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# Hydrothermal synthesis of mpg-C<sub>3</sub>N<sub>4</sub> and Bi<sub>2</sub>WO<sub>6</sub> nest-like structure nanohybrids with enhanced visible light photocatalytic activities†

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To overcome the shortcomings of low photocatalytic efficiency, mpg-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> photocatalysts have been successfully designed via a facile hydrothermal method. A succession of techniques was used to explore the morphology, structure, surface composition and photocatalytic property of the mpg-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> material. The mpg-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> nanohybrid has high photocatalytic performance for the degradation of tetracycline hydrochloride (TC) and rhodamine B (RhB). Holes, ·O<sub>2</sub><sup>−</sup> and ·OH radicals are determined to be the active species in the process of photocatalytic degradation by ESR and capture experiments. The ultrathin thickness of nest-like Bi<sub>2</sub>WO<sub>6</sub> and the introduction of mpg-C<sub>3</sub>N<sub>4</sub> into the Bi<sub>2</sub>WO<sub>6</sub> matrix can improve the photocatalytic efficiency. The photocatalytic Z-scheme mechanism of the system was also discussed in detail. This work paves the way for preparing visible-light-driven nanocomposites for pollutant degradation.

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## 1. Introduction

Heterogeneous photocatalysis, in which limitless and environmentally friendly sunlight can be secured as a practical technology, has been widely utilized<sup>1–3</sup> in various fields such as in environmental remediation,<sup>4,5</sup> electrode materials,<sup>6</sup> water splitting,<sup>7</sup> bioimaging<sup>8</sup> and hydrogen production.<sup>9</sup> However, traditional photocatalysts still cannot fully meet the standards of practical applications in environmental protection and hydrogen generation driven by solar energy owing to their wide band gaps and rapid recombination of photo-generated electrons and holes. Accordingly, it is of great significance and necessity to exploit novel photocatalysts with visible-light activity as well as highly efficient photogenerated charge separation.<sup>10</sup>

Very recently, researchers have fabricated many highly effective bismuth-based photocatalysts under visible light, such as Bi<sub>2</sub>MoO<sub>6</sub>,<sup>11</sup> BiVO<sub>4</sub>,<sup>12,13</sup> Bi<sub>2</sub>S<sub>3</sub>,<sup>14</sup> BiOX (X = Cl, Br, I),<sup>15–17</sup> Bi<sub>2</sub>O<sub>3</sub>,<sup>18</sup> etc. Among them, Bi<sub>2</sub>WO<sub>6</sub> has been become one of the most potential photocatalysts because of its proper band gap, unique layer-structures and fascinating properties such as ferroelectric piezoelectricity, etc.<sup>19</sup> As we all know, the photocatalytic activity

closely contacts with the structure, morphology and size of photocatalysts.<sup>20–22</sup> Moreover, ultrathin thickness can make photo-excited carriers easily transferring to the surface from the interior, and therefore reduces the bulk recombination according to the diffusion equation  $t = d^2/k^2D$  ( $t$  is the diffusion time;  $k$ , the constant;  $d$ , the particle size;  $D$ , the diffusion coefficient of photo-excited carrier).<sup>23,24</sup> Although shape engineering can enhance the photocatalytic activity of Bi<sub>2</sub>WO<sub>6</sub>, high recombination rate of photogenerated carriers between the hybrid orbital of O 2p and Bi 6s to the empty W 5d orbital gives rise to low photo quantum efficiency of Bi<sub>2</sub>WO<sub>6</sub>.<sup>25–27</sup> Consequently, it is still necessary to search for suitable components to combine with Bi<sub>2</sub>WO<sub>6</sub> for extending the light response range, facilitating photo-generated electron–hole separation, and remarkably improving the visible light photocatalytic activity of Bi<sub>2</sub>WO<sub>6</sub>.

Recently, the polymeric metal-free graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), a kind of new visible-light-driven photocatalyst reported by Wang *et al.*<sup>28</sup> has attracted intensive attention for its applications. However, photocatalytic efficiency and photo-excited carrier separation rate of g-C<sub>3</sub>N<sub>4</sub> were very low due to it was the bulk state of the material. On this basis, mesoporous g-C<sub>3</sub>N<sub>4</sub> (mpg-C<sub>3</sub>N<sub>4</sub>) catalysts have been prepared by generating holey structures into the g-C<sub>3</sub>N<sub>4</sub> matrix to enhance their electronic and structural functions for solar energy conversion.<sup>29</sup> Many research groups have combined g-C<sub>3</sub>N<sub>4</sub> and semiconductor photocatalysts to improve photocatalytic efficiency, such as ZnO,<sup>30</sup> BiPO<sub>4</sub>.<sup>31</sup> Notably, Bi<sub>2</sub>WO<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composites have also been reported.<sup>32</sup> Wang *et al.*<sup>33</sup> have synthesized the g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> nanocomposite by chemical adsorption of g-C<sub>3</sub>N<sub>4</sub> on Bi<sub>2</sub>WO<sub>6</sub> surface. Ge *et al.*<sup>33</sup> have also prepared g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> nanocomposite by

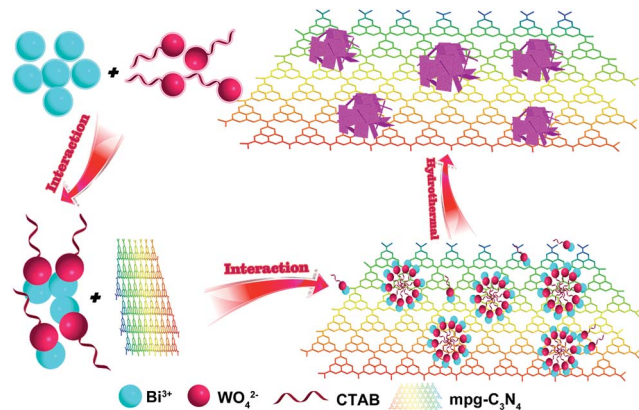
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Scheme 1 The possible schematic illustration of the preparation of CNBW.

simple mechanical agitation followed by heating of  $\text{g-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$ . Nevertheless, the photocatalytic activity of the materials synthesized by these methods is relatively low: only low concentrations of pollutants can be degraded.

