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1	One-pot preparation of Bi/Bi <sub>2</sub> WO <sub>6</sub> /reduced graphene oxide as a
2	plasmonic photocatalyst with improved activity under visible
3	$\mathbf{light}^\dagger$
4	Yan Zhou, Sushan Ren, Qimei Dong, Yingying Li, Hanming Ding*
5	School of Chemistry and Molecular Engineering, East China Normal University, 500
6	Dongchuan Road, Shanghai 200241, China
7	
8	Abstract

A novel nanocomposite, Bi nanorods and  $Bi_2WO_6$  nanosheets supported on reduced 9 graphene oxide ( $Bi/Bi_2WO_6/rGO$ ), was synthesized *via* a facile one-pot solvothermal 10 method. In the reaction process, Bi<sub>2</sub>WO<sub>6</sub> nanosheets and Bi nanorods were in situ 11 12 grown on the rGO sheets, which were simultaneously achieved by the reduction of GO. Such a synthetic strategy can form effective close interfacial contacts and strong 13 interactions among Bi<sub>2</sub>WO<sub>6</sub>, Bi and rGO, leading to efficient separation and transfer 14 of photogenerated electron-hole pairs. As a result, the ternary plasmonic photocatalyst 15 exhibited a much higher photocatalytic activity than pure Bi<sub>2</sub>WO<sub>6</sub> and the binary 16 17 composites in the photocatalytic degradation of rhodamine B and p-chlorophenol under visible light irradiation, which could be ascribed to the synergic effects of the 18 improved electron-hole pair separation efficiency, enhanced visible-light harvesting 19 and the good adsorptive capacity to dye molecules. 20

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available.

# 1 Introduction

Semiconductor-based photocatalysis is a promising technology to solve the current energy shortage and environmental pollution using the abundant solar light.<sup>1-3</sup> Undoubtedly, the semiconductor TiO<sub>2</sub> is known as one of the most excellent photocatalysts for the redox decomposition of a range of organic pollutants.<sup>4, 5</sup> However, TiO<sub>2</sub> has a wide band gap, which has limitation in visible light absorption.<sup>6-8</sup> Therefore, it is important to develop visible-light-driven photocatalysts to efficiently utilize the solar light in the visible region.

As a new visible light-responding non-titania-based photocatalyst, Bi<sub>2</sub>WO<sub>6</sub> with 9 a unique layered structure has attracted increasing interest recently.<sup>9-11</sup> However, there 10 are two main drawbacks that limit the application of  $Bi_2WO_6$  photocatalyst. At first, 11 pure Bi<sub>2</sub>WO<sub>6</sub> can only absorb light with wavelengths shorter than 420 nm.<sup>12, 13</sup> 12 Secondly, the high recombination of photogenerated charges after light absorption 13 seriously confines the light energy conversion efficiency.<sup>14, 15</sup> It was suggested that if 14 a high optical absorption could be maintained and meanwhile the charge 15 recombination could be significantly suppressed, a good photocatalytic activity will 16 be anticipated. To solve these problems, one way is to fabricate heterojunction 17 composite photocatalysts by coupling of another material with appropriate Fermi 18 energy. The recombination of photogenerated electron-hole pairs thus can be 19 effectively suppressed, resulting in increased probability of the photogenerated 20 charges to be available for photocatalytic reactions.<sup>16, 17</sup> Reduced graphene oxide 21 (rGO) has recently attracted tremendous attention owing to its fascinating electrical 22

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and chemical properties.<sup>18, 19</sup> When rGO is hybridized with a photocatalyst, the excellent electronic conductivity of rGO will promote the charge transfer through its conjugated structure, inhibiting the recombination of the photoexcited electron-hole pairs<sup>20, 21</sup> Furthermore, rGO nanosheets can act as adsorptive centers due to their large  $\pi$ -conjugation system and 2D planar structure, which make dye molecules adsorb easily onto their surface via strong  $\pi$ - $\pi$  interactions between rGO and dye molecules.<sup>22</sup>

Lately, bismuth (Bi) have been observed to exhibit surface plasmon resonance 8 (SPR) properties.<sup>23</sup> Compared to the general noble metals such as Au and Ag, Bi is 9 much cheap and easily prepared. It is documented that several Bi-modified 10 photocatalysts, such as  $Bi/g-C_3N_4$  and  $Bi/Bi_2O_2CO_3$  exhibited highly promoted 11 photocatalytic performance, which is ascribed to the SPR effect of Bi.24, 25 12 Considering the salient characteristics of Bi, Bi<sub>2</sub>WO<sub>6</sub>, and rGO, it prompts us to 13 consider whether we can use a facile method to prepare a Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO triple 14 nanocomposite, in which their synergic effects could improve the photocatalytic 15 16 activity.

