Peroxydisulfate-assisted for facilitating photocatalytic degradation performance of 2D/2D WO₃/BiOBr S-scheme heterojunction. *Chem. Eng. J.* **2022**, *430*, 132806. [\[CrossRef\]](#)
31. Dang, W.; Wang, W.; Yang, Y.; Wang, Y.; Huang, J.; Fang, X.; Wu, L.; Rong, Z.; Chen, X.; Li, X.; et al. One-step hydrothermal synthesis of 2D WO₃ nanoplates@ graphene nanocomposite with superior anode performance for lithium ion battery. *Electrochim. Acta* **2019**, *313*, 99–108. [\[CrossRef\]](#)
32. Wan, J.; Tao, F.; Shi, Y.; Shi, Z.; Liu, Y.; Wu, G.; Kan, J.; Zhou, R. Designed preparation of nano rod shaped CeO₂-MnO catalysts with different Ce/Mn ratios and its highly efficient catalytic performance for chlorobenzene complete oxidation: New insights into structure–activity correlations. *Chem. Eng. J.* **2022**, *433*, 133788. [\[CrossRef\]](#)
33. Li, H.; Bian, Z.; Zhu, J.; Huo, Y.; Li, H.; Lu, Y. Mesoporous Au/TiO₂ Nanocomposites with Enhanced Photocatalytic Activity. *J. Am. Chem. Soc.* **2007**, *129*, 4538–4539. [\[CrossRef\]](#)

34. Lo, A.-Y.; Taghipour, F. Ordered mesoporous photocatalysts for CO₂ photoreduction. *J. Mater. Chem. A* **2021**, *9*, 26430–26453. [\[CrossRef\]](#)
35. Tok, A.I.Y.; Boey, F.Y.C.; Dong, Z.; Sun, X.L. Hydrothermal synthesis of CeO₂ nano-particles. *J. Mater. Process. Technol.* **2007**, *190*, 217–222. [\[CrossRef\]](#)
36. Zhang, X.-Y.; Wang, J.-J.; Li, P.; Tan, Z.-Y.; Zeng, J.-H.; He, Y.-R.; Habibul, N. Removal of U(VI) from aqueous solution via photocatalytic reduction over WO₃/g-C₃N₄ composite under visible light. *Chem. Eng. J.* **2022**, *428*, 131209. [\[CrossRef\]](#)
37. Li, P.; Wang, B.; Qin, C.; Han, C.; Sun, L.; Wang, Y. Band-gap-tunable CeO₂ nanoparticles for room-temperature NH₃ gas sensors. *Ceram. Int.* **2020**, *46*, 19232–19240. [\[CrossRef\]](#)
38. Kwong, W.L.; Savvides, N.; Sorrell, C.C. Electrodeposited nanostructured WO₃ thin films for photoelectrochemical applications. *Electrochim. Acta* **2012**, *75*, 371–380. [\[CrossRef\]](#)
39. Liu, R.; Li, H.; Duan, L.; Shen, H.; Zhang, Y.; Zhao, X. In situ synthesis and enhanced visible light photocatalytic activity of C-TiO₂ microspheres/carbon quantum dots. *Ceram. Int.* **2017**, *43*, 8648–8654. [\[CrossRef\]](#)
40. Yang, Y.; Wang, Y.; Yin, S. Oxygen vacancies confined in SnO₂ nanoparticles for desirable electronic structure and enhanced visible light photocatalytic activity. *Appl. Surf. Sci.* **2017**, *420*, 399–406. [\[CrossRef\]](#)
41. Grätzel, M. Photoelectrochemical cells. *Nature* **2001**, *414*, 338–344. [\[CrossRef\]](#)
42. Li, H.; Yu, H.; Quan, X.; Chen, S.; Zhang, Y. Uncovering the Key Role of the Fermi Level of the Electron Mediator in a Z-Scheme Photocatalyst by Detecting the Charge Transfer Process of WO₃-metal-gC₃N₄ (Metal = Cu, Ag, Au). *ACS Appl. Mater. Interfaces* **2016**, *8*, 2111–2119. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Shen, C.-H.; Wen, X.-J.; Fei, Z.-H.; Liu, Z.-T.; Mu, Q.-M. Novel Z-scheme W₁₈O₄₉/CeO₂ heterojunction for improved photocatalytic hydrogen evolution. *J. Colloid Interface Sci.* **2020**, *579*, 297–306. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Huang, Z.-F.; Song, J.; Wang, X.; Pan, L.; Li, K.; Zhang, X.; Wang, L.; Zou, J.-J. Switching charge transfer of C₃N₄/W₁₈O₄₉ from type-II to Z-scheme by interfacial band bending for highly efficient photocatalytic hydrogen evolution. *Nano Energy* **2017**, *40*, 308–316. [\[CrossRef\]](#)
