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## A direct Z-scheme $\text{Bi}_2\text{WO}_6/\text{NH}_2\text{-UiO-66}$ nanocomposite as an efficient visible-light-driven photocatalyst for NO removal†

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To explore an efficient photocatalyst for NO pollution, a direct Z-scheme photocatalytic system is successfully fabricated by coupling  $\text{Bi}_2\text{WO}_6$  with  $\text{NH}_2\text{-UiO-66}$  via a simple hydrothermal synthesis technique. The Z-scheme system promotes the NO photocatalytic oxidation activity with an optimum NO removal rate of 79%, which is 2.7 and 1.2 times that obtained by using only pristine  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ , respectively. Simultaneously, superior selectivity for converting NO to  $\text{NO}_3^-/\text{NO}_2^-$  is observed. The enhanced photocatalytic performance of the  $\text{Bi}_2\text{WO}_6/\text{NH}_2\text{-UiO-66}$  hybrids is attributed to the following two aspects: (i) large specific area of  $\text{NH}_2\text{-UiO-66}$ , which exposes more active sites and is beneficial to the adsorption and activation of NO; (ii) outstanding Z-scheme structure constructed between  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ , which can improve the efficiency of the separation of electron-hole pairs and preserves the strong oxidation ability of hybrids. ESR analysis shows that  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  contribute to NO removal. A possible photocatalytic mechanism of NO oxidation on the direct Z-scheme photocatalyst ( $\text{BWO/2NU}$ ) under visible light irradiation is proposed. This work displays the BWO/2NU hybrid's potential for treating low-concentration air pollutants, and the proposed Z-scheme photocatalyst design and promotion mechanism may inspire more rational synthesis of highly efficient photocatalysts for NO removal.

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### 1. Introduction

Rapid industrialization and urbanization have led to a sharp increase in harmful gas emissions, such as volatile organic compounds (VOCs) and nitrogen oxides ( $\text{NO}_x$ ), which have become the most significant pollutants in prominent environmental issues.<sup>1,2</sup> NO is a typical air pollutant and results in many hazards, such as tropospheric ozone depletion, global climate warming, acid rain, and human diseases.<sup>3</sup> Different techniques including physical and chemical adsorption,<sup>4</sup> heterogeneous catalytic reduction,<sup>5</sup> and oxidation and so on<sup>6</sup> are usually adopted to eliminate NO from gas emissions from combustion sources. However, these technologies are usually employed to treat NO at relatively high concentrations.<sup>7</sup> For practical ppb-level NO, it widely exists in both indoor and

outdoor atmospheric environments, which has severe impacts on ecology and human health. Photocatalytic oxidation appears to be an environment friendly and easy approach to removing NO at ppb levels in air.<sup>3,8,9</sup>

Among the various reported photocatalysts, it's difficult for a single-component material to achieve superior performance, including stability, effective separation of photogenerated charges, utilization efficiency of solar energy and strong redox ability.<sup>10</sup> Therefore, a variety of strategies have been developed and applied to improve the performance of single-component materials, such as size and morphology control,<sup>11</sup> surface modification,<sup>12</sup> defect engineering<sup>13</sup> and heterojunction construction.<sup>14</sup> Among them, the constructed heterojunctions are promising due to high separation efficiency of electron-hole pairs, including type II heterojunctions and Z-scheme photocatalysts and so on. In comparison with type II heterojunctions, Z-scheme photocatalytic system can minimize unfavorable backward reaction at two different redox sites during the photocatalytic process<sup>15</sup> and preserve the higher redox potentials of the photo-induced charges, showing excellent photocatalytic performance.<sup>14,16-18</sup> Thus, direct Z-scheme photocatalysts have been studied and applied,<sup>15,16,19,20</sup> ever since Yu *et al.* pioneered the direct Z-scheme photocatalyst  $\text{g-C}_3\text{N}_4\text{-TiO}_2$  and applied it to decompose formaldehyde in air.<sup>21</sup>

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Bismuth tungstate ( $\text{Bi}_2\text{WO}_6$ ), an environment-friendly material, has been widely studied and applied in photocatalysis owing to its unique properties, such as nontoxicity, a visible light response range and a regulable band gap of 2.75 eV.<sup>22</sup> Moreover, its unique band structure makes the valence band largely dispersed and does benefits to the mobility of photo-induced carriers.<sup>23</sup> However, a few drawbacks limit the photocatalytic performance of  $\text{Bi}_2\text{WO}_6$ , including high recombination of photoinduced electron–hole pairs and low utilization of visible light.<sup>24</sup> Therefore, it is imperative to overcome these disadvantages. Coupling  $\text{Bi}_2\text{WO}_6$  with other materials to construct Z-scheme heterojunction photocatalysts could help achieve this objective. For example, Hu *et al.*<sup>25</sup> designed and synthesized a Z-scheme photocatalytic system (2D/2D BP/monolayer  $\text{Bi}_2\text{WO}_6$ ). The Z-scheme photocatalyst showed superior performance in photocatalytic water splitting and photocatalytic NO removal. And the NO removal ratio was as high as 67%.

$\text{NH}_2\text{-UiO-66}$ , a typical metal–organic frameworks (MOFs) material, have been widely applied in different areas owing to their high specific surface areas, tailorabile pore sizes, easy functional groups, stability and designed frame structures.<sup>26</sup> Combing  $\text{NH}_2\text{-UiO-66}$  with  $\text{Bi}_2\text{WO}_6$  can provide extra pathways for the charge migration and facilitate the efficient separation of photo-induced carriers. In addition, the incorporation may lead to the formation of a Z-scheme photocatalytic system and maintaining high redox potential, which are beneficial for good catalytic activity and selectivity.<sup>27</sup>

Here, we constructed a novel direct Z-scheme photocatalyst to promote NO removal and selectivity at a ppb level under visible light irradiation in a continuous gas flow. In our work,  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$  were chosen to form an interactive interface between them *via* a simple hydrothermal method, and a novel direct Z-scheme system,  $\text{Bi}_2\text{WO}_6/x\text{NH}_2\text{-UiO-66}$  (BWO/ $x$ NU), was fabricated. On the one hand, bismuth tungstate ( $\text{Bi}_2\text{WO}_6$ ), an environment-friendly material, is being extensively studied for photocatalysis owing to unique properties.  $\text{NH}_2\text{-UiO-66}$  displays superior features in owing to large surface areas, high stability, visible-light response, and semiconductor properties.<sup>27–31</sup> One the other hand, the band position of  $\text{NH}_2\text{-UiO-66}$  matched well with that of  $\text{Bi}_2\text{WO}_6$ . Combining  $\text{NH}_2\text{-UiO-66}$  with  $\text{Bi}_2\text{WO}_6$  can lead to forming a Z-scheme band structure, which ensures high separation efficiency of photogenerated electrons and holes. More importantly, the BWO/ $x$ NU hybrids can preserve the strong oxidation ability on the valence band (VB) of  $\text{NH}_2\text{-UiO-66}$  and high reduction ability on the conduction band (CB) of  $\text{Bi}_2\text{WO}_6$  simultaneously. The as-prepared BWO/ $x$ NU hybrids exhibited both higher photocatalytic ability for NO oxidation and improved selectivity for  $\text{NO}_3^-/\text{NO}_2^-$  conversion. Hence, this work provides a basis for designing a MOFs-based direct Z-scheme photocatalytic system, simultaneously improving photocatalytic activity and selectivity for NO oxidation, and presents a mechanism of Z-scheme photocatalytic reaction for NO oxidation.

## 2. Experimental

### 2.1 Materials

Zirconium tetrachloride ( $\text{ZrCl}_4$ ), *N,N*-dimethyl formamide (DMF), glacial acetic acid (HAc), and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd.  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were purchased from Aladdin Industrial Corporation. 2-NH<sub>2</sub>-terephthalic acid was procured from Sigma-Aldrich Chemistry. All the reagents were of analytical grade and were used without further purification.