In this study, we have developed a one-pot hydrothermal method to prepare a Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO nanocomposite, in which the formation of Bi<sub>2</sub>WO<sub>6</sub>, reduction of graphene oxide (GO) into rGO, and reduction of Bi<sup>3+</sup> ions into metal Bi are simultaneously accomplished in the same synthetic system. Notably, besides being a solvent, ethylene glycol (EG) also plays as a mild reductant for the reduction of GO and Bi<sup>3+</sup> ions, and therefore no additional reductants are required. The

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Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO nanocomposite exhibit a high photocatalytic activity to degrade
 rhodamine B (RhB) solutions under visible light irradiation. And the photocatalytic
 mechanism has been proposed as well.

4

# 5 **Experimental section**

# 6 Synthesis of graphene oxide (GO) and Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO composites

7 GO was synthesized via a modified Hummer's method (see Supporting Information 8 for experimental details). For the synthesis of  $Bi/Bi_2WO_6/rGO$ , an optimal molar ratio of  $Bi(NO_3)_3$  to  $Na_2WO_4$  was adopted as 3.5:1. Typically, 3 mg of GO was dispersed 9 in 20 mL of ethylene glycol followed by ultrasonication for 1 h. Then, 1 g of PVP 10 (polyvinylpyrrolidone K-30) and 3.5mmol of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were added under 11 stirring. Complete dissolution was required to obtain a uniform mixture. Subsequently, 12 0.5 mL of Na<sub>2</sub>WO<sub>4</sub> solution (2 mol/L) was added into the mixture and stirred for 30 13 min, getting a homogeneous suspension. After that, the suspension was transferred to 14 15 a 25 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 180  $^{\circ}$ C and kept at this temperature for 24 h. After the autoclave was cooled naturally to room 16 temperature, the product was separated, washed with absolute ethanol and distilled 17 water for several cycles, and dried at 60 °C in vacuum. According to the added dosage 18 of GO in the synthesize process, four Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO samples were synthesized and 19 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-2, denoted Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-1, Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 20 as and Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-4 corresponding to the adding weight of GO of 1, 2, 3 and 4 mg. For 21 comparison, pure Bi<sub>2</sub>WO<sub>6</sub>, Bi<sub>2</sub>WO<sub>6</sub>/rGO and Bi/Bi<sub>2</sub>WO<sub>6</sub> were prepared using similar 22

- methods (see Supporting Information for experimental details).
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# 3 Characterization

X-ray powder diffraction (XRD) analysis was conducted using a Bruker D8 Advance 4 X-ray powder diffractometer with Cu K $\alpha$  radiation. The morphology was observed 5 with a JEOL JEM-100C II transmission electron microscope (TEM) with an 6 7 accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were carried out 8 using a Kratos AXIS Ultra DLD XPS system with an Al K $\alpha$  (1486.6 eV) line at 150 W. UV-vis diffused reflectance spectra (DRS) were recorded using a LAMBDA 950 9 UV/Vis/NIR spectrophotometer. Fluorescence (FL) spectra were determined by a 10 Hitachi F-4500 FL spectrophotometer. Raman spectra were obtained on a Thermo 11 12 Scientific DXR Raman microscope at room temperature with 532 nm laser excitation. Nitrogen adsorption-desorption isotherms and the Brunauer-Emmett-Teller (BET) 13 surface areas were collected at 77 K using ASAP 2020 system (Quantachrome 14 15 Instruments). Photo-electrochemical measurements were performed in a constructed three electrode quartz cell system. Pt sheet was used as a counter electrode and 16 Ag/AgCl was used as reference electrodes, while the thin film on fluorine doped tin 17 oxide (FTO) was used as the working electrode for investigation. The 18 photoelectrochemical experimental results were obtained with a CHI 760C 19 electrochemical system. An aqueous solution of 0.2 M Na<sub>2</sub>SO<sub>4</sub> was used as the 20 electrolyte. 21

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# **1 Photocatalytic experiments**

2 The photocatalytic activities of the as-prepared samples were evaluated by the degradation of rhodamine B (RhB) or colorless *p*-chlorophenol (4-CP) under visible 3 light irradiation using a 500 W metal halide lamp with a 420 nm cutoff filter as the 4 light source. In a typical process, 20 mg of the photocatalyst was dispersed into 50 mL 5 RhB (10 mg L<sup>-1</sup>) or 4-CP (10 mg L<sup>-1</sup>) solution under magnetic stirring. Prior to 6 7 irradiation, the suspension was agitated in darkness for 30 min to ensure 8 adsorption-desorption equilibrium. Subsequently, the suspension was kept magnetically stirred under visible light irradiation, and 2 mL of the sample solution 9 was taken from the reaction system at a certain time interval. After the catalyst was 10 isolated by centrifugation, the supernatant was analyzed using a UV-vis spectrometer 11 (UV-8000). The degradation efficiency was calculated in accordance with  $C/C_0$ , 12 13 where C is the concentration of the remaining pollutant solution at each time interval, while  $C_0$  is the initial concentration. 14

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## 16 Results and discussion

