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1 **Double Z-scheme FeVO₄/Bi₄O₅Br₂/BiOBr ternary heterojunction photocatalyst for**
2 **simultaneous photocatalytic removal of hexavalent chromium and rhodamine B**

3

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16

17

1 **Abstract**

2 *Hypothesis*

3 Fabrication of the heterojunction photocatalyst with appropriate band potentials as a
4 promising method of inhibiting electron-hole pair recombination leading to enhanced
5 photocatalytic properties.

6 *Experiments*

7 Herein, BiOBr, Bi₄O₅Br₂, and binary BiOBr/Bi₄O₅Br₂ composite were selectively
8 synthesized by employing a one-step microwave irradiation method. Then, double Z-scheme
9 FeVO₄/Bi₄O₅Br₂/BiOBr ternary composites with different weight percentages (%wt) of FeVO₄
10 were fabricated and their photocatalytic applications were studied. The photodegradation of
11 organic compounds (rhodamine B (RhB), methylene blue (MB) and salicylic acid (SA)), along
12 with the photoreduction of hexavalent chromium (Cr(VI)) were investigated.

13 *Findings*

14 Comparing with the single and binary photocatalysts, and a commercial TiO₂, the
15 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst demonstrated superior visible-light-driven
16 photocatalytic performance. In a Cr(VI)/RhB combined system, Cr(VI) photoreduction was
17 further improved and coexisting RhB molecules were simultaneously degraded. Removal of
18 Cr(VI) and RhB were maximized by adjusting both pH values and catalyst dosages. Based on
19 UV-vis diffuse reflectance spectroscopy, photoluminescence spectroscopy, electrochemical
20 investigations, active-species trapping, nitrotetrazolium blue transformation, and silver photo-
21 deposition experiments, a double Z-scheme charge transfer mechanism with an RhB-sensitized
22 effect was proposed. This special mechanism has led to significant enhancement in charge
23 segregation and migration, along with higher redox properties of the ternary composite, which
24 were responsible for the excellent photocatalytic activity.

25

1 **Keywords:** Ternary heterojunction; Double Z-scheme; Dye-sensitization; Cr(VI)
2 photoreduction; Photodegradation; Microwave irradiation method

4 **1. Introduction**

5 With massive increases in water pollution, the removal of pollutants from water bodies
6 has become a critical issue. This can be accomplished through various techniques such as
7 adsorption [1], photocatalysis [2,3], and electrocatalysis [3]. Semiconductor photocatalysis is
8 a promising technology that can be used to address the environmental pollution that is related
9 to organic and inorganic pollutants in industrial wastewater. In order to fully utilize renewable
10 and clean solar energy, which is mainly comprised of visible light, there have been significant
11 attempts to develop and synthesize visible-light active photocatalysts [4,5]. Bismuth
12 oxyhalides (BiOX, X = Cl, Br and I) have exhibited striking photocatalytic activities due to
13 their layered structures with [Bi₂O₂] slabs interleaved by double slabs of halide atoms. Such
14 layered structure induces an internal static electric field, which then facilitates segregation of
15 electron-hole pairs and favors an enhanced photocatalytic activity [6–9]. Among them,
16 bismuth oxybromide (BiOBr) exhibited the highest photocatalytic activity due to its relatively
17 high photo-oxidation power of the photoactivated holes [10–13]. However, this photocatalyst
18 usually suffers from a low absorption efficiency in the visible light region, which can limit the
19 utilization of visible light to generate electron-hole pairs.