### 2.2 Synthesis

**2.2.1 Synthesis of  $\text{NH}_2\text{-UiO-66}$ .**  $\text{NH}_2\text{-UiO-66}$  was synthesized in accordance with a procedure reported in the literature.<sup>32</sup> In a typical synthesis,  $\text{ZrCl}_4$  (0.136 g, 0.585 mmol) and 2-NH<sub>2</sub>-terephthalic acid (0.106 g, 0.585 mmol) were dissolved in DMF (130 mL) containing 15.6 mL HAc, and the solution was transferred to a 200 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated in an oven at 120 °C for 24 h under autogenous pressure. Until it cooled naturally to room temperature, the solid particles were obtained *via* filtration with a mixture of methanol and DMF (v/v = 1 : 4) to remove residual DMF. The obtained pale yellow product was dried in vacuum at 90 °C for 12 h.

**2.2.2 Synthesis of  $\text{Bi}_2\text{WO}_6/\text{NH}_2\text{-UiO-66}$ .** The  $\text{Bi}_2\text{WO}_6/\text{NH}_2\text{-UiO-66}$  composites were synthesized *via* a simple one-step solvothermal method.<sup>28</sup> In detail,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (0.142 g, 0.430 mmol) was dissolved in deionized water (60 mL), vigorously stirring at room temperature. A series of different  $\text{Bi}_2\text{WO}_6/\text{NH}_2\text{-UiO-66}$  mass ratios of 1 : 0.5, 1 : 1, 1 : 2, 1 : 3, and 1 : 5 was obtained by adding 0.15 g, 0.30 g, 0.60 g, 0.90 g, and 1.20 g, respectively, of  $\text{NH}_2\text{-UiO-66}$  to the  $\text{Na}_2\text{WO}_4$  solution, and the resultant mixtures were stirred for 0.5 h. Then,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.417 mg, 0.860 mmol) was added to DMF (60 mL) to form a homogenous white solution. Subsequently, the reaction precursor was stirred for 1 h. And then, it was transferred to a 200 mL Teflon-lined stainless steel autoclave, where the reaction proceeded at 120 °C for 12 h. After naturally cooling, the final products were collected by centrifugation, washed with deionized water, and dried at 60 °C for 12 h. According to the  $\text{Bi}_2\text{WO}_6/\text{NH}_2\text{-UiO-66}$  mass ratios, the samples were denoted as BWO/ $x$ NU; the labels BWO/0.5NU, BWO/NU, BWO/2NU, BWO/3NU, and BWO/5NU, correspond to  $\text{Bi}_2\text{WO}_6/\text{NH}_2\text{-UiO-66}$  mass ratios of 1 : 0.5, 1 : 1, 1 : 2, 1 : 3, and 1 : 5, respectively.

### 2.3 Characterization

The crystal phases of the samples were observed *via* X-ray diffraction (XRD) with Cu K $\alpha$  radiation (Shimadzu XRD-6000, Japan). The morphologies and structures of the catalysts were characterized using a scanning electron microscopy (SEM, SU-8010, Hitachi, Japan) and a transmission electron microscopy (TEM, H-9500, HITACHI, Japan). The N<sub>2</sub> adsorption/desorption isotherms were collected on an N<sub>2</sub> adsorption apparatus (JW-BK 132F, Beijing JWGB Sci & Tech Co., China) and used the Brunauer–Emmett–Teller (BET) method. The pore size distribution was acquired *via* the Barrett–Joyner–Halenda (BJH) desorption

method. X-ray photoelectron spectroscopy (XPS) experiments were carried out on an XPS instrument (ESCALAB 250Xi, Thermo, USA) to investigate the surface chemical compositions. The binding energies were referenced to C 1s at 284.8 eV. To explore the light absorption properties, the ultraviolet-visible light diffuse reflection spectra (UV-vis DRS) were obtained using a UV-vis diffuse reflection spectrophotometer (Lambda 750 S, PerkinElmer, USA) with a spectral range 200–800 nm. The electron spin resonance (ESR) signals of spin-trapped radicals were detected using a JES FA200 spectrometer (JEOL Ltd., Japan). The photoluminescence spectra were obtained using a fluorescence spectrometer (FLS920, Edinburgh Instruments, England) and the excitation source used was a laser source emitting at 380 nm. The photocurrent, electrochemical AC impedance, and the parameters required for Mott–Schottky plots were measured using an electrochemical workstation (CHI 660E, China). And standard three-electrode system and 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as the electrolyte are necessary for the electrochemical workstation.

#### 2.4 Photocatalytic activity tests

The photocatalytic activity for NO removal was performed at room temperature in a continuous-flow stainless steel rectangular reactor. There are five channels in the reactor, and photocatalyst (50 mg) was dispersed uniformly on five glass slides, which were placed in the channels. The light source for photocatalytic reaction used a 500 W Xenon lamp (CEL-LAX500, Beijing AuLight Tech Co., Ltd, China), equipped with a 420 nm UV cut-off filter. The NO gas used in the tests was continuously obtained from a NO compressed gas cylinder (50 ppm, N<sub>2</sub> balance). Air stream was used to dilute the concentration of NO to around 500 ppb. Simultaneously, air stream was delivered through a bubbler to adjust the relative humidity (RH) of the reaction gas to 55%. The volume flow rate of the reaction gas was about 0.8 L min<sup>-1</sup>, with corresponding residence time being 18.75 s. NO adsorption–desorption equilibrium should be achieved before switching on the Xe lamp with a current of 7 A. The concentrations of NO, NO<sub>2</sub>, and NO<sub>x</sub>

were recorded using an online analyzer (NO–NO<sub>2</sub>–NO<sub>x</sub> Analyzer, Model 42i, Thermo Scientific). Based on the following formulae, NO and NO<sub>x</sub> removal efficiencies could be calculated.

$$\text{NO removal} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}})/\text{NO}_{\text{in}},$$

$$\text{NO}_2 \text{ formation} = \text{NO}_{x,\text{out}} - \text{NO}_{\text{out}},$$

where NO<sub>in/out</sub> represent the concentrations of NO at the inlet and outlet, respectively. And NO<sub>x,in/out</sub> has the similar meaning.

### 3. Results and discussion

#### 3.1 Crystal phases and structures

To confirm the phases and crystal structures of pure NH<sub>2</sub>-UiO-66, Bi<sub>2</sub>WO<sub>6</sub>, and the BWO/xNU nanocomposites with different mass ratios of NH<sub>2</sub>-UiO-66, the catalysts were characterized *via* XRD. The XRD results are shown in Fig. S1† and 1a. The XRD patterns of pure NH<sub>2</sub>-UiO-66 are consistent with those reported previously,<sup>26,28,32,33</sup> while pristine Bi<sub>2</sub>WO<sub>6</sub> shows the characteristic peaks ascribed to russellite (JCPDS: 79-2020). After combining Bi<sub>2</sub>WO<sub>6</sub> with NH<sub>2</sub>-UiO-66, similar XRD patterns at  $2\theta = 5\text{--}10^\circ$  are observed in all of the as-prepared catalysts, which are ascribed to NH<sub>2</sub>-UiO-66.<sup>26,28,32,33</sup> Compared with those of pure NH<sub>2</sub>-UiO-66, the characteristic peaks of BWO/xNU at low angles become weaker as the Bi<sub>2</sub>WO<sub>6</sub> content increases. What is noteworthy in Fig. 1b is that the diffraction peaks shift to lower angles at  $2\theta = 7\text{--}9^\circ$ . According to Bragg's law, the negative shift can be ascribed to the lattice expansion of NH<sub>2</sub>-UiO-66 in the hybrids.<sup>34</sup> Moreover, no other impurity peaks can be seen, which indicates that the BWO-NU heterojunctions are successfully obtained and BWO/xNU is a two-phase composite.<sup>35</sup>

The samples's SEM images are shown in Fig. 2. As illustrated in Fig. 2a, pure NH<sub>2</sub>-UiO-66 displays a regular octahedral cubic morphology with clean and smooth surfaces and its size is approximately 200–500 nm. Pristine Bi<sub>2</sub>WO<sub>6</sub> exhibits nanoparticle-like morphology (Fig. 2d). Interestingly, after the Bi<sub>2</sub>WO<sub>6</sub> loading process, the NH<sub>2</sub>-UiO-66's surface from BWO/