The crystalline structure of the products was investigated by the XRD method. The results shown in Fig. 1 display that the diffraction peaks of pure  $Bi_2WO_6$  and Bi are in good agreement with the orthorhombic phase of  $Bi_2WO_6$  (JCPDS card no. 39-0256) and the hexagonal phase of Bi (JCPDS card no. 44-1246), respectively. As for the Bi/Bi<sub>2</sub>WO<sub>6</sub> composite, all the diffraction peaks can be indexed to the orthorhombic phase of Bi<sub>2</sub>WO<sub>6</sub> and the hexagonal phase of Bi respectively. Furthermore, the

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diffraction peak intensities of Bi in the Bi/Bi<sub>2</sub>WO<sub>6</sub> composites strengthened gradually 1 2 when increasing  $Bi(NO_3)_3$  in the precursor solutions (Fig. S1), suggesting that the Bi content in the  $Bi/Bi_2WO_6$  composite can be controlled in the synthesize process. The 3 XRD pattern of the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 composite is comparable to that of Bi/Bi<sub>2</sub>WO<sub>6</sub> 4 (Fig. 1f). However, the full width at half maximum (FWHM) of the diffraction peaks 5 of Bi and Bi<sub>2</sub>WO<sub>6</sub> is broadened for the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO composites (Fig. S2), which 6 7 is attributed to the existence of rGO restricts the degree of crystallization in the synthesize process.<sup>26</sup> In addition, no characteristic diffraction peaks for rGO are 8 observed in the pattern because of the low amount and relatively low diffraction 9 intensity.<sup>27</sup> However, the existence of rGO in the nanocomposite can be confirmed by 10 the Raman spectra. 11





13 Fig. 1. XRD patterns of (a) GO, (b) Bi, (c) Bi<sub>2</sub>WO<sub>6</sub>, (d) Bi/Bi<sub>2</sub>WO<sub>6</sub>, (e) Bi<sub>2</sub>WO<sub>6</sub>/rGO, and (f)

14  $Bi/Bi_2WO_6/rGO-3$ . Triangle and solid dot refer to Bi and  $Bi_2WO_6$  respectively.

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As shown in Fig. 2, the Raman peak at 303 cm<sup>-1</sup> is assigned to the translation

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modes involving simultaneous motions of Bi<sup>3+</sup> and WO6<sup>6-.28</sup> These two peaks at 763 1 and 817  $\mbox{cm}^{-1}$  are attributed to antisymmetric and symmetric  $A_g$  modes of the O-W-O 2 group terminus, respectively.<sup>29</sup> Compared to Bi<sub>2</sub>WO<sub>6</sub>, the intensity of Raman peaks of 3 Bi/Bi<sub>2</sub>WO<sub>6</sub> composites are slightly enhanced. This phenomenon could be attributed to 4 the surface enhanced Raman scattering effect of metal Bi.<sup>30</sup> As for rGO, there are two 5 typical Raman bands at ~1611 cm<sup>-1</sup> (G band) and at ~1359 cm<sup>-1</sup> (D band) for its 6 graphitized structure.<sup>31</sup> In Raman spectrum of Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3, these two 7 characteristic bands were also observed. In comparison with GO ( $I_D/I_G = 0.98$ ), an 8 increased D/G intensity ratio ( $I_D/I_G = 1.03$ ) was observed, which revealed that the GO 9 has been partially reduced after the solvothermal reaction.<sup>32</sup> Furthermore, the 10 positions of D band and G band in the ternary composites were slightly shifted (inset 11 of the Fig. 2), due to the reduction of GO and the combination of Bi and Bi<sub>2</sub>WO<sub>6</sub> with 12 rGO.<sup>33, 34</sup> 13



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15 Fig. 2 Raman spectra of (a) GO, (b) Bi<sub>2</sub>WO<sub>6</sub>, (c) Bi/Bi<sub>2</sub>WO<sub>6</sub> and (d) Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3. Inset: the

16 enlarged Raman spectra of GO and  $Bi/Bi_2WO_6/rGO-3$ .

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2	The chemical states and the surface composition of $\mathrm{Bi}/\mathrm{Bi}_2\mathrm{WO}_6/\mathrm{rGO}$ -3 sample
3	has been analyzed by XPS (Fig. 3). In the full XPS spectrum of Fig. 3A, the different
4	binding energies were assigned to W 4f, Bi 4f, W 4d, Bi 4d, C 1s, O 1s, and Bi 4p
5	states emission peaks, respectively. These peaks at 34.9 and 35.1 eV in
6	$Bi/Bi_2WO_6/rGO\text{-}3$ correspond to W $4f_{5/2}$ and W $4f_{7/2}$ (Fig. 3B), respectively, both of
7	which can be assigned to the $W^{6+}$ oxidation state. <sup>35</sup> The O 1s peaks for
8	$Bi/Bi_2WO_6/rGO-3$ (Fig. 3C) can be deconvoluted into two bands at 529.8 and 530.7
9	eV, which are associated with OH hydroxyl groups and oxygen species in the lattice
10	oxygen, respectively. <sup>36</sup> Two main peaks with binding energies of 158.8 eV and 164.1
11	eV can be observed in Fig.3D, which can be ascribed to the $\mathrm{Bi}^{3+}$ 4f $_{7/2}$ and $\mathrm{Bi}^{3+}$ 4f $_{5/2}$
12	binding energies, respectively. <sup>37</sup> Moreover, apart from the two peaks discussed above,
13	there are two peaks at 162.5 eV and 157.2 eV with low intensity, which can be
14	ascribed to metallic Bi. <sup>38</sup> As shown in Fig. 3E, the peak at 288.7 eV for the C=O
15	bonding exists but its peak intensity is very low. To illustrate the reduction degree of
16	the GO sheets in the $Bi/Bi_2WO_6/rGO-3$ , the peak area ratios of C=O bonds to the total
17	area are calculated to be 0.16 by the XPS C 1s peak area analysis, proving the
18	transformation from GO to rGO. <sup>39, 40</sup> Therefore, the results confirm the successful
19	reduction of Bi <sup>3+</sup> and GO into metal Bi and rGO via the facile hydrothermal process.