To our knowledge, there are no reports on the application and preparation of  $\text{mpg-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$  (CNBW) composites. Herein, we report the synthesis of CNBW composites by oriented ultrathin nanoplates ( $\sim 12$  nm) of  $\text{Bi}_2\text{WO}_6$  via a facile hydrothermal method as shown in Scheme 1. We used CTAB as a surfactant to promote the formation of nest-like structures of  $\text{Bi}_2\text{WO}_6$ . Due to the electrostatic force, the positively charged  $\text{CTA}^+$  and the negatively charged  $\text{WO}_4^{2-}$  attract each other to form a more stable intermediate product. In this way, the formation rate of  $\text{Bi}_2\text{WO}_6$  nanoparticles is reduced. Due to the anisotropic growth of  $\text{Bi}_2\text{WO}_6$ , the zero dimensional (0D) nanoparticles can be transformed into two dimensional (2D) nanosheets. With the increase of reaction time, the nanosheets will be changed to three-dimensional (3D) nest-like structures because of self assembly. The visible-light photocatalytic activities are evaluated sufficiently with the degradation of the model dye and the antibiotics, demonstrating that the composites exhibit much improved photocatalytic activity than bare  $\text{mpg-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$ . In addition, this work may also provide a useful method for the synthesis of the composite photocatalyst with enhanced photocatalytic performance.

## 2. Experimental

### 2.1. Synthesis of photocatalysts

**2.1.1 Synthesis of  $\text{mpg-C}_3\text{N}_4$ .** All chemicals were of AR and used without any further purification. The  $\text{mpg-C}_3\text{N}_4$  was prepared according to Thomas and Xu *et al.*<sup>34,35</sup> Typically experiment, the 40 wt% HS-40 (colloidal silica 40 wt% suspension in  $\text{H}_2\text{O}$ , Sigma-Aldrich) was slowly soaked in an aqueous solution, which contained 8 mL deionized water and 8 g cyanamide.<sup>36,37</sup> The water was removed after stirring for 12 h at  $35^\circ\text{C}$  and a white solid was obtained. Then, the white solid was heated to  $550^\circ\text{C}$  into a quartz crucible with a ramp rate of  $2.5^\circ\text{C min}^{-1}$  under  $\text{N}_2(\text{g})$  flow and kept for 4 h in a horizontal quartz-tube. Next, the yellow powders obtained via these two similar procedures were

reacted with 4 M, 300 mL of  $\text{NH}_4\text{HF}_2$  (95%, Sigma-Aldrich) solution for 24 h to remove the silica template. After that, the sample was washed several times with deionized water and ethanol, and dried at  $60^\circ\text{C}$  for 12 h in an electric oven. Finally, the mesoporous graphitic carbon nitride ( $\text{mpg-C}_3\text{N}_4$ ) was obtained.

**2.1.2 Synthesis of  $\text{mpg-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$  photocatalysts.** In a typical procedure, the  $\text{mpg-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$  (CNBW) nanohybrids were fabricated by a hydrothermal method as follows: to begin with, an appropriate amount of as-prepared  $\text{mpg-C}_3\text{N}_4$  ultra-sonically dispersed in 8.0 mL water for 30 min. Then, 194 mg  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 20 mg CTAB were put into the former solution and sonicated for another 30 min. Next, 66 mg  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved into the above solution under vigorous stirring. Finally, the mixture was poured into a 20 mL Teflon-lined autoclave and heated at  $140^\circ\text{C}$  for 12 h, and then the sample was washed repeatedly with deionized water and ethanol, and dried at  $60^\circ\text{C}$  for 12 h in an oven. In comparison, the pure  $\text{Bi}_2\text{WO}_6$  sample was prepared without adding  $\text{mpg-C}_3\text{N}_4$  in the same conditions. In addition, the yield of the product depends only on the volume of the autoclave. For the sake of convenience, the  $\text{mpg-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$  photocatalysts were labeled as X% CNBW (X denotes wt% of  $\text{mpg-C}_3\text{N}_4$  in  $\text{mpg-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ ). The added contents of  $\text{mpg-C}_3\text{N}_4$  in  $\text{mpg-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$  composites were the 6.7 wt%, 12.5 wt% and 22.3 wt%, respectively.

### 2.2. Characterization of the photocatalysts

X-ray powder diffraction (XRD) spectra were obtained on Shimadzu XRD-6000 diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) as source in the range of  $2\theta = 10\text{--}80^\circ$  at a scan rate of  $0.1167^\circ \text{ s}^{-1}$ . Fourier transform infrared (FT-IR) spectra were recorded on Nicolet FT-IR spectrometer (Nexus 470, Thermo Electron Corporation). X-ray photoelectron spectroscopy (XPS) measurements were performed on a ESCALab MKII spectrometer with  $\text{Mg K}\alpha$  radiation at 20 kV. The  $\text{N}_2$ -sorption measurements were performed on Micromeritics Tristar 3000 at 77.35 K. The field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy measurements were carried out with a field-emission scanning electron microscope (JEOL JSM-7001F) operating at an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) analyses were performed by a JEOL-JEM-2010 spectrometer (JEOL, Japan) operating at 200 kV. Atomic force microscopy (AFM) images were obtained by FM-Nanoview 6800 AFM. The photoabsorption performance was characterized by a ultraviolet-visible (UV-vis) diffuse reflection spectroscopy (DRS, Shimadzu UV-2450, Japan), and  $\text{BaSO}_4$  was utilized as the standard material. The specific surface area (SSA) and the pore size distribution (PSD) were determined by Micromeritics Instrument, respectively. All the spectra have been normalized to the incident beam. Electron spin resonance (ESR) patterns were recorded on a Bruker model ESR JES-FA200 spectrometer in methanol and water, respectively.