20 Density functional theory (DFT) calculations [14] indicated that the valence band of
21 BiOBr is mainly occupied by O 2*p* and Br 4*p* hybrid orbitals and its conduction band is
22 composed of Bi 6*p* orbital. This suggests that tuning bismuth and bromide contents in BiOBr
23 could modulate its band edge potentials, and consequently change its band gap energy. In
24 addition, bismuth-rich strategy strengthens the hybridization of the conduction band and
25 reinforces the internal static electric field, which in turn promotes electron migration and

1 segregation of the photoactivated electron–hole pairs. Therefore, the bismuth-rich strategy has
2 received significant interest over its potential to improve the photocatalytic performance of
3 BiOBr. Bismuth-rich BiOBr photocatalysts have been previously reported with a narrow band
4 gap and for possessing higher visible light absorption properties than the ordinary BiOBr
5 material [15]. Bi₄O₅Br₂, one of the known bismuth-rich BiOBr materials, exhibited higher
6 visible-light-driven photocatalytic activity than BiOBr in terms of the degradation of bisphenol
7 A [16,17], resorcinol [18], rhodamine b [19], and ciprofloxacin [20], as well as in the
8 photocatalytic reduction of CO₂ [21]. Although Bi₄O₅Br₂ exhibited strong visible light
9 photocatalytic properties, its quantum efficiency is still rather poor due to undesirable electron-
10 hole recombination [22]. Therefore, there is need to improve the lifetime of the photoactivated
11 electron-hole pairs in an attempt to overcome the unsatisfied quantum efficiency of the
12 material.

13 Some previous publications [23,24] have reported that the BiOBr/Bi₄O₅Br₂
14 heterojunction photocatalyst exhibited significant enhancement in photocatalytic activity due
15 to a suitable band alignment that ultimately led to an effective charge separation between the
16 two individual semiconductors. However, the synthesis of the BiOBr/Bi₄O₅Br₂ heterostructure
17 required harsh synthetic conditions [18,19,25–28]. For example, at high temperature, Bi₄O₅Br₂
18 was produced from a gradual loss of bromide ion in the BiOBr crystal accompanied by phase
19 transformations [24]. Compared with the binary heterojunction system, a ternary
20 heterojunction system had greatly satisfied electron-hole pair separation efficiency and much
21 prolonged the charge carrier's lifetime, both of which resulted from the multistep charge-
22 transfer processes and led to better photocatalytic activity [29,30]. In this research work, the
23 iron (III) vanadate, FeVO₄, was chosen as a visible-light photosensitizer for the construction
24 of the ternary FeVO₄/Bi₄O₅Br₂/BiOBr heterostructures owing to its narrow energy band gap,
25 visible-light active properties, and high stability [31,32]. Moreover, according to the outcomes

1 of our previous studies [33,34], we also found that by coupling the optimum content of FeVO_4
2 with bismuth-based compounds, compatible electronic band structure alignments can be
3 formed at the interface between the individual semiconductors to exhibit the enhancement of
4 photocatalytic activity. This likely would have resulted from the effective segregation of the
5 charge carriers and led to improved visible light responsibility.

6 Herein, we firstly synthesized the binary $\text{BiOBr}/\text{Bi}_4\text{O}_5\text{Br}_2$ composite using the facile
7 one-step microwave irradiation method. After that, the synthesized $\text{BiOBr}/\text{Bi}_4\text{O}_5\text{Br}_2$ composite
8 was hybridized with FeVO_4 using the wet-impregnation method to fabricate the ternary
9 $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ composites. The weight percentages (%wt) of FeVO_4 in the ternary
10 composites were varied in order to enhance their photocatalytic activities, which were then
11 investigated by the photocatalytic degradation of organic pollutants under visible light
12 irradiation. Using $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ composite with an optimum %wt of FeVO_4 , we also
13 investigated its photocatalytic performance towards the photoreduction efficiency of $\text{Cr}(\text{VI})$.
14 Since the co-existence of organic and inorganic pollutants is commonly found in real industrial
15 wastewater, for example, the coexistence of $\text{Cr}(\text{VI})$ and dyes/non-dyes in the effluents from the
16 leather tanning process [35–37], we further investigated the photoreduction of $\text{Cr}(\text{VI})$ in the
17 $\text{Cr}(\text{VI})/\text{RhB}$ combined pollution system. A series of experiments under the combined pollution
18 system was carried out to optimize photocatalytic conditions. Possible charge transfer and
19 photocatalytic mechanisms for the removal of $\text{Cr}(\text{VI})$ and RhB in the combined pollutant
20 system were discussed in detail.