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Fig. 3 XPS spectra of the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 sample: (A) full spectrum, (B) W 4f, (C) O 1s, (D) Bi 4f,
and (E) C 1s.

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TEM images showing the morphology and microstructure of the as-prepared Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 are presented in Fig. 4. It can be seen that the rGO sheets exhibit a typical rippled and crumpled structure and the Bi/Bi<sub>2</sub>WO<sub>6</sub> composites overspread on the rGO surface. (Fig. 4a). The apparent contrast between the darker nanorods and brighter nanosheets as illustrated in Fig. 4b suggests the formation of Bi nanorods and Bi<sub>2</sub>WO<sub>6</sub> nanosheets on the surface of rGO. The Bi nanorods appear distinctly darker

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1	than the $Bi_2WO_6$ due to the higher electron density, which could be further confirmed
2	by HRTEM (Fig. 4c). <sup>41-43</sup> The Bi nanorods with an average length of 50 nm have
3	been observed in the TEM images (Figs. 4b and S6a). As can be observed in Fig. 4c,
4	the fringe interval of 0.315 nm is in accordance with the interplanar spacing of (131)
5	plane of $Bi_2WO_6$ , whereas the periodic fringe spacing of 0.325 nm can be indexed as
6	the (102) plane of the hexagonal Bi. To further obtain information about the Bi
7	structure, the special region of Bi nanorods was analyzed (Fig. 4d). The spacing of
8	0.227 nm between neighboring lattice fringes corresponds to the distance between two
9	(110) planes, indicating [100] as the growth direction for the Bi nanorods. <sup>44</sup> These
10	results agree well with the XRD results. Moreover, the stacking width is calculated to
11	be 0.37 nm for rGO layers corresponding to the spacing of the (002) lattice planes. <sup>45,</sup>
12	<sup>46</sup> This spacing is very close to pristine graphite, indicating that GO has been well
13	reduced to graphene (rGO).





4 Fig. 4 TEM images (a, b) and HRTEM image (c, d) of Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3.

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1	Fig. 5 shows the nitrogen adsorption-desorption isotherms for samples of
2	Bi <sub>2</sub> WO <sub>6</sub> , Bi/Bi <sub>2</sub> WO <sub>6</sub> , Bi <sub>2</sub> WO <sub>6</sub> /rGO, Bi/Bi <sub>2</sub> WO <sub>6</sub> /rGO-3. The typical IV isotherms and
3	hysteresis loops of the sample are characteristic of mesoporous materials. <sup>37, 38</sup> The
4	BET surface areas of the as-prepared Bi2WO6, Bi/Bi2WO6, Bi2WO6/rGO, and
5	$Bi/Bi_2WO_6/rGO-3$ are 27.87, 39.12, 67.42, and 67.67 m <sup>2</sup> /g, respectively. Notably, the
6	higher surface area of $Bi/Bi_2WO_6/rGO-3$ is attributed to the presence of rGO
7	nanosheets in the nanocomposite. Moreover, the pore volume determined by the
8	Barrett-Joyner-Halenda (BJH) model indicated broad distributions with a pore volume
9	of 24.65, 35.14, 68.43, and 69.26 cm <sup>3</sup> /g for $Bi_2WO_6$ , $Bi/Bi_2WO_6$ , $Bi_2WO_6/rGO$ , and
10	$Bi/Bi_2WO_6/rGO-3$ respectively. The pore size distribution of $Bi/Bi_2WO_6/rGO-3$ is
11	shown in the inset in Fig. 5, which shows an average pore diameter of 20 nm. Owing
12	to its high surface area and large pore volume, the mesoporous photocatalyst will
13	provide efficient adsorption sites and enhance transportation of charge carriers, which
14	would lead to an improvement of the photocatalytic activity.