### 2.3. Photocatalytic performance measurement

Photocatalytic performance of the CNBW composite samples was determined in an opening quartz chamber (50 mL) by the



decomposition of TC and RhB under simulated solar light of a 300 W Xe lamp with a 420 nm cut off filter. The irradiation area was *ca.* 25 cm<sup>2</sup>. Reaction conditions: temperature, 25 ± 0.5 °C; *C*<sub>0</sub>(TC) = 50 mg L<sup>-1</sup>; *C*<sub>0</sub>(RhB) = 20 mg L<sup>-1</sup>; *C*(CNBW) = 0.5 g L<sup>-1</sup>. Prior to irradiation, the solution was stirred under atmosphere for 30 min in darkness to achieve adsorption-desorption equilibrium. TC and RhB solution were collected, centrifuged and analyzed using UV-vis spectrometer (UV-2450, Shimadzu Ltd.) at wavelength 356 nm and 553 nm, respectively. The degradation efficiency ( $\eta$ ) was determined using  $\eta$  (%) = (1 - *C*/*C*<sub>0</sub>) × 100%, where *C*<sub>0</sub> represents the original solution concentration after achieving pollution-photocatalyst equilibrium and *C* was the concentration after reaction for time *t*.

To investigate the active species produced in the photo-degradation process of photocatalytic, hydroxyl radicals ( $\cdot\text{OH}$ ), superoxide radical ( $\cdot\text{O}_2^-$ ) and holes ( $h^+$ ) were probed by adding 5 mM *tert*-butyl alcohol (*t*-butanol), N<sub>2</sub> and EDTA-2Na, respectively.<sup>38–40</sup>

#### 2.4. Photoelectrochemical measurements

Electrochemical measurements were performed with a CHI 660B (Chenhua Instrument Company, Shanghai, China) electrochemical workstation, using a three-electrode system. A platinum plate electrode and an Ag/AgCl electrode (3 M KCl) were used as counter electrode and reference electrode, respectively. The working electrode was photocatalyst (0.1 mg) films coated on ITO (0.5 × 1 cm<sup>2</sup>). The electrolyte was 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution and the photocurrent measurement were performed under visible light from a 500 W Xe lamp with 420 nm cutoff filters. The electrochemical impedance spectroscopy (EIS) measurements were recorded in 5 mM K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> (1 : 1) containing 0.1 mol L<sup>-1</sup> KCl.

### 3. Results and discussion

#### 3.1. Compositional and structural information

In order to correlate the photocatalytic performance of the as-synthesized CNBW photocatalysts with their structural performances, the CNBW samples are characterized by XRD, FT-IR and XPS in detail.

The crystal structure of the CNBW samples is rated by XRD analysis, as shown in Fig. 1 and S1.† For the mpg-C<sub>3</sub>N<sub>4</sub>, the characteristic peak located at 27.5° indicated the diffraction interplanar staking peak of the aromatic conjugated system, which can be indexed to the (002) crystal plane (JCPDS no. 87-1526).<sup>29</sup> For the Bi<sub>2</sub>WO<sub>6</sub>, the distinct diffraction peaks at 28.3°, 32.8°, 32.9°, 47.1°, 56.0°, 58.5°, and 68.8° corresponding to the (131), (200), (002), (202), (133), (262) and (400) crystallographic planes (JCPDS no. 39-0256), respectively.<sup>41</sup> No impurity is found in CNBW samples. Furthermore, no mpg-C<sub>3</sub>N<sub>4</sub> phase is observed in CNBW samples, which may be due to the restrictions on the use of mpg-C<sub>3</sub>N<sub>4</sub> and high dispersion in CNBW samples. In addition, the sole peak of mpg-C<sub>3</sub>N<sub>4</sub> overlaps with one of the Bi<sub>2</sub>WO<sub>6</sub> peaks, which can be the reason that it cannot be discern clearly in the composites.

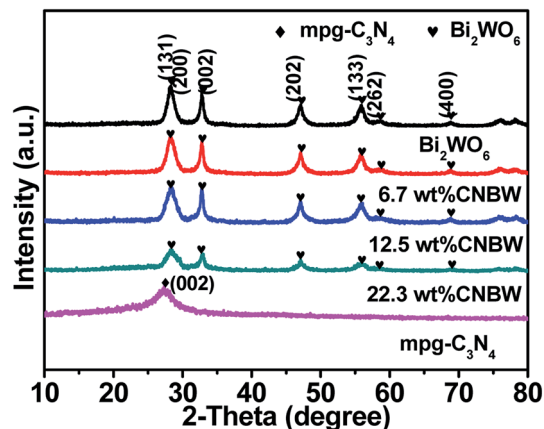


Fig. 1 XRD pattern of the as-prepared mpg-C<sub>3</sub>N<sub>4</sub>, Bi<sub>2</sub>WO<sub>6</sub> and CNBW composites.

The chemical bonding and composition information of CNBW are further characterized by FT-IR analysis (Fig. S1†). In FT-IR spectrum of mpg-C<sub>3</sub>N<sub>4</sub>, a series of the peaks located between 1200 cm<sup>-1</sup> to 1750 cm<sup>-1</sup> conformed to the stretching vibration modes of the mpg-C<sub>3</sub>N<sub>4</sub> heterocycles, while the sharp band located at 812 cm<sup>-1</sup> is due to the breathing vibration of triazine ring in mpg-C<sub>3</sub>N<sub>4</sub>.<sup>42</sup> In addition, the stretching vibrations of C–H can be observed at 2921 cm<sup>-1</sup> and 2972 cm<sup>-1</sup>, possibly due to the existence of few CTAB.<sup>43</sup> The absorption peaks at 571 cm<sup>-1</sup>, 736 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> are owing to Bi–O, W–O stretching and W–O–W bridging stretching modes, suggesting the presence of the Bi<sub>2</sub>WO<sub>6</sub>.