21

22 **2. Experimental procedures**

23 **2.1. Synthesis of photocatalysts**

24 FeVO_4 was synthesized using a similar method to that which had been used in our
25 previous publications [33,34]. For the synthesis of bismuth oxybromide photocatalysts,

1 Bi(NO₃)₃·5H₂O (1 mmol; Sigma-Aldrich, Co., 95%) and KBr (1 mmol; RCI Labscan Limited,
2 99.9%) were separately dissolved in 20.0 mL of ethylene glycol (Carlo Erba Reagents, 99.5%)
3 and then mixed for 30 min. Next, the mixed solution was irradiated using 2.45 GHz microwave
4 radiation operated at 600 W for 8, 60, and 110 cycles in order to obtain BiOBr, BiOBr/Bi₄O₅Br₂
5 binary heterostructure, and Bi₄O₅Br₂, respectively. Each cycle was performed at 30-s on at
6 every 90-s interval. The obtained powder was filtered, washed with deionized water, and dried
7 at 70 °C overnight.

8 For the preparation of ternary FeVO₄/Bi₄O₅Br₂/BiOBr composites, a certain amount of
9 FeVO₄ powder was dispersed in 40.0 mL of methanol (RCI Labscan Limited, 99.9%) and kept
10 under sonication for 30 min. Then, a certain amount of the BiOBr/Bi₄O₅Br₂ powder was added
11 into the suspension and was constantly stirred at room temperature for 24 h. Finally, the
12 obtained powder was dried at 70 °C and heated at 200 °C for 30 min. The
13 FeVO₄/Bi₄O₅Br₂/BiOBr composites were then denoted as xFV/Br where x represents the
14 weight percentages of FeVO₄ (0.5, 1, 3, 6.25 and 12.5%wt) and Br represents the
15 BiOBr/Bi₄O₅Br₂ host material. For the purposes of comparison, a physical mixing sample,
16 denoted as PM, was also prepared by grinding the FeVO₄ powder with the BiOBr/Bi₄O₅Br₂
17 powder.

18

19 **2.2. Characterizations**

20 X-ray diffraction spectroscopy (XRD, Rigaku Smartlab) was used to investigate the
21 purity, structure and crystallinity of the powders. Chemical compositions and oxidation states
22 of the constituent elements were determined by X-ray photoelectron spectroscopy (XPS, AXIS
23 Ultra DLD, Kratos Analytical Ltd.) using Al K α X-ray source at 1.4 keV radiation. XPS spectra
24 were corrected by referencing the binding energy of an adventitious carbon (C 1s) peak at 284.6
25 eV. Morphology, microstructure and the elemental composition of the samples were

1 investigated with the use of a field emission scanning electron microscope (FESEM, JEOL
2 JSM-6335F) and a transmission electron microscope (TEM, JEOL JEM-2010). These were
3 used in conjunction energy dispersive X-ray spectrometry (EDS). Optical properties were
4 examined by UV-vis diffuse reflectance spectroscopy (UV-vis DRS, UV-1800 Shimadzu) that
5 was equipped with a specular reflectance measurement attachment. The results were referenced
6 against BaSO₄. Photoluminescence (PL) spectra were recorded using a photoluminescence
7 spectrometer (PL, Avantes Avaspec-2048TEC-USB2) with an excitation wavelength of 345
8 nm. Zeta potential of the ternary composite was measured on a Zetasizer (Malvern Nano ZS).
9 The Brunauer-Emmett-Teller N₂ gas adsorption (BET, Quantachrome, Quadrasorb-*evo*) and
10 the Barret–Joyner–Halenda (BJH) methods were used