16 Fig. 5 Nitrogen adsorption-desorption isotherms of various samples. Inset: the pore size distribution of

1 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3. 2 3 The formation mechanism of Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO nanocomposites Based on the above experimental results and analysis, a possible synthesis process of 4 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO is proposed. The *in situ* one-step synthetic route of Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO 5 nanocomposites is illustrated in Scheme 1. The reactions involved in the formation of 6 7 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO structures can be summarized as follows: 8  $Bi(NO_3)_3 \rightarrow Bi^{3+} + 3NO_3^{-1}$ 9 (1) $Na_2WO_6 \rightarrow 2Na^+ + WO_4^{2-}$ (2)10  $2\mathrm{Bi}^{3+} + \mathrm{WO_4}^{2-} \rightarrow \mathrm{Bi}_2\mathrm{WO_6}$ (3)11  $Bi^{3+} + HOCH_2CH_2OH \rightarrow$ Bi  $+2H^{+}$ (4)12 Ð  $+ WO_4^{2-} \rightarrow Bi_2WO_6 + HOCH_2CH_2OH$ Bi 2 (5)13  $2HOCH_2CH_2OH \rightarrow 2CH_3CHO$ (6) 14  $6CH_3CHO + 2Bi^{3+} \rightarrow 3CH_3COCOCH_3 + Bi + 6H^+$ (7)15 16 The overall synthesis can be divided into four consecutive stages. At the early 17

17 The overall synthesis can be divided into four consecutive stages. At the early 18 stage of the reaction process, when  $Bi(NO)_3$  is dissolved in the GO solution (Eq. 1), 19 the positively charged  $Bi^{3+}$ could be uniformly adsorbed onto the surface of the GO 20 sheets, which is negatively charged due to the existence of OH and C=O functional

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1	groups (Scheme 1A-B). After $Bi^{3+}$ ions have been adsorbed, the reaction between $Bi^{3+}$
2	and EG takes place on the surface of GO, forming EG-Bi <sup>3+</sup> complexes via the
3	coordination between Bi <sup>3+</sup> ions and OH groups (Eq. 4, Scheme 1C). <sup>47</sup> Then, in the
4	following solvothermal treatment at high operating temperature, the complex is
5	gradually decomposed to release the ${\rm Bi}^{3+}$ ions, which are then reacted with ${\rm WO_4}^{2-}$
6	ions to form $Bi_2WO_6$ nanosheets on the surface of the graphene components (Eq. 5). <sup>48</sup>
7	Meanwhile, metal Bi and rGO can be formed simultaneously (Eqs. 6 and 7, Scheme
8	1D) during the hydrothermal treatment. When $Bi(NO_3)_3$ is excessive in the reaction,
9	there are still many residual $\mathrm{Bi}^{3+}$ ions absorbed on the surface of GO after the
10	formation of $Bi_2WO_6$ . These residual $Bi^{3+}$ ions can be reduced into Bi nanorods by the
11	reductant of EG in the presence of PVP. Therefore, the content of Bi nanorods can be
12	easily tuned just by varying the precursor ratios. It has been reported that only
13	urchin-like bismuth structures were obtained by self-assemble of Bi nanorods in pure
14	EG solution, in which a typical coordinative reduction course was suggested. <sup>49</sup> It is
15	believed that the anisotropic effects of crystal and the face inhibitor function of PVP
16	play crucially important roles in the formation of 1D nanostructures. <sup>50</sup> In the
17	solvothermal reaction process, PVP molecules could preferentially adsorb onto the
18	primary surfaces of Bi crystals through O-Bi bonding as reported in the previous
19	work. <sup>44</sup> The polymer molecules adsorbed on some surfaces of the Bi crystals could
20	significantly decrease their growth rates and lead to highly anisotropic growth. <sup>51</sup>
21	Therefore, the isolated Bi nanorods were formed in the presence of PVP under
22	appropriate reaction conditions.

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UV-vis diffuse reflectance spectra (DRS) of the as-prepared samples are shown 4 in Fig. 6. Compared with that of pure  $Bi_2WO_6$ , the light-harvesting ability of 5 Bi/Bi<sub>2</sub>WO<sub>6</sub> is apparently enhanced, ranging from UV to visible light region. This 6 enhancement is attributed to the SPR effect of plasmonic Bi.<sup>52</sup> Additionally, the 7 absorption of  $Bi/Bi_2WO_6$  is gradually intensified with increasing the content of Bi 8 (Fig. S3). For Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO, the continuous background absorption from 400-800 9 nm is enhanced due to the black body effect of graphene.<sup>53</sup> In addition, this 10 observation also clearly indicates that more visible light can be absorbed in the 11 as-prepared Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO nanocomposite to generate more electron-hole pairs, and 12 thus its photocatalytic activity will be improved under visible light irradiation. This 13

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hypothesis was confirmed by measuring the degradation of RhB over the obtained
samples under the same conditions. With increasing the amount of rGO, the
Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO composites show a continuously enhanced visible-light absorption in
the range of 400-800 nm, which is in agreement with the previous report.<sup>54</sup> Therefore,
the incorporation of Bi nanorods and rGO sheets increased the light absorption of the
ternary composites in the visible region.



8 Fig. 6 UV-vis diffuse reflection spectra of (a) Bi<sub>2</sub>WO<sub>6</sub>, (b) Bi/Bi<sub>2</sub>WO<sub>6</sub>, (c) Bi<sub>2</sub>WO<sub>6</sub>/rGO, (d)
9 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-1, (e) Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-2, (f) Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3, and (g) Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-4.