To analyze the surface chemical conditions of the Bi, W, O, C and N elements in the 12.5 wt% CNBW nanohybrid as shown in Fig. S2a,† XPS measurements were conducted (Fig. 2 and S2†). As shown in Fig. S2b,† the binding energies of Bi 4f<sub>7/2</sub> and Bi 4f<sub>5/2</sub> peaks are at approximate 159.2 and 164.6 eV, which is assigned to Bi<sup>3+</sup> in crystal structure, respectively.<sup>41,44</sup> In the W 4f spectra (Fig. 2a), peaks at 35.5 and 37.6 eV were ascribed to W 4f<sub>7/2</sub> and W 4f<sub>5/2</sub> of W<sup>6+</sup> oxidation state,<sup>19,41</sup> respectively. Three main peaks of O 1s at 529.9, 530.5 and 531.1 eV are assigned to the Bi–O, W–O and H–O on the surface of Bi<sub>2</sub>WO<sub>6</sub>,<sup>27</sup> respectively, which are shown in Fig. 2b. In Fig. 2c, the C 1s peaks of the sample centered at *ca.* 284.5, 285.0, 286.0 and 287.0 eV. The peak at *ca.* 284.5 eV is graphite carbon, but the peak at around 285.0 eV is ascribable to C–O species.<sup>45</sup> The binding energy centered at 286.0 and 287.0 eV correlated with the sp<sup>2</sup>-hybridized bonds in N–C=N and O–C=O,<sup>45,46</sup> respectively. The broad N 1s peak of mpg-C<sub>3</sub>N<sub>4</sub> in the spectrum is deconvoluted into four peaks centered at *ca.* 397.8, 399.0, 400.0 and 404.1 eV (Fig. 2d), which can be ascribed to pyridinic nitrogen, tertiary nitrogen (N–C3), amino functions (N–H), and the charging effects,<sup>47</sup> respectively.

#### 3.2. Morphology and textural property

The FE-SEM and EDS images of the as-prepared samples are presented in Fig. 3. As shown in Fig. 3a and b, all the pure Bi<sub>2</sub>WO<sub>6</sub> products have a nest-like morphology, with diameters





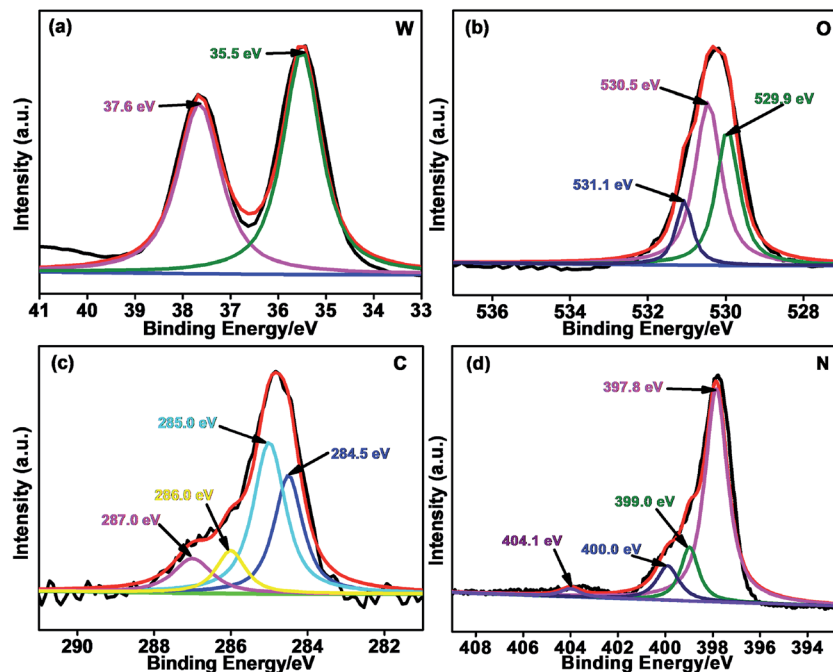


Fig. 2 XPS spectra of W 4f (a), O 1s (b), C 1s (c) and N 1s (d).

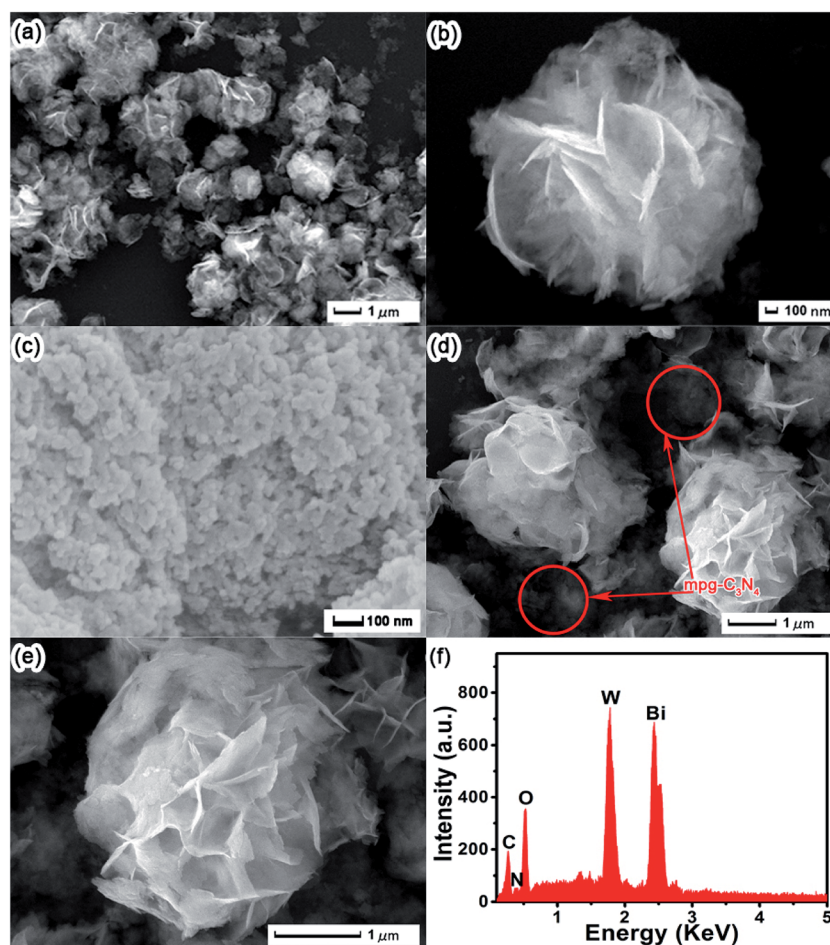


Fig. 3 FE-SEM images of  $\text{Bi}_2\text{WO}_6$  (a and b),  $\text{mpg-C}_3\text{N}_4$  (c), 12.5 wt% CNBW composite (d and e); EDS (f) of the 12.5 wt% CNBW composite.