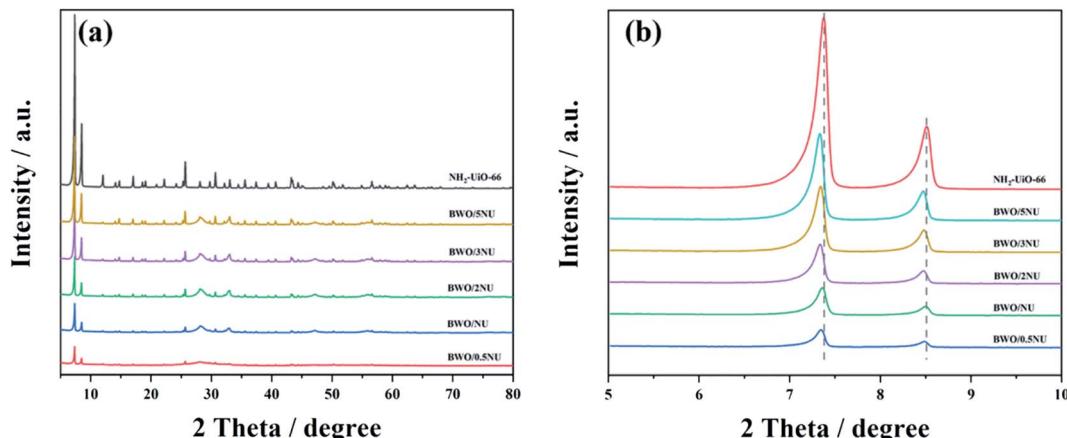


Fig. 1 (a) XRD patterns of NH<sub>2</sub>-UiO-66 and BWO/xNU samples, and (b) diffraction peaks of pure NH<sub>2</sub>-UiO-66 and of BWO/xNU ascribed to NH<sub>2</sub>-UiO-66.



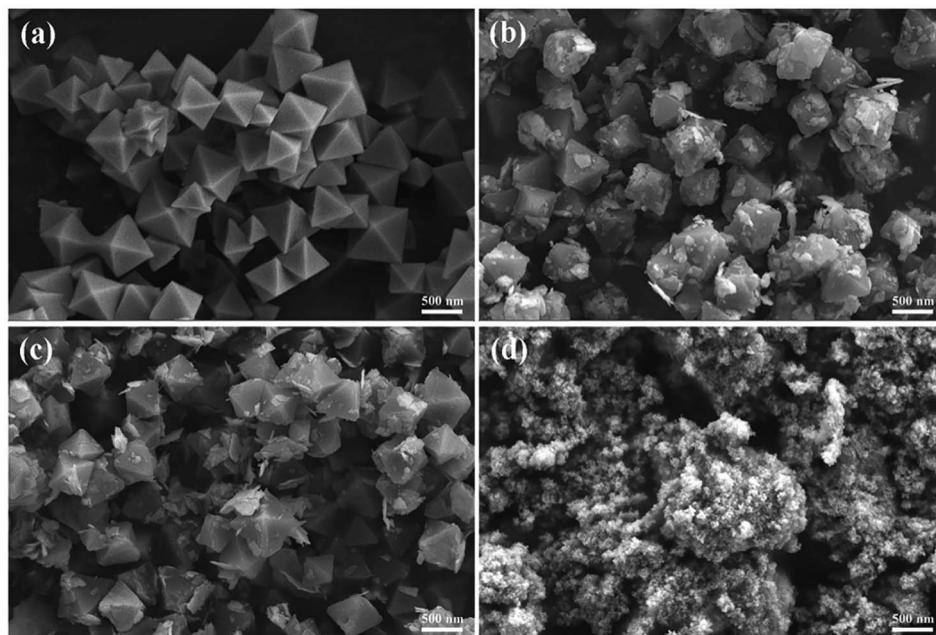


Fig. 2 (a) SEM patterns of  $\text{NH}_2\text{-UiO-66}$  samples, (b and c) SEM patterns of BWO/2NU samples, and (d) SEM patterns of  $\text{Bi}_2\text{WO}_6$  samples.

2NU hybrid becomes rough (Fig. 2b and c). In the SEM patterns of BWO/2NU (Fig. 2b and c), large number of nanoplates insert among the  $\text{NH}_2\text{-UiO-66}$  nanocubes. We believe that these nanoplates are  $\text{Bi}_2\text{WO}_6$ , introduced by the addition of  $\text{NH}_2\text{-UiO-66}$  during the growth of  $\text{Bi}_2\text{WO}_6$ . To further confirmation, TEM and energy dispersive spectroscopy (EDS) analyses were conducted. These  $\text{Bi}_2\text{WO}_6$  nanoplates decorate and disperse on the surface of  $\text{NH}_2\text{-UiO-66}$ .

The morphology and structure of samples were additionally analyzed *via* TEM and high-resolution TEM (HRTEM). It is shown in Fig. 3a that pure  $\text{NH}_2\text{-UiO-66}$  has a cube-like morphology, of which size is approximately 200–500 nm. The results are in accordance with the SEM analysis. After hybridization with  $\text{Bi}_2\text{WO}_6$  (Fig. 3b and c), the  $\text{NH}_2\text{-UiO-66}$  in the BWO/2NU hybrids can still be observed. Meanwhile,  $\text{Bi}_2\text{WO}_6$  displays a nanoplate-like morphology. Further observations show that  $\text{NH}_2\text{-UiO-66}$  and  $\text{Bi}_2\text{WO}_6$  are closely bonded, which is consistent with the XRD and SEM analysis. This structure does benefits to the rapid separation of photo-induced charges between  $\text{NH}_2\text{-UiO-66}$  and  $\text{Bi}_2\text{WO}_6$  with improving its photocatalytic activity. Additionally, pristine  $\text{Bi}_2\text{WO}_6$  displays the morphology of small nanoparticles (Fig. S2<sup>†</sup>), which differs from that of  $\text{Bi}_2\text{WO}_6$  in the BWO/2NU hybrid. The HRTEM image (Fig. 3d) of as-prepared  $\text{Bi}_2\text{WO}_6$  shows clear fringes. And lattice spacings of 0.248 nm and 0.255 nm are measured, which can be assigned to the (115) and (022) planes of russelite  $\text{Bi}_2\text{WO}_6$ , respectively. The EDS spectrum (Fig. 3e and f) confirms that the BWO/2NU hybrid contains elements including Zr, Bi, W, C, N, and O.

The  $\text{N}_2$  adsorption–desorption measurements were performed to explore the BET surface areas and pore structures of the as-prepared photocatalysts. The results are shown in Fig. 4.  $\text{NH}_2\text{-UiO-66}$  has a large surface area ( $673.58 \text{ m}^2 \text{ g}^{-1}$ ) and its isotherm is of type I, which indicates that the  $\text{NH}_2\text{-UiO-66}$

sample has a microporous structure.<sup>36–38</sup> The BET surface area of pure  $\text{Bi}_2\text{WO}_6$  is  $52.67 \text{ m}^2 \text{ g}^{-1}$  (Fig. 4), which is relatively low. Moreover, the isotherm of pure  $\text{Bi}_2\text{WO}_6$  has a H3 type hysteresis loop, indicating its mesoporous structure. The BET surface areas of BWO/2NU and BWO/0.5NU are  $685.41 \text{ m}^2 \text{ g}^{-1}$  and  $313.20 \text{ m}^2 \text{ g}^{-1}$ , respectively (Fig. 4). After the combination of  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ , the specific surface areas of different samples increase with decrease in the content of  $\text{Bi}_2\text{WO}_6$ . It's worth noting that the  $\text{N}_2$  adsorption–desorption isotherms of all the hybrids present obvious hysteresis loops, revealing the formation of a mesoporous structure in  $\text{NH}_2\text{-UiO-66}$  after the hybridization of  $\text{Bi}_2\text{WO}_6$ . The combination of micropores and mesopores can be further confirmed using the pore size distributions (Fig. S3 and S4<sup>†</sup>). Photocatalysts with higher BET surface areas can be expected to produce more active sites for photocatalytic reaction and exhibit improved photocatalytic performance.