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The degree of charge recombination can be evaluated by photoluminescence (PL) spectroscopy (Fig. 7). The lower PL intensity reflects the lower recombination rate of photogenerated electrons and holes.<sup>55</sup> Obviously, Bi/Bi<sub>2</sub>WO<sub>6</sub> shows a significantly diminished PL intensity in comparison with pure Bi<sub>2</sub>WO<sub>6</sub>, which suggests that the deposition of Bi results in a remarkable decline in the recombination rate of

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photogenerated electron-hole pairs.<sup>25</sup> In Bi<sub>2</sub>WO<sub>6</sub>/rGO, photogenerated electrons could

be transferred efficiently from Bi<sub>2</sub>WO<sub>6</sub> to rGO due to the high charge carrier mobility

of the rGO sheets, leading to a low charge recombination rate. The PL results

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12 Fig. 7 Photoluminescence spectra of various photocatalysts.

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Fig. 8 shows the transient photocurrent responses of the obtained samples. The photocurrents were stable and reversible at light-on and light-off for all samples. In

comparison with Bi<sub>2</sub>WO<sub>6</sub>, Bi/Bi<sub>2</sub>WO<sub>6</sub>, and Bi<sub>2</sub>WO<sub>6</sub>/rGO, Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3
composite exhibited an increased current density, about 1.6, 1.2, and 1.15 times than
that of Bi<sub>2</sub>WO<sub>6</sub>, Bi/Bi<sub>2</sub>WO<sub>6</sub>, and Bi<sub>2</sub>WO<sub>6</sub>/rGO, respectively. The improvement of
photocurrent indicated an enhanced photogenerated electron-hole separation
efficiency, which is in good agreement with the PL measurements.



Fig. 8 Photocurrent responses of (a) Bi<sub>2</sub>WO<sub>6</sub>, (b) Bi/Bi<sub>2</sub>WO<sub>6</sub>, (c) Bi<sub>2</sub>WO<sub>6</sub>/rGO, and (d)
8 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3.

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The photocatalytic activities of the samples were evaluated by the degradation of 10 RhB under visible light irradiation ( $\lambda$ >420nm), as shown in Fig. 9. A blank control 11 test (without photocatalyst) confirmed that the self-degradation of RhB can be 12 negligible. The Bi/Bi<sub>2</sub>WO<sub>6</sub> composite has a higher photocatalytic activity than that of 13 14  $Bi_2WO_6$ , which is due to the SPR effect of Bi. In addition, the photocatalytic activity 15 was further enhanced by increasing the Bi amount in the composites (Fig. S4), which is consistent with the results of DRS. Compared with pure Bi<sub>2</sub>WO<sub>6</sub> and Bi/Bi<sub>2</sub>WO<sub>6</sub>, 16 the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO photocatalysts exhibited much higher photocatalytic activity (Fig. 17

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9A). About 99.9% of the RhB molecules was decomposed in 120 min when

 $Bi/Bi_2WO_6/rGO-3$  was used as the photocatalyst, while only 49% and 83% of the

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3	RhB molecules were degraded when pure Bi <sub>2</sub> WO <sub>6</sub> and Bi/Bi <sub>2</sub> WO <sub>6</sub> were employed,
4	respectively. Moreover, the photocatalytic activity of the $Bi/Bi_2WO_6/rGO$ composites
5	increases with increasing the rGO content, and $Bi/Bi_2WO_6/rGO-3$ shows the highest
6	degradation efficiency. However, when more GO was added, the photocatalytic
7	activity of the Bi/Bi <sub>2</sub> WO <sub>6</sub> /rGO photocatalyst is decreased. It is probably because the
8	dense black layers of excessive rGO shield the light irradiation on Bi and Bi <sub>2</sub> WO <sub>6</sub> ,
9	which could weaken the photocatalytic activity of the composite. Furthermore,
10	excessive rGO also can act as a recombination center, which then decreases the
11	efficiency of charge separation. <sup>57</sup>
12	In order to directly shown the photocatalytic activity enhancement of
13	Bi/Bi <sub>2</sub> WO <sub>6</sub> /rGO, Langmuir-Hinshelwood kinetics model was applied to calculate the
14	apparent pseudo-first order rate constant $k$ . <sup>58</sup> As can be seen in Fig. 9B, the rate
15	constants corresponding to, Bi/Bi <sub>2</sub> WO <sub>6</sub> , Bi <sub>2</sub> WO <sub>6</sub> /rGO, Bi/Bi <sub>2</sub> WO <sub>6</sub> /rGO-1,

lied to calculate the n Fig. 9B, the rate Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-1, Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-2, Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 and Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-4 were estimated to be 16 0.0111, 0.0099, 0.0115, 0.0203, 0.0355 and 0.0147 min<sup>-1</sup>, which are about 2.27, 2.02, 17 2.35, 4.14, 7.24 and 3 times as much as that over  $Bi_2WO_6$  (0.0049 min<sup>-1</sup>), respectively. 18 These results clearly indicated that introducing appropriate amount of Bi and rGO into 19 the Bi<sub>2</sub>WO<sub>6</sub> photocatalyst system can greatly enhance its photocatalytic activity. 20



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Fig. 9 (A) Photocatalytic degradation curves of RhB as a function of irradiation time over various
photocatalysts under visible light irradiation (the time before 0 min means in the dark). (B) Kinetic
curves of photocatalytic degradation of RhB fitted from the data of Figure 9A.