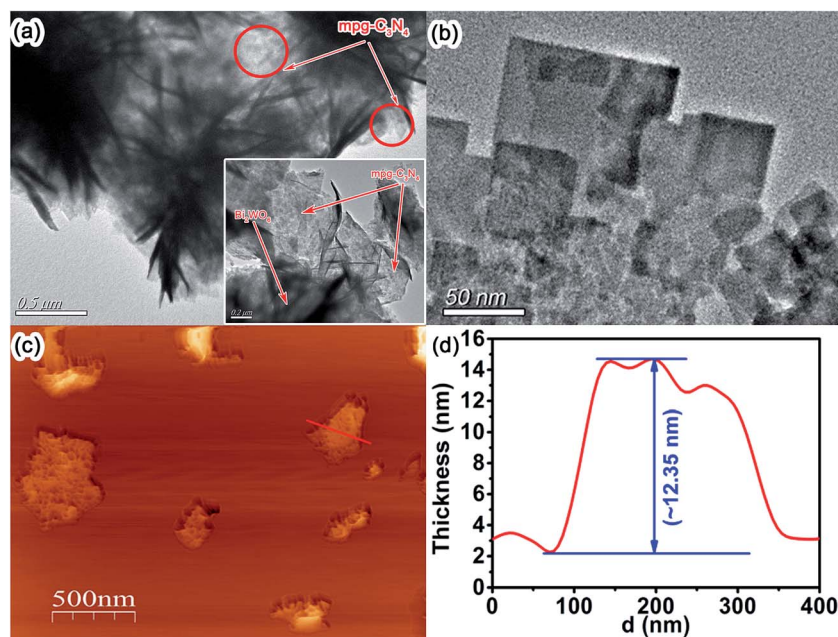


Fig. 4 TEM (a and b) and AFM (c and d) images of 12.5 wt% CNBW composite.

ranging from 2 to 4  $\mu\text{m}$ . In Fig. 3c, the FE-SEM image of mpg- $\text{C}_3\text{N}_4$  presents a typical multihole layered structure of the graphitic mesoporous of carbon nitride. Nevertheless, the microstructures of the 12.5 wt% CNBW composite (Fig. 3d and e) are found the nest-like structure intermingled with multihole stacking structure. The contact region between mpg- $\text{C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$  may enhance the photo-excited carrier separation rate. Moreover, the EDS pattern (Fig. 3f) indicates that the 12.5 wt% CNBW composite contains C, N, O, W and Bi elements, which is in accordance with the XPS results. In Fig. S3,† the mapping results reveal that the C (b) and N (c) elements are uniformly distributed in 12.5 wt% CNBW nanocomposite and that the O (d), Bi (e) and W (f) elements are dispersed like microspheres in the 12.5 wt% CNBW samples.

TEM and AFM are used to further analyze the microstructure of CNBW composite, as shown in Fig. 4. Fig. 4a is the TEM image of 12.5 wt% CNBW, it can be clearly seen that  $\text{Bi}_2\text{WO}_6$  is a nest-like structure composed of thin sheets, as well as the nest-like structure of  $\text{Bi}_2\text{WO}_6$  is anchored on the mesoporous structure of surface mpg- $\text{C}_3\text{N}_4$ . Concurrently, few peeled fragments can also be found, which further evidences the  $\text{Bi}_2\text{WO}_6$  thin films, as indicated in Fig. 4b. We further investigate the thickness of  $\text{Bi}_2\text{WO}_6$  sheet by AFM, which show that the thickness of  $\text{Bi}_2\text{WO}_6$  is around 12 nm (ref. 48) (Fig. 4c and d). It can greatly improve the photocatalytic activity by reducing the bulk recombination rate, because ultrathin thickness can make photo-excited carrier easily transferring to the surface from the interior.<sup>23,24,49</sup>

Fig. S4† depicts the  $\text{N}_2$  adsorption-desorption pattern and the homologous pore size distribution curves for mpg- $\text{C}_3\text{N}_4$ ,  $\text{Bi}_2\text{WO}_6$  and CNBW samples. It can be seen that specific surface area (SSA) of mpg- $\text{C}_3\text{N}_4$ ,  $\text{Bi}_2\text{WO}_6$ , 6.7 wt% CNBW, 12.5 wt% CNBW and 22.3 wt% CNBW samples are about 128.4, 27.9, 37.6, 40.2, 43.5  $\text{m}^2 \text{g}^{-1}$ , respectively. In theory, the high porosity of

mpg- $\text{C}_3\text{N}_4$  constructed herein can result in large surface areas and greater numbers of active sites for various application-driven photocatalyses.<sup>10</sup> Fig. S4,† the isotherms are type IV with a H3 hysteresis loop in the scope of 0.65–1.00  $P/P_0$ , which can be also indicated by its pore-size distribution and suggested there are both mesopores and micropores. It also shows that the increase of  $\text{Bi}_2\text{WO}_6$  did not significantly change or block the pore structure of mpg- $\text{C}_3\text{N}_4$ . The improved surface area is favorable for the adsorption of more reactants and active substances, so as to improve the photocatalytic activity.