The XPS spectra of the as-prepared  $\text{NH}_2\text{-UiO-66}$ ,  $\text{Bi}_2\text{WO}_6$ , and BWO/2NU samples were obtained to further clarify the interfacial interaction between  $\text{NH}_2\text{-UiO-66}$  and  $\text{Bi}_2\text{WO}_6$ . The XPS survey spectrum (Fig. S5<sup>†</sup>) reveals that the BWO/2NU hybrid is composed of Zr, Bi, W, O, N, and C, which is consistent with the results of EDS. The characteristic peaks of the four elements with different valence states are ascribed to Zr  $3d^{5/2}$  and Zr  $3d^{3/2}$  (Fig. 5a), N 1s (Fig. 5b), Bi  $4f^{7/2}$  and Bi  $4f^{5/2}$  (Fig. 5c), and W  $4f^{7/2}$  and W  $4f^{5/2}$  (Fig. 5d). Compared with those of pure  $\text{NH}_2\text{-UiO-66}$ , the high-resolution XPS spectra of Zr  $3d^{5/2}$  and Zr  $3d^{3/2}$  in BWO/2NU shift to lower binding energies by approximately 0.1 eV. It is noticeable that the shift in the binding energies of N 1s exhibits a similar result, indicating strong interfacial interaction between  $\text{NH}_2\text{-UiO-66}$  and  $\text{Bi}_2\text{WO}_6$ .<sup>15</sup> Meanwhile, the characteristic peaks of Bi  $4f^{7/2}$  and Bi  $4f^{5/2}$ , and of W  $4f^{7/2}$  and W  $4f^{5/2}$ , attributed to the BWO/2NU hybrid, exhibit positive shifts of



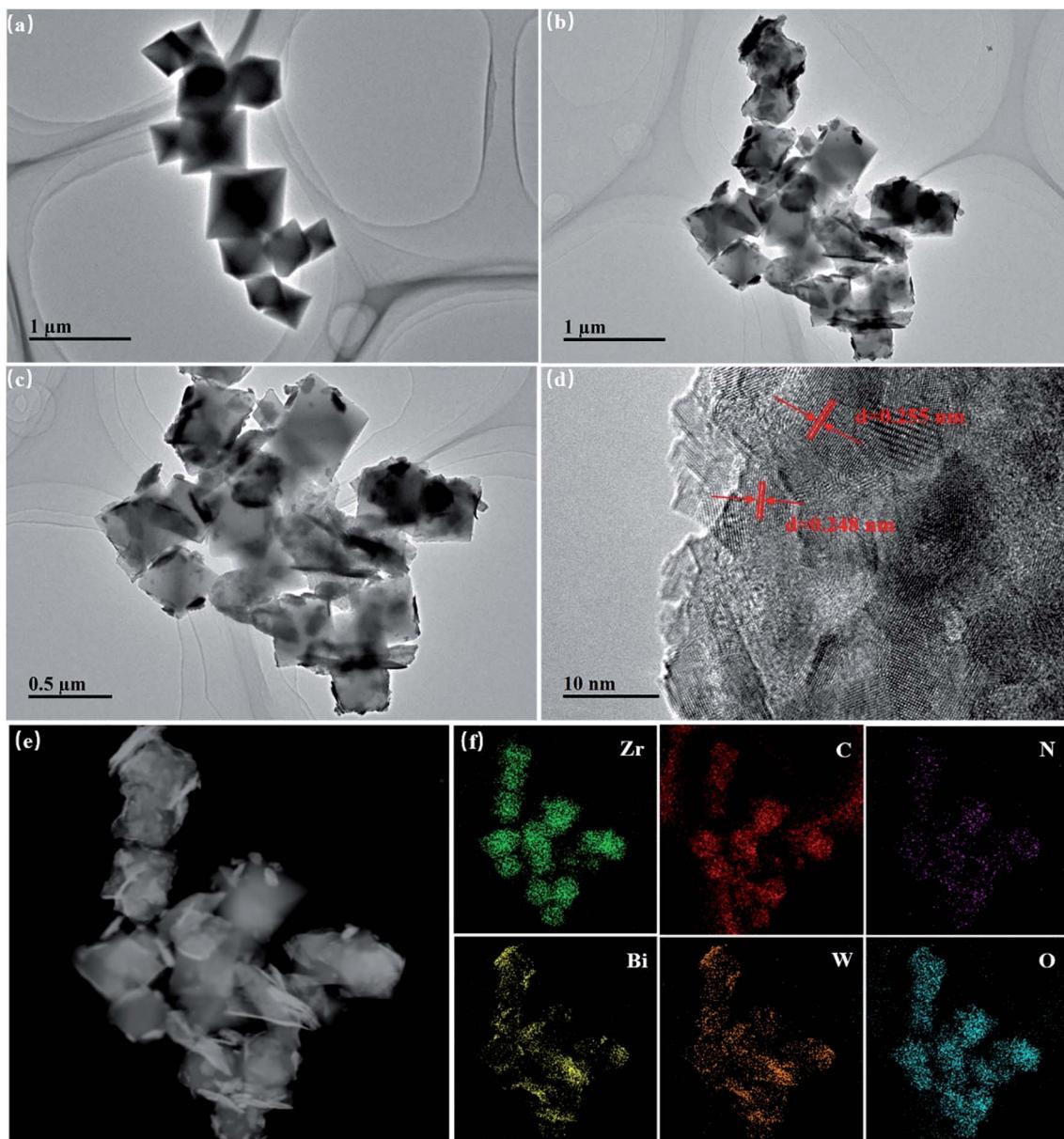


Fig. 3 TEM image of (a)  $\text{NH}_2\text{-UiO-66}$  samples, (b and c) BWO/2NU samples, (d) HRTEM image of  $\text{Bi}_2\text{WO}_6$  samples, and (e and f) EDS elemental mapping images of BWO/2NU samples.

0.2 eV and 0.3 eV, when compared with those observed for pure  $\text{Bi}_2\text{WO}_6$ . The shifts in the binding energy of a specific element suggest the electron migration from  $\text{Bi}_2\text{WO}_6$  to  $\text{NH}_2\text{-UiO-66}$  with the formation of a built-in electric field at the interface in the direction from  $\text{Bi}_2\text{WO}_6$  to  $\text{NH}_2\text{-UiO-66}$  and a strong interfacial interaction between them.

### 3.2 Photocatalytic activities for NO removal

NO is chosen as the target pollutant to assess the photocatalytic performance of photocatalysts. An adsorption–desorption equilibrium between the test samples and NO was attained before the latter were irradiated using the Xe lamp. Fig. 6a shows that the blank test with no photocatalysts is not active for photocatalytic NO oxidation and the NO concentrations of the

as-prepared samples decrease with increase in illumination time. The maximum NO removal ratio of pure  $\text{NH}_2\text{-UiO-66}$  is 63% but that of pristine  $\text{Bi}_2\text{WO}_6$  is only 29%. Moreover, the time taken to achieve stable efficiency is longer in the case of  $\text{NH}_2\text{-UiO-66}$  and  $\text{Bi}_2\text{WO}_6$  than in the case of the hybrids. As the  $\text{NH}_2\text{-UiO-66}$  content increases, the optimal activities of the as-prepared BWO/ $x$ NU ( $x = 0.5, 1, 2, 3, 5$ ) hybrids assume an inverted V-shaped trend. When the  $\text{NH}_2\text{-UiO-66}$  content of BWO/ $x$ NU is 66.7%, the BWO/2NU exhibits an optimum NO removal efficiency of 79%, which is an increase of 272.41% and 118.44% over those achieved with pristine  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ , respectively. It is interesting that the compounds, especially BWO/2NU, could achieve a state of balance rapidly, *i.e.*, in only a few minutes. The photocatalytic NO oxidation of



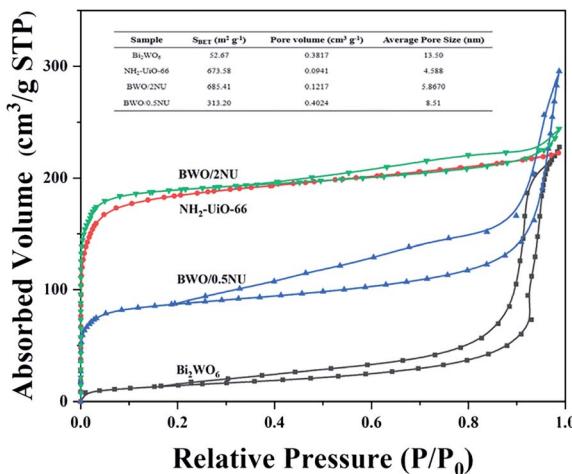


Fig. 4  $\text{N}_2$  adsorption–desorption isotherms and BET surface areas (inset table) of  $\text{Bi}_2\text{WO}_6$ ,  $\text{NH}_2\text{-UiO-66}$ , BWO/0.5NU, and BWO/2NU.

different catalysts displays small error variety (error bar < 5%) (Fig. S7†). And Table S1† shows other reported works in the field of photocatalytic NO removal. Among them, the BWO/2NU hybrid displays superior performance.