6

7 It is usually accepted that the degrading RhB over the photocatalyst would occur
8 partially via photosensitization pathway. In order to eliminate the photosensitization
9 effect, colorless *p*-chlorophenol (4-CP) was used as the model pollutant. The

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1	photocatalytic degradation results are shown in Fig. 10. In contrast to $Bi_2WO_6$ ,
2	Bi/Bi <sub>2</sub> WO <sub>6</sub> , and Bi <sub>2</sub> WO <sub>6</sub> /rGO, an enhanced photocatalytic activity was observed for
3	the Bi/Bi <sub>2</sub> WO <sub>6</sub> /rGO-3 composite. As shown in Fig. 10A, a similar trend to the
4	photocatalytic degradation of RhB was observed under visible light irradiation. The
5	$Bi/Bi_2WO_6/rGO-3$ composite exhibits the highest photocatalytic performance among
6	all the tested samples for RhB and 4-CP removal. Fig. S5 shows the evolution of
7	UV-vis spectra for RhB and 4-CP solution in the presence of $Bi/Bi_2WO_6/rGO-3$ under
8	visible light irradiation. The UV-vis peak intensity of RhB at 553 nm decreased
9	gradually with irradiation time, while its position remained unchanged, suggesting
10	that the RhB molecules were directly destroyed through the cleavage of the
11	chromophore ring structure rather than a de-ethylation process. <sup>59</sup> The UV-vis intensity
12	of 4-CP also decreased with irradiation time, but slowly compared with that of RhB.
13	Only 52% 4-CP was removed, while almost 99% RhB was degraded after 120 min.
14	Thus, the degradation efficiency for 4-CP is lower than that for RhB (Fig. 10B),
15	which implies that photosensitization plays a role in the RhB degradation.





Fig. 10 (A) Photocatalytic degradation of 4-CP as a function of irradiation time over the different four
samples. (B) The comparison of removal efficiencies for RhB and 4-CP over Bi<sub>2</sub>WO<sub>6</sub>, Bi/Bi<sub>2</sub>WO<sub>6</sub>,
Bi<sub>2</sub>WO<sub>6</sub>/rGO and Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 after 120-min visible light irradiation.

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As is known, various active species (•OH, •O<sub>2</sub><sup>-</sup>, and  $h^+$ ) generated in the 6 photocatalytic processes played key roles. Therefore, the trapping experiments were 7 carried out to explore the main active species. Isopropyl alcohol (IPA), 8 p-benzoquinone (BQ), and triethanolamine (TEOA) were adopted as the traps for • 9 OH,  $\bullet O_2^-$ , and  $h^+$ , respectively.<sup>60</sup> Fig. 11 shows the effect of different scavengers on 10 the photocatalytic degradation RhB and 4-CP over Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3. It can be easily 11 seen that the addition of IPA does not cause deactivation of the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 12 photocatalyst in both cases, indicating that •OH was not the major active species 13 involved in the photocatalytic processes. However, the photocatalytic performance of 14 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 significantly decreases by the addition of TEOA and BQ. Thus, 15

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 $\cdot O_2^-$  radicals and h<sup>+</sup> were proved to be the dominant active species in the 1 photocatalytic degradation of RhB and 4-CP over the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 composite 2 photocatalyst under visible light irradiation. According to the previous report, the CB 3 electrons of Bi<sub>2</sub>WO<sub>6</sub> possess a poor reduction power owing to its more positive 4 potential (+0.3 V, vs. SHE) than the one-electron oxygen reduction ( $O_2 + H^+ + e^-$ 5 HO<sub>2</sub>, -0.046 V vs. SHE).<sup>61</sup> It seem plausible that the conduction band potential of 6  $Bi_2WO_6$  is incapable to reduce the dissolved  $O_2$  to  $\bullet O_2^-$  radicals. However, with the 7 addition of rGO, the electronic interaction and charge equilibrium between  $Bi_2WO_6$ 8 and rGO lead to the negative shift of the Fermi level and the change in energy levels 9 of the conduction band and valence band, indicating that the photocatalytic 10 performance of reduction reactions is enhanced.<sup>62, 63</sup> 11





2 Fig. 11 Effects of different scavengers on (A) RhB and (B) 4-CP degradation over Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3