### 3.3. Optical and electronic properties

The light absorption behaviors of  $\text{Bi}_2\text{WO}_6$ , mpg- $\text{C}_3\text{N}_4$  and CNBW photocatalysts are probed by optical diffuse-reflection spectra (DRS), and the result is depicted in Fig. 5. The absorption edges of pure mpg- $\text{C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$  photocatalysts are around 450 and 445 nm, corresponding band gap ( $E_g$ )

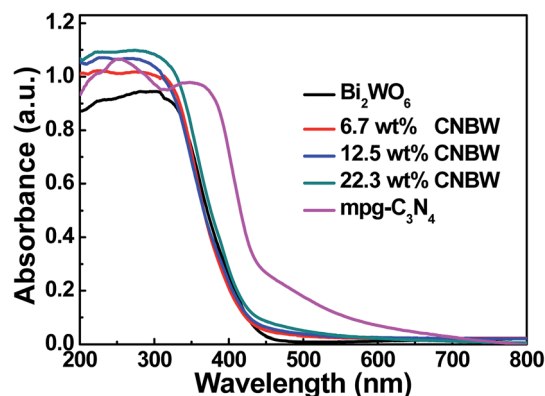


Fig. 5 UV-vis diffuse reflectance spectra of the as-prepared samples.



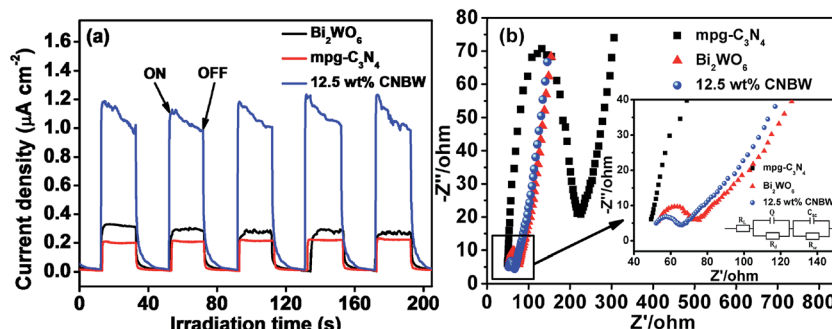


Fig. 6 Transient photocurrent responses (a) and electrochemical impedance spectroscopy (b) of  $\text{Bi}_2\text{WO}_6$ ,  $\text{mpg-C}_3\text{N}_4$  and 12.5 wt% CNBW under visible light irradiation.

calculated to be 2.7 (ref. 9) and 2.8 eV,<sup>19,22</sup> respectively. Combining  $\text{mpg-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$  caused a redshift in the absorption edges with increasing the mass ratio of  $\text{mpg-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$ , improving the absorption in the light range of visible, and indicating that all the CNBW composites possessed visible light response. The enhanced optical absorption may result in the generation of more photogenerated carriers, thereby enhancing the photocatalytic activity.

It is well-known that the photocurrent is widely considered as the reliable testimony to prove the separation efficiency of the photogenerated electron-hole pairs in the semiconductor photocatalysis process. The photogenerated current measurements of  $\text{Bi}_2\text{WO}_6$ ,  $\text{mpg-C}_3\text{N}_4$ , and 12.5 wt% CNBW samples are performed, it can be clearly detected that the transient photocurrent of CNBW is about 3.5 times higher than that of the  $\text{Bi}_2\text{WO}_6$  and  $\text{mpg-C}_3\text{N}_4$ , as shown in Fig. 6a. This displays that the electrodes are stable and the photosensitivity is completely

reversible. This result supported that more efficient transportation and separation of the photogenerated electron-hole pairs are realized, which can be attributed to the heterostructure built between  $\text{mpg-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$ .

To assess the charge-transfer and recombined process at semiconductor-electrolyte interfaces, the EIS is performed. Fig. 6b indicates that the CNBW Nyquist plot diameter is much smaller than  $\text{Bi}_2\text{WO}_6$  and  $\text{mpg-C}_3\text{N}_4$ , suggesting that interfacial charge transfer is faster and low resistance. It also means that the separation and transmission rate of photogenerated electrons are elevated significantly *via* interfacial interaction between  $\text{mpg-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$ .

### 3.4. Photocatalytic tests

The photocatalytic performance of  $\text{Bi}_2\text{WO}_6$ ,  $\text{mpg-C}_3\text{N}_4$  and CNBW samples with different mass ratios are evaluated by 20  $\text{mg L}^{-1}$  RhB degradation under visible light ( $\lambda > 420 \text{ nm}$ ).

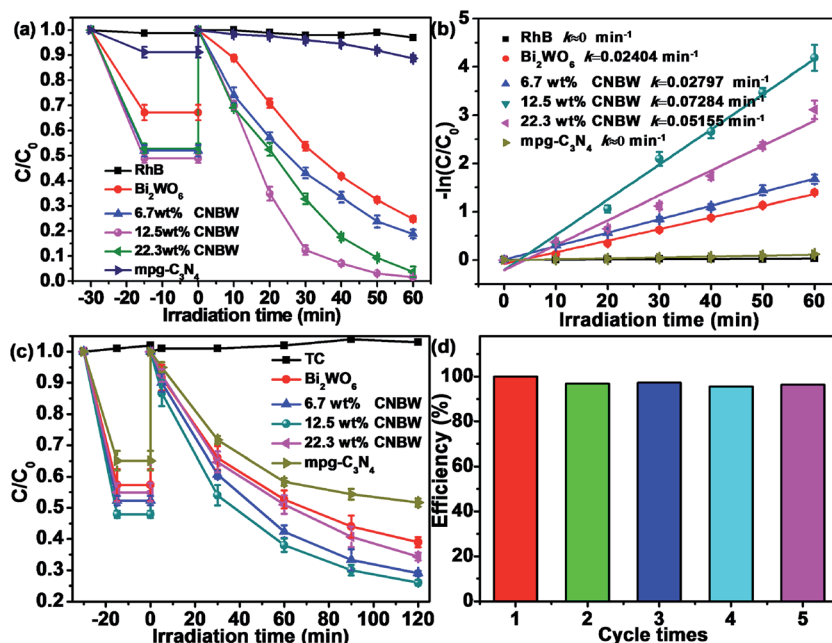


Fig. 7 Photocatalytic degradation of RhB (a), the corresponding rate constant  $k$  values (b) and photocatalytic degradation of TC (c) in the presence of  $\text{mpg-C}_3\text{N}_4$ ,  $\text{Bi}_2\text{WO}_6$  and CNBW composites under visible light irradiation; recycling experiments (d) of visible-light photocatalytic degradation of RhB over the 12.5 wt% CNBW.