$\text{NO}_3^-$  is the desired product<sup>39</sup> during the photocatalytic oxidation of NO, while  $\text{NO}_2$ , as one of the reaction intermediates, is not desired. The formation of  $\text{NO}_2$  can be used to estimate the product selectivity and photooxidation ability of the materials.<sup>39</sup> Therefore, the  $\text{NO}_2$  formation was detected online

and the results are shown in Fig. 6b. It is noteworthy that the  $\text{NO}_2$  formation in the case of BWO/xNU hybrids decreases dramatically and is as low as 1.97 ppb when BWO/2NU is used. This quantity can reach 67.89 ppb and 56.22 ppb in the case of pristine  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ , respectively, after stabilization. The above results indicate that the BWO/2NU hybrids are beneficial to the conversion of NO to  $\text{NO}_3^-/\text{NO}_2^-$  owing to their superior oxidation ability.

In addition, stability is usually used as an index to estimate the usefulness of photocatalysts in practical applications. Five-cycle experiments were performed to investigate the BWO/2NU's stability (Fig. 6c). After the first four runs, the efficiency of NO removal decreases slightly with increase in irradiation time. When the photocatalysts were washed with deionized water after four runs, their photocatalytic activity remained nearly unchanged. It is suggested in the literature<sup>40,41</sup> that photocatalytic activity is weakened by the accumulation of  $\text{HNO}_3/\text{HNO}_2$  on the surfaces of the catalysts, as the active sites of the as-prepared samples are likely covered. However, the powder XRD patterns (Fig. S6†) of the BWO/2NU hybrid used for photocatalysis shows no distinct differences in comparison with a fresh specimen, indicating no structural changes.

### 3.3 Enhanced mechanism of visible-light photocatalytic activities

To further investigate the enhanced photocatalytic activities, steady-state photoluminescence (PL) spectroscopy, time-resolved photoluminescence (TRPL) spectroscopy, photocurrent, and

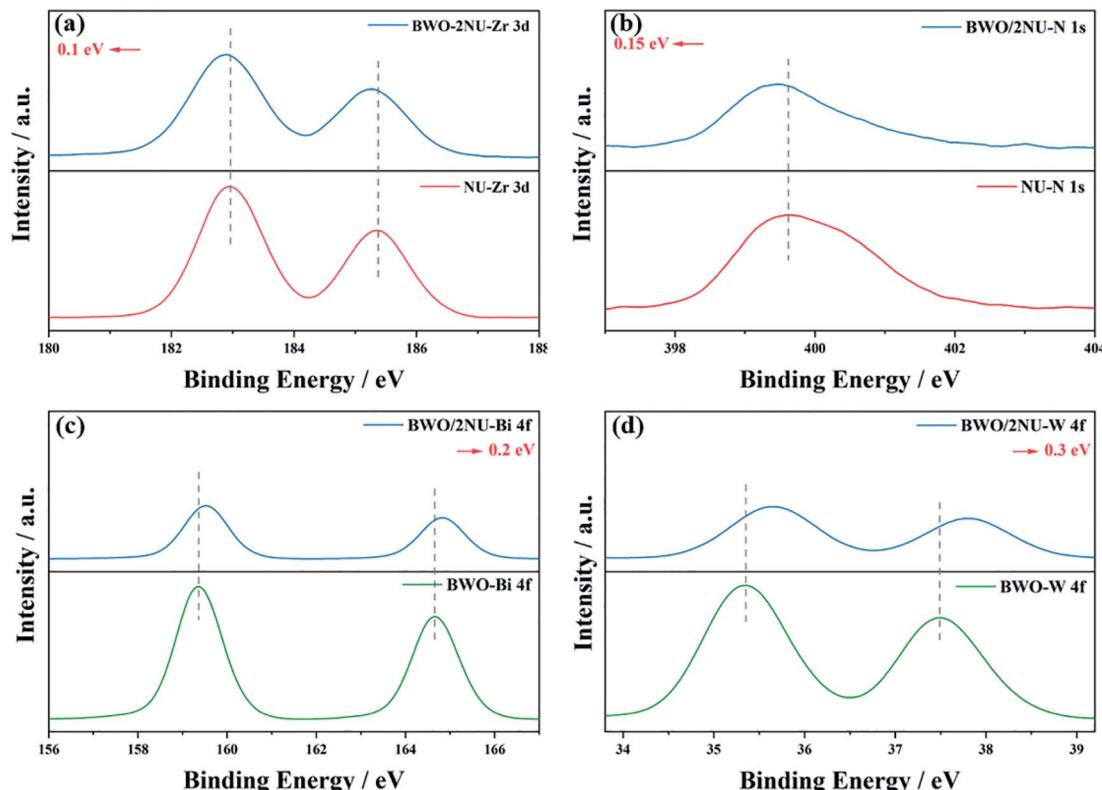


Fig. 5 XPS spectra of (a) Zr 3d, (b) N 1s, (c) Bi 4f, and (d) W 4f.



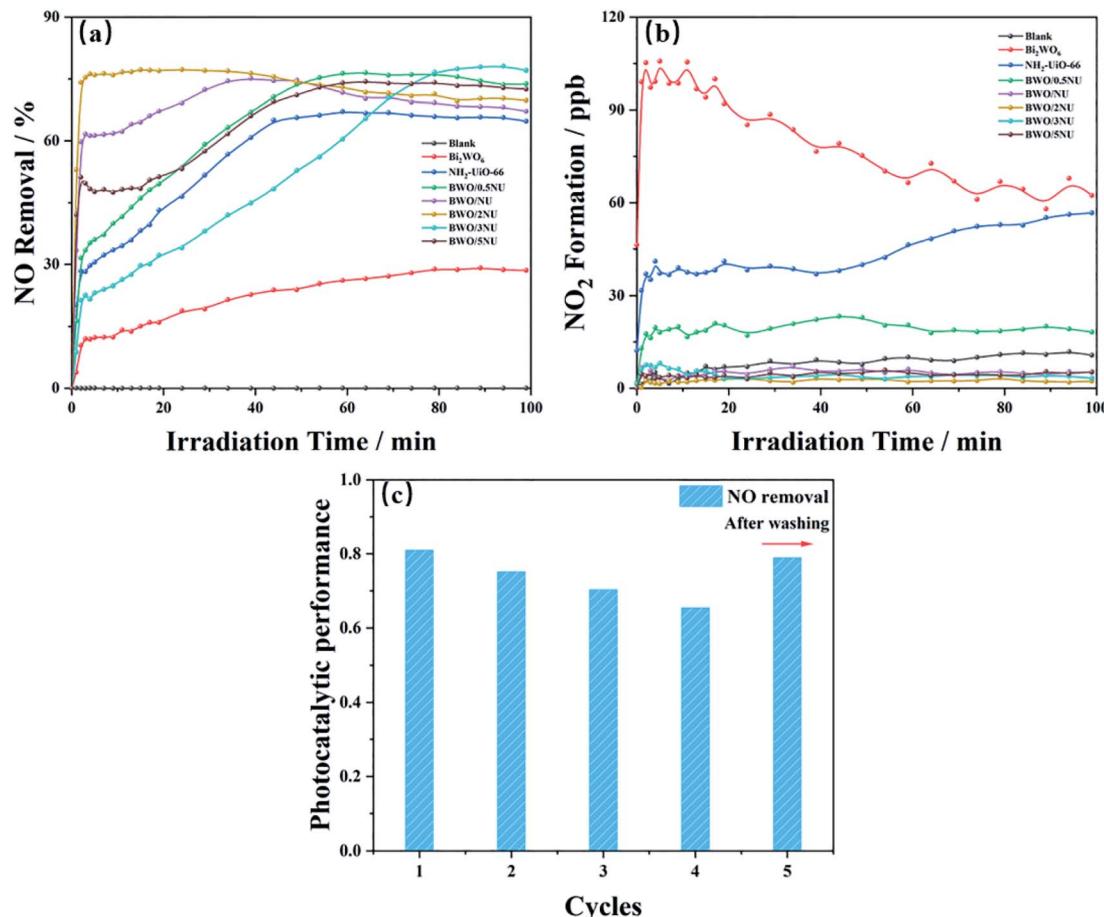


Fig. 6 (a) NO removal efficiencies, and (b) quantities of  $\text{NO}_2$  formation using different as-prepared samples; and (c) consecutive cycles of photocatalytic reaction of NO on BWO/2NU.