- 3 under visible light irradiation.
- 4

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In addition to photocatalytic efficiency, the stability of photocatalysts is another 5 important issue for its practical application. To study the photocatalytic stability and 6 7 reusability of Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3, the photocatalysis process was repeated five times under the same conditions. As shown in Fig. 12A, the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 composite 8 had a high and stable activity for photocatalytic degradation of RhB under visible 9 light irradiation. After five cycling runs, the photocatalyst has no detectable loss of its 10 photocatalytic activity. XRD patterns of Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 before and after the 11 photocatalytic reaction were comparable in Fig. 12B. There is no apparent change 12 13 observed in the XRD patterns. TEM and XPS analysis proved that there is no apparent change in composition and morphology for Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 during the 14 photocatalytic process (Figs. S6 and S7), which also confirmed the stability of the 15 structure. It can be concluded that Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO possesses an efficient 16

- 1.0 А 3rd 5th 4th 1st 2nd 0.8 0.6 ပိုပ 0.4 0.2 0.0 0 100 200 300 400 500 600 Time (min) В after Intensity (a.u.) before Bi JCPDS no. 44-1246 Bi2WO6 JCPDS no. 39-0256 20 40 60 80 2 Theta (degree)
- 1 photocatalytic activity and can be easily separated for reuse.

2

4 Fig. 12 (A) Cycling runs in the photocatalytic degradation of RhB in the presence of
5 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3. (B) XRD diffraction patterns of Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO-3 measured before and after a
6 photocatalytic reaction under visible light irradiation.

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8 The enhanced photocatalytic activities of the Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO composites could 9 be ascribed to the synergic effects of the following factors. Firstly, the introduction of

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Bi nanorods in the composite broadened the light absorption in the visible region,
which could be ascribed to the SPR effect of metal Bi. Secondly, due to their
matching energy levels, the interfacial charge transfer could effectively enhance the
separation efficiency of photogenerated electrons and holes. Finally, the presence of
rGO provides more active adsorption sites on the surface of rGO in the photocatalytic
reaction. A proposed mechanism for the separation and transportation of
photogenerated electron-hole pairs at the $\mathrm{Bi}/\mathrm{Bi}_2\mathrm{WO}_6/\mathrm{rGO}$ interface is shown in
Scheme 2. Electrons and holes could be generated from both the photo-excited
$\mathrm{Bi}_{2}\mathrm{WO}_{6}$ and the SPR-excited Bi under visible light irradiation. Since the Fermi
energy level of Bi ( $E_f = -0.17$ eV vs. SHE) is more negative than the conduction band
(CB) of $Bi_2WO_6$ (E <sub>CB</sub> = 0.24 eV vs. SHE). <sup>64, 65</sup> It is energetically favorable for the
SPR-excited electrons transferring from Bi to the CB of $Bi_2WO_6$ . Subsequently, these
electrons can transfer from the CB of $Bi_2WO_6$ to the surface of rGO nanosheets, due
to their two-dimensional conjugated $\pi$ -structure and ultrahigh charge carrier mobility.
Concomitantly, the holes transfer to the $Bi_2WO_6$ and $Bi$ surfaces, which corresponds
to the oxidation of dye molecules into CO <sub>2</sub> . Thus, in the case of $Bi/Bi_2WO_6/rGO$ , rGO
sheets served as an acceptor of the photogenerated electrons of $\mathrm{Bi}_2\mathrm{WO}_6$ and $\mathrm{Bi}$ , which
will suppress the recombination of photogenerated electron-hole pairs. The electrons
in rGO can be captured by the dissolved O <sub>2</sub> molecules to generate superoxide anion
radicals ( $^{\bullet}O_2$ ) and then react with RhB (or 4-CP). In the meantime, the holes in the
composite can directly oxidize the pollutants into $CO_2$ and $H_2O$ , and other
intermediates.



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## 5 Conclusions

In summary, the excellent heterojunction structure of rGO supported Bi nanorods 6 and  $Bi_2WO_6$  nanosheets was obtained via a one-pot solvothermal process. The 7 8 obtained composite possesses an enhanced visible light harvesting, good adsorptive capacity and efficient charge separation of the photogenerated electron-hole pairs. The 9 ternary composite photocatalyst had a better performance for RhB photocatalytic 10 degradation compared with the pristine Bi<sub>2</sub>WO<sub>6</sub> and the binary composite of 11 Bi/Bi<sub>2</sub>WO<sub>6</sub>. Such excellent performance should be attributed to the SPR effect of Bi, 12 visible light response of Bi<sub>2</sub>WO<sub>6</sub>, vectorial charge carrier transfer in the 13 Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO heterojunctions and rGO sheets. In addition, the photocatalyst 14 exhibits a high stability and can be reused for five times without any degeneration in 15

Scheme 2. Proposed mechanism degradation of RhB over Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO composite.

1	its photocatalytic activity. This work provides a new possibility in the investigation of	
2	Bi/Bi	<sub>2</sub> WO <sub>6</sub> /rGO composites and promotes their practical applications in waste water
3	treatn	nent.
4		
5	Ackn	owledgments
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The Bi/Bi<sub>2</sub>WO<sub>6</sub>/rGO nanocomposite for simultaneous RhB adsorption and photocatalysis were synthesized by an one-pot hydrothermal method.