Fig. 7 displays the standard concentration of RhB illumination time for photocatalytic degradation under visible light irradiation. The blank experiment proves the RhB is stable in the lack of photocatalysts, suggesting that the degradation of RhB can be negligible. Among the photocatalysts tested, the CNBW composites exhibited higher photocatalytic performance than  $\text{Bi}_2\text{WO}_6$  and  $\text{mpg-C}_3\text{N}_4$ , and the photocatalytic activity of CNBW is enhanced with the increase of  $\text{mpg-C}_3\text{N}_4$  ratio, as shown in Fig. 7a. But further increase in the amount of  $\text{mpg-C}_3\text{N}_4$  causes a rapid decrease in photocatalytic activity, which may be due to excessive  $\text{mpg-C}_3\text{N}_4$  coverage in the surface confined CNBW. Moreover, 12.5 wt% CNBW shows the best photocatalytic performance, the photocatalytic degradation of  $20 \text{ mg L}^{-1}$  RhB achieves 100% within 60 min. Fig. S5† shows the instantaneous evolution of the absorption spectra during the degradation of RhB in the existence of the 12.5 wt% CNBW samples, indicating the excellent photocatalytic activity. At the same time, the photocatalytic reaction kinetics of RhB by using CNBW composites is also evaluated, and the results are displayed in Fig. 7b. As we can see, the degradation rate of 12.5 wt% CNBW is determined to be  $0.07284 \text{ min}^{-1}$ , which is approximately 3 times higher than that of  $\text{Bi}_2\text{WO}_6$  ( $0.02404 \text{ min}^{-1}$ ) and much larger than that of  $\text{mpg-C}_3\text{N}_4$  ( $0 \text{ min}^{-1}$ ).

The broad-spectrum antibiotic, TC, is widely utilized for combating microbial infections. TC may cause adverse effects on ecosystems in nature, so it is important to remove TC.<sup>50,51</sup> TC is slowly photodegraded in the existence of  $\text{Bi}_2\text{WO}_6$  or  $\text{mpg-C}_3\text{N}_4$  under visible light; however, the photocatalytic activity is enhanced remarkably after a marriage of  $\text{mpg-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$ . True to form, 12.5 wt% CNBW shows the best

photocatalytic performance, and the photocatalytic degradation of TC attains 75% within 120 min (Fig. 7c). Hence, the composite helps to improve the photocatalytic efficiency under visible light.

The regeneration and reusability of the 12.5 wt% CNBW composite is analyzed for RhB degradation by performing recycling experiments under visible light. As can be seen from Fig. 7d, after five consecutive cycles, there is no significant change in the photocatalytic activity, illustrating the high durability of the photocatalyst under visible light. XRD spectra not only show that the crystalline information of photocatalyst has not changed during the photocatalysis process, but also clearly indicate that the photocatalyst is very stable (Fig. S6†). Based on the above results, we conjecture that the interaction between  $\text{mpg-C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$  promotes the formation of the efficient and stable CNBW photocatalyst.

### 3.5. Mechanism of pollutant photodegradation

In order to further investigate the catalytic mechanism, the active species formed during the reaction are identified by the trapping experiment of radicals in TC photodegradation over 12.5 wt% CNBW (Fig. 8a). The EDTA-2Na, *t*-butanol and  $\text{N}_2$  are used as  $\text{h}^+$ ,  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  scavengers,<sup>38–40</sup> respectively. The photocatalytic activity is greatly inhibited when EDTA is added, which means that  $\text{h}^+$  plays an important role in the photocatalytic degradation of TC. Similarly, after the addition of  $\text{N}_2$  and *t*-butanol, the photocatalytic rate is greatly reduced, which indicates that  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  also play an important role in the photocatalytic process. Therefore,  $\text{h}^+$ ,  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  are the primary active species.

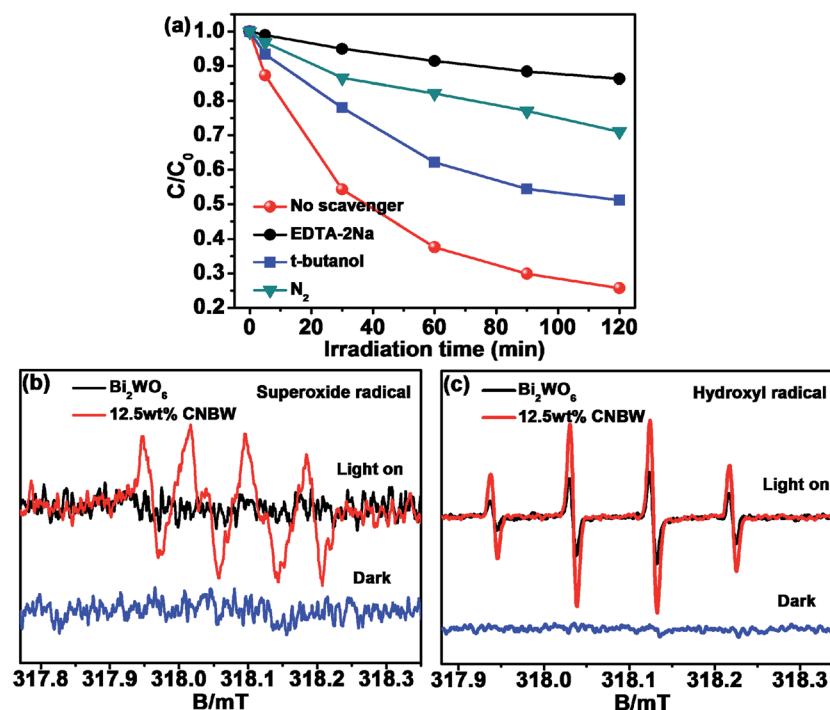


Fig. 8 Effects of different scavengers (a) on the photocatalytic activity of 12.5 wt% CNBW; ESR spectra of radical adducts trapped (b and c) by DMPO in 12.5 wt% CNBW aqueous dispersion under visible light irradiation.



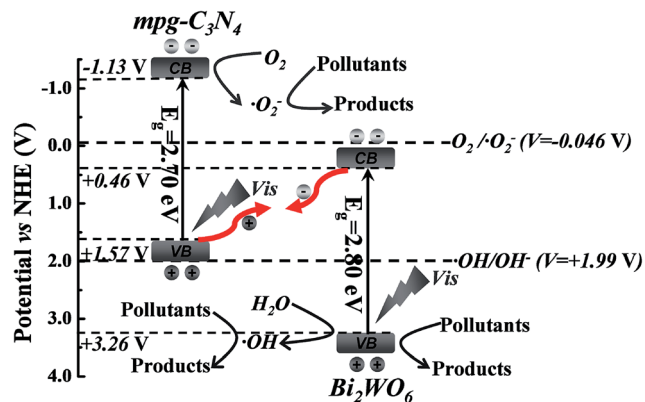


Fig. 9 Visible-light-induced-carrier generation and the postulated mechanism of CNBW.

The ESR spectroscopy with DMPO spin-trapping adducts allows the observation of superoxide radical ( $\text{DMPO}\cdot\text{O}_2^-$ ) and hydroxyl radical ( $\text{DMPO}\cdot\text{OH}$ ) during the irradiation of 12.5 wt% CNBW.<sup>52</sup> As indicated in Fig. 8, six characteristic peaks of  $\text{DMPO}\cdot\text{O}_2^-$  spin-trapping adducts are obviously detected under visible light illumination (Fig. 8b), and four characteristic peaks of  $\text{DMPO}\cdot\text{OH}$  signals can also be detected (Fig. 8c). In addition, no  $\text{DMPO}\cdot\text{O}_2^-$  signals are found in  $\text{Bi}_2\text{WO}_6$  and the peak intensity of  $\text{DMPO}\cdot\text{OH}$  adducts of CNBW is distinctively higher than that of  $\text{Bi}_2\text{WO}_6$ , which is due to the synergistic effect of mpg- $\text{C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$ . These results agree with the trapping experiment results, which show that  $\text{h}^+$ ,  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  are the main active species in the photocatalysis degradation process.

Based on the aforementioned experimental results and related literature, we propose the possible Z-scheme mechanism of CNBW to enhance the photocatalytic performance by increasing the separation efficiency of photogenerated electron-hole pairs at the surface of heterostructure under visible light (Fig. 9). The conduction band minimum (CBM) and valence band maximum (VBM) positions of mpg- $\text{C}_3\text{N}_4$  are ca.  $-1.13$  V and  $+1.57$  V, respectively,<sup>53</sup> while those of  $\text{Bi}_2\text{WO}_6$  are about  $+0.46$  V and  $+3.26$  V, respectively.<sup>54</sup> Both mpg- $\text{C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$  can be used to generate electron-hole pairs under visible light. Then, the photogenerated electrons in the CBM of  $\text{Bi}_2\text{WO}_6$  can recombine the holes in the VBM of mpg- $\text{C}_3\text{N}_4$  at the interface of the heterostructure.<sup>55</sup> It can accumulate more reductive electrons and oxidative holes to involve in the redox reactions, resulting in high photocatalytic efficiency. Consequently, the strong reductive electrons can reduce oxygen in the air to generate  $\cdot\text{O}_2^-$ , because the CBM edge potential of mpg- $\text{C}_3\text{N}_4$  is more negative than that of  $\text{O}_2/\cdot\text{O}_2^-$  ( $-0.046$  V),<sup>56</sup> and superoxide radical can further induce the mineralization of organic pollutants. At the same time, the strong oxidizing holes in the  $\text{Bi}_2\text{WO}_6$  interface can also degrade organic pollutants. Furthermore, the holes in the VBM of  $\text{Bi}_2\text{WO}_6$  can oxidize  $\text{H}_2\text{O}$  to  $\cdot\text{OH}$  because the VBM potential of  $\text{Bi}_2\text{WO}_6$  is more positive than the potential of  $\cdot\text{OH}/\text{OH}^-$  ( $+1.99$  V), and then induced the organic pollutants degradation.<sup>56</sup> Based on the above discussion, it can be seen that the band structure and the interaction

of mpg- $\text{C}_3\text{N}_4$  and  $\text{Bi}_2\text{WO}_6$  lead to the improvement of photocatalytic performance, and the CNBW system is a type of Z-scheme photocatalysis.

## 4. Conclusions

A novel mpg- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$  composite photocatalytic material is first prepared by a simple hydrothermal method. The composite photocatalytic materials show strong photocatalytic activity under visible light irradiation, which is notably higher than that of pristine mpg- $\text{C}_3\text{N}_4$  or  $\text{Bi}_2\text{WO}_6$ . The  $\text{h}^+$ ,  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  are the main active species in the photocatalytic degradation process. Relied on the experimental results and theoretical analysis, the photocatalytic Z-scheme mechanism of the system was also discussed. The high photocatalytic performance is due to the high rate of photogenerated carrier separation. Furthermore, the ultrathin thickness of nest-like structure  $\text{Bi}_2\text{WO}_6$  can make photo-excited carrier easily transferred to the surface from the interior, and therefore reduces the bulk reorganization. Such a strategy may give a good understanding of the development of other similar photocatalytic materials.

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