electrochemical impedance spectroscopy (EIS) analyses were performed. The PL emission can be utilized to investigate the recombination of photo-induced electron–hole pairs.<sup>42</sup> The PL spectrum of pure  $\text{NH}_2\text{-UiO-66}$  (Fig. 7a) reveals an emission peak centered at 450 nm. And the PL emission peak of the BWO/2NU hybrid is significantly weaker than that of pure  $\text{NH}_2\text{-UiO-66}$ , indicating efficient charge separation between  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ . Fig. 7b presents the TRPL spectra of  $\text{Bi}_2\text{WO}_6$ ,  $\text{NH}_2\text{-UiO-66}$ , BWO/0.5NU, and BWO/2NU. Multiexponential decay is observed from the plot. The cubic exponential models were adopted to fit the decay spectra and obtain three radiative lifetimes with different percentages (inset of Fig. 7b). The three lifetimes ( $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ ) of the BWO/2NU hybrid are all 0.452 ns, which is shorter than the corresponding lifetimes of pristine  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ . Moreover, the BWO/2NU hybrid has a shorter average fluorescence lifetime (0.452 ns) than those of pure  $\text{Bi}_2\text{WO}_6$  (0.962 ns) and  $\text{NH}_2\text{-UiO-66}$  (0.602 ns). The recombination of free excitons can lead to a longer lifetime. Therefore, the obvious quenching of all the lifetimes in the transients for BWO/2NU hybrid leads to a shorter decay lifetime, which indicates that interfacial electrons transfer faster at the BWO/2NU hybrid, otherwise charges will recombine and result in enhanced photoluminescence. The above result can be responsible for BWO/2NU's higher photocatalytic performance owing to

the efficient suppressed recombination of charges in  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ . The spectra of the transient photocurrent response and electrochemical impedance spectroscopy were analyzed to investigate the separation efficiency of electron–hole pairs. Fig. 7c provides the transient photocurrent responses of  $\text{Bi}_2\text{WO}_6$ ,  $\text{NH}_2\text{-UiO-66}$ , BWO/0.5NU, and BWO/2NU under discontinuous visible light irradiation. When the light is switched on, the intensity of photocurrent response for pristine  $\text{Bi}_2\text{WO}_6$  or  $\text{NH}_2\text{-UiO-66}$  is weak. After the incorporation of  $\text{NH}_2\text{-UiO-66}$  into  $\text{Bi}_2\text{WO}_6$ , both BWO/0.5NU and BWO/2NU hybrids show stronger photocurrent intensity than pristine  $\text{Bi}_2\text{WO}_6$  or  $\text{NH}_2\text{-UiO-66}$ . Generally, the transient photocurrent responses have positive correlations with the separation efficiency of electron–hole pairs, so the above result indicates more efficient separation of photo-induced charges and transfer over the BWO/2NU hybrid.<sup>43</sup> As shown in Fig. 7d, BWO/2NU shows smaller diameter of the arc radius on the Nyquist plot compared with that of pristine  $\text{Bi}_2\text{WO}_6$  or  $\text{NH}_2\text{-UiO-66}$ , suggesting a considerably smaller charge transfer resistance between the interface of  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$ .<sup>44</sup> That is to say the BWO/2NU hybrid has higher efficiency of photo-induced charge separation and migration.<sup>45</sup> All the results reveal that the BWO/2NU hybrid has superior performance of the electron–hole separation and migration than the single component, leading to enhanced photocatalytic abilities.



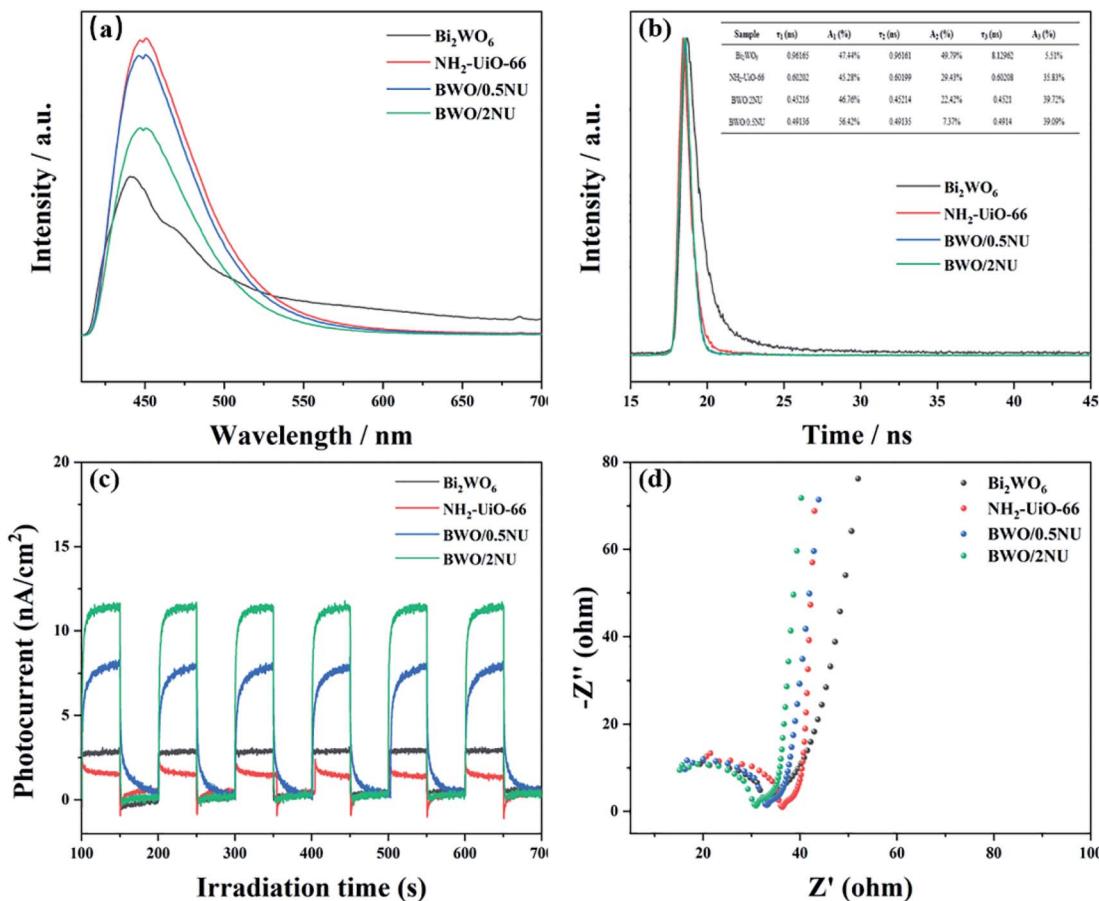


Fig. 7 (a) Stable state PL, and (b) TRPL spectra, (c) photocurrent responses, and (d) EIS images of Bi<sub>2</sub>WO<sub>6</sub>, NH<sub>2</sub>-UiO-66, BWO/0.5NU and BWO/2NU.

Additional experiments were carried out to investigate the detailed band structures/positions of the photocatalysts. The UV-vis DRS analysis (Fig. 8) reveals that pristine Bi<sub>2</sub>WO<sub>6</sub> holds an absorption edge of 440 nm, which is close to the reported values.<sup>46,47</sup> NH<sub>2</sub>-UiO-66 exhibits strong absorption in the range 200–440 nm.<sup>26</sup> When compared with those of pure Bi<sub>2</sub>WO<sub>6</sub> and NH<sub>2</sub>-UiO-66, the absorption edges of the hybrids occur with a slight red shift and the BWO/2NU sample shows the strongest response in the visible region, indicating the production of more electron–hole pairs and thereby enhanced photocatalytic performance.<sup>26</sup> The equation,  $\alpha h\nu = A(h\nu - E_g)^{n/2}$ ,<sup>36,48</sup> is used to calculate the band gaps of pristine Bi<sub>2</sub>WO<sub>6</sub> and NH<sub>2</sub>-UiO-66, where  $\alpha$ ,  $h$ ,  $\nu$ ,  $A$ , and  $E_g$  stand for the absorption coefficient, Planck's constant, optical frequency, a constant, and the band gap, *i.e.*, highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap, respectively.  $n$ 's values depend on the types of optical transitions in different semiconductors. Hence, the values obtained are  $n = 4$  for Bi<sub>2</sub>WO<sub>6</sub> (indirect semiconductor) and  $n = 1$  for NH<sub>2</sub>-UiO-66 (direct semiconductor).<sup>36,49</sup> From the plots of  $(\alpha h\nu)^{2/n}$  versus  $h\nu$  (Fig. S8†), the band gaps/HOMO–LUMO gaps of the as-prepared Bi<sub>2</sub>WO<sub>6</sub> and NH<sub>2</sub>-UiO-66 samples are determined to 2.82 eV and 2.86 eV, respectively. Moreover, the HOMO–LUMO gap of the BWO/2NU hybrid is estimated to be 2.80 eV from the absorption

edge in Fig. 8. The result suggests that the BWO/2NU hybrid is not a simple mixture of Bi<sub>2</sub>WO<sub>6</sub> and NH<sub>2</sub>-UiO-66, but entails the formation of an interfacial interaction, which indicates the formation of a heterojunction structure.

It's demonstrated in Fig. 9 that the CBs of Bi<sub>2</sub>WO<sub>6</sub>, NH<sub>2</sub>-UiO-66, and BWO/2NU were determined using the Mott–Schottky method.

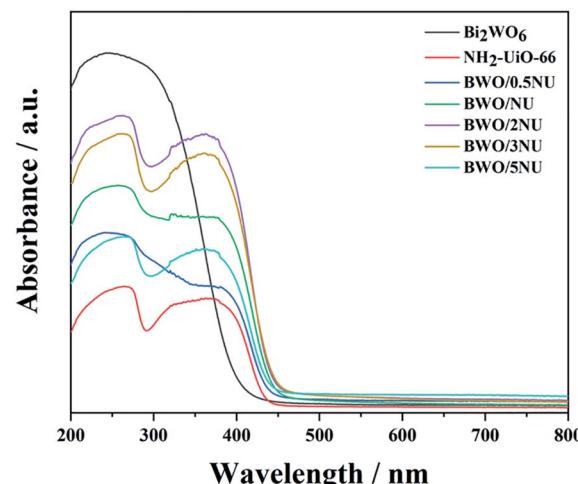


Fig. 8 UV-vis DSR spectra of as-prepared samples.

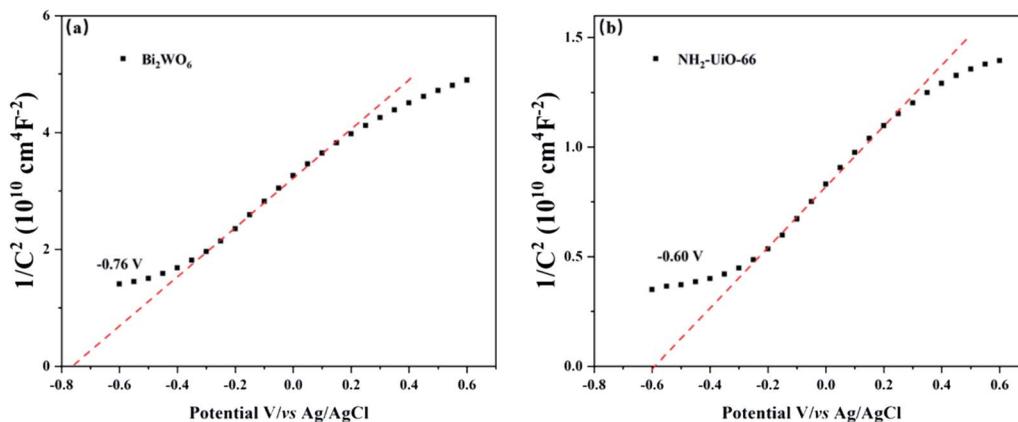


Fig. 9 Mott–Schottky plots for (a)  $\text{Bi}_2\text{WO}_6$ , and (b)  $\text{NH}_2\text{-UiO-66}$ .

The slopes of the Mott–Schottky curves are positive, indicating that both  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$  are n-type semiconductors.<sup>26</sup> The flat-band potentials of  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$  are approximately  $-0.76\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  (*i.e.*,  $-0.56\text{ V}$  vs. normal hydrogen electrode (NHE)) and  $-0.60\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  (*i.e.*,  $-0.40\text{ V}$  vs. NHE), respectively. Generally, the flat band potential is about  $0\text{--}0.2\text{ V}$  below the bottom of the CB in n-type semiconductors.<sup>50</sup> Here, the voltage difference between the CB and flat band potential was set to  $0.1\text{ eV}$ .<sup>50</sup> Therefore, the CB positions of  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$  can be calculated to be  $-0.66\text{ V}$  and  $-0.50\text{ V}$  (vs. NHE), respectively. By combining these results with the band gap values of the as-prepared photocatalysts derived from the UV-vis DRS analysis (Fig. 8), the VB positions of  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$  are determined to be  $+2.16\text{ V}$  and  $+2.36\text{ V}$  (vs. NHE), respectively.

To confirm and investigate the mechanism of the Z-scheme BWO/2NU system, the ESR spin-trap (with 5,5-dimethyl-1-pyrroline N-oxide (DMPO)) was employed. Fig. 10 shows that no characteristic peaks of  $\cdot\text{OH}$  or  $\cdot\text{O}_2^-$  are observed in pristine  $\text{Bi}_2\text{WO}_6$ ,  $\text{NH}_2\text{-UiO-66}$ , and the BWO/0.5NU, BWO/2NU, and BWO/5NU hybrids without irradiation. Under visible light irradiation (Fig. 10a), strong ESR signals corresponding to the DMPO- $\cdot\text{O}_2^-$  adduct are clearly observed for both pristine  $\text{Bi}_2\text{WO}_6$  and the BWO/xNU hybrids, whereas no signal is

observed in the case of pure  $\text{NH}_2\text{-UiO-66}$ . Moreover, the signals of DMPO- $\cdot\text{O}_2^-$  attributed to the hybrids are generally much stronger than those in the case of pristine  $\text{Bi}_2\text{WO}_6$ . As depicted in Fig. 10b, the DMPO- $\cdot\text{OH}$  signals of the BWO/xNU hybrids are detected under visible light irradiation but not in the case of pure  $\text{Bi}_2\text{WO}_6$  or  $\text{NH}_2\text{-UiO-66}$ . The above results suggest that the BWO/xNU hybrids, with  $\text{Bi}_2\text{WO}_6$  incorporated into the  $\text{NH}_2\text{-UiO-66}$  catalysts, can produce more active radicals, thereby enhancing photocatalytic activity.

Based on the UV-vis DRS analysis and Mott–Schottky plots, the VB/CB (HOMO/LUMO) positions of  $\text{Bi}_2\text{WO}_6$  and  $\text{NH}_2\text{-UiO-66}$  are determined to be  $+2.16\text{--}0.66\text{ V}$  and  $+2.36\text{--}0.5\text{ V}$  (vs. NHE), respectively. The CB potential of  $\text{Bi}_2\text{WO}_6$  ( $-0.66\text{ V}$  vs. NHE) is more negative than the standard potential of  $\text{O}_2/\cdot\text{O}_2^-$  ( $-0.33\text{ V}$  vs. NHE),<sup>51</sup> and hence, the  $\cdot\text{O}_2^-$  generated by  $\text{Bi}_2\text{WO}_6$  can be detected. In addition, the CB potential of  $\text{NH}_2\text{-UiO-66}$  ( $-0.5\text{ V}$  vs. NHE) is more negative than that of  $\text{O}_2/\cdot\text{O}_2^-$ , but no  $\cdot\text{O}_2^-$  signal is observed in the case of pure  $\text{NH}_2\text{-UiO-66}$ , which is probably owing to the production of a few DMPO- $\cdot\text{O}_2^-$  adducts. Meanwhile, the HOMO energy of  $\text{NH}_2\text{-UiO-66}$  is higher than the potential energy of  $\text{H}_2\text{O}/\cdot\text{OH}$  ( $2.27\text{ V}$  vs. NHE),<sup>52</sup> but  $\cdot\text{OH}$  was not generated for reasons similar to those mentioned above.  $\text{Bi}_2\text{WO}_6$  has lower VB potential and hence, the production of

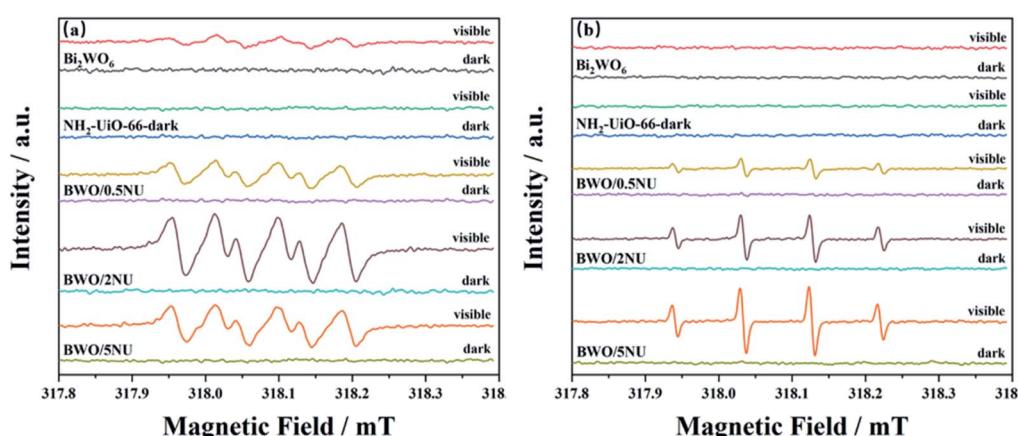


Fig. 10 DMPO spin-trapping ESR spectra for (a) DMPO- $\cdot\text{O}_2^-$ , and (b) DMPO- $\cdot\text{OH}^-$ .



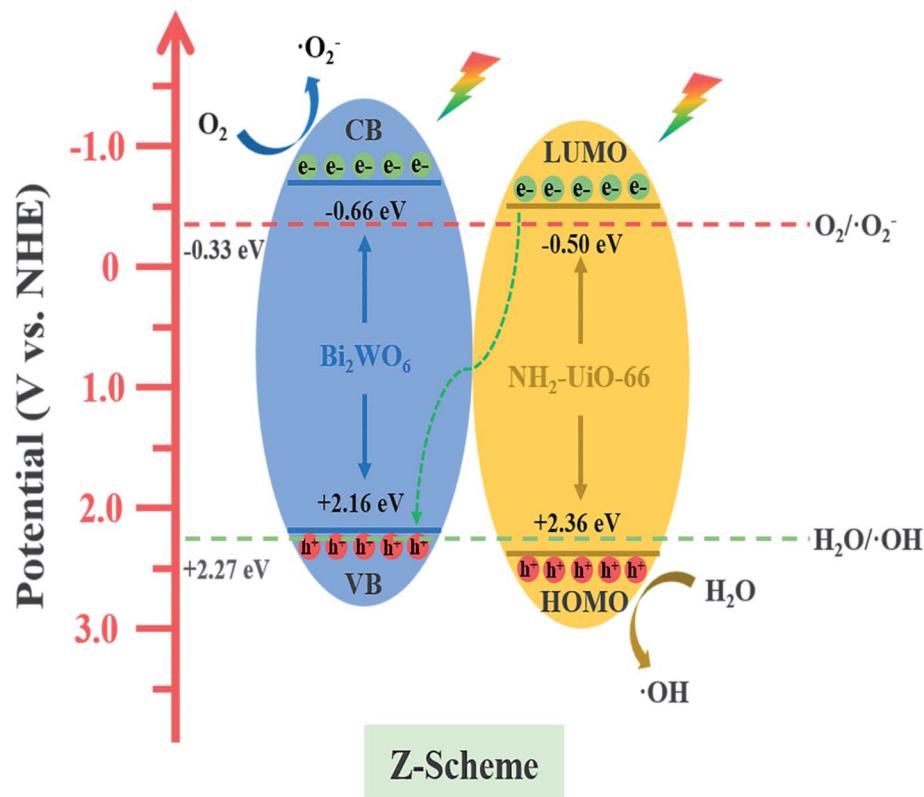


Fig. 11 Schematic diagram of direct Z-scheme system for photocatalysis and charge migration pathway.

$\cdot\text{OH}$  is prohibited. Both  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  signals are observed in the case of the BWO/xNU hybrids. Therefore, a direct Z-scheme photocatalytic system is proposed, which is displayed in Fig. 11.

Moreover, the potential  $E_F$  (Fermi level) of pristine  $\text{Bi}_2\text{WO}_6$  is about  $-0.89$  eV (vs. SCE),<sup>23</sup> negative than that of pure  $\text{NH}_2\text{-UiO-66}$  about  $-0.58$  eV (vs. SCE).<sup>53</sup> When the  $\text{Bi}_2\text{WO}_6$  and the  $\text{NH}_2\text{-UiO-66}$  get into contact, the electrons will migrate from the surface of  $\text{Bi}_2\text{WO}_6$  to the surface of  $\text{NH}_2\text{-UiO-66}$  to achieve their Fermi level equilibrium.<sup>16</sup> After Fermi level equilibrium is achieved, the region close to the interface of BWO/xNU is charged, which results in the formation of a built-in electric field in the direction from  $\text{Bi}_2\text{WO}_6$  to  $\text{NH}_2\text{-UiO-66}$ .

The photo-induced electrons from the CB of  $\text{NH}_2\text{-UiO-66}$  transfer to the interface and combine with the photo-induced holes on the VB of  $\text{Bi}_2\text{WO}_6$ . In addition, the formation of the built-in electric field pointing from  $\text{Bi}_2\text{WO}_6$  to  $\text{NH}_2\text{-UiO-66}$  will accelerate the electron transfer from the LUMO of  $\text{NH}_2\text{-UiO-66}$  to the VB of  $\text{Bi}_2\text{WO}_6$ . This promotes the accumulation of electrons on the CB of  $\text{Bi}_2\text{WO}_6$  and of holes on the VB of  $\text{NH}_2\text{-UiO-66}$ , resulting in the preservation of the strong reducibility of electrons and strong oxidation ability of holes. The direct Z-scheme photocatalytic mechanism proposed is in excellent agreement with the results of ESR analysis.

## 4. Conclusion

In this study, a novel direct Z-scheme photocatalytic system composed of  $\text{NH}_2\text{-UiO-66}$  and  $\text{Bi}_2\text{WO}_6$  for efficient NO oxidation

under visible light irradiation was proposed. The incorporation of  $\text{NH}_2\text{-UiO-66}$  into  $\text{Bi}_2\text{WO}_6$  can not only effectively improve its photocatalytic activity for NO oxidation, but also increase the selectivity for converting NO to  $\text{NO}_3^-/\text{NO}_2^-$ , truly diminishing the potential secondary pollution of  $\text{NO}_2$ . The introduction of  $\text{NH}_2\text{-UiO-66}$  produces abundant active sites to promote the adsorption and photocatalytic reaction. Meanwhile, combining  $\text{NH}_2\text{-UiO-66}$  with  $\text{Bi}_2\text{WO}_6$  can narrow the band gaps of the hybrids to some extent to enhance their light adsorption. The fabrication of a direct Z-scheme system improves the separation efficiency of electron-hole pairs. Simultaneously it preserves their strong redox abilities. This work provides a new idea for the construction of a direct Z-scheme photocatalytic system without cocatalysts for NO photocatalytic removal. We hope this work can provide some inspiration on the design and synthesis of more advanced photocatalysts for environmental protection.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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