45. Wang, H.; Liao, B.; Lu, T.; Ai, Y.; Liu, G. Enhanced visible-light photocatalytic degradation of tetracycline by a novel hollow BiOCl@CeO₂ heterostructured microspheres: Structural characterization and reaction mechanism. *J. Hazard. Mater.* **2020**, *385*, 121552. [\[CrossRef\]](#)
46. Lai, C.; Xu, F.; Zhang, M.; Li, B.; Liu, S.; Yi, H.; Li, L.; Qin, L.; Liu, X.; Fu, Y.; et al. Facile synthesis of CeO₂/carbonate doped Bi₂O₂CO₃ Z-scheme heterojunction for improved visible-light photocatalytic performance: Photodegradation of tetracycline and photocatalytic mechanism. *J. Colloid Interface Sci.* **2021**, *588*, 283–294. [\[CrossRef\]](#)
47. Ye, Z.; Li, J.; Zhou, M.; Wang, H.; Ma, Y.; Huo, P.; Yu, L.; Yan, Y. Well-dispersed nebula-like ZnO/CeO₂@HNTs heterostructure for efficient photocatalytic degradation of tetracycline. *Chem. Eng. J.* **2016**, *304*, 917–933. [\[CrossRef\]](#)
48. Zhang, K.; Gu, S.; Wu, Y.; Fan, Q.; Zhu, C. Preparation of pyramidal SnO/CeO₂ nano-heterojunctions with enhanced photocatalytic activity for degradation of tetracycline. *Nanotechnology* **2020**, *31*, 215702. [\[CrossRef\]](#)
49. Wen, X.-J.; Niu, C.-G.; Ruan, M.; Zhang, L.; Zeng, G.-M. AgI nanoparticles-decorated CeO₂ microspheres photocatalyst for the degradation of organic dye and tetracycline under visible-light irradiation. *J. Colloid Interface Sci.* **2017**, *497*, 368–377. [\[CrossRef\]](#)
50. Chen, C.; Wang, D.; Li, Y.; Huang, H.; Ke, Y. Flower-like AgBr/CeO₂ Z-scheme heterojunction photocatalyst with enhanced visible light photocatalytic and antibacterial activities. *Appl. Surf. Sci.* **2021**, *565*, 150534. [\[CrossRef\]](#)
51. Shen, J.; Shen, J.; Zhang, W.; Yu, X.; Tang, H.; Zhang, M.; Zulfiqar, L.; Liu, Q. Built-in electric field induced CeO₂/Ti₃C₂-MXene Schottky-junction for coupled photocatalytic tetracycline degradation and CO₂ reduction. *Ceram. Int.* **2019**, *45*, 24146–24153. [\[CrossRef\]](#)
52. Su, F.; Li, P.; Huang, J.; Gu, M.; Liu, Z.; Xu, Y. Photocatalytic degradation of organic dye and tetracycline by ternary Ag₂O/AgBr-CeO₂ photocatalyst under visible-light irradiation. *Sci. Rep.* **2021**, *11*, 85. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Zhang, E.; Zhu, Q.; Huang, J.; Liu, J.; Tan, G.; Sun, C.; Li, T.; Liu, S.; Li, Y.; Wang, H.; et al. Visually resolving the direct Z-scheme heterojunction in CdS@ZnIn₂S₄ hollow cubes for photocatalytic evolution of H₂ and H₂O₂ from pure water. *Appl. Catal. B Environ.* **2021**, *293*, 120213. [\[CrossRef\]](#)
54. Deng, Y.; Zhang, Z.; Du, P.; Ning, X.; Wang, Y.; Zhang, D.; Liu, J.; Zhang, S.; Lu, X. Embedding Ultrasmall Au Clusters into the Pores of a Covalent Organic Framework for Enhanced Photostability and Photocatalytic Performance. *Angew. Chem. Int. Ed.* **2020**, *59*, 6082–6089. [\[CrossRef\]](#)
55. Feng, C.; Wu, Z.P.; Huang, K.W.; Ye, J.; Zhang, H. Surface Modification of 2D Photocatalysts for Solar Energy Conversion. *Adv. Mater.* **2022**, *34*, e2200180. [\[CrossRef\]](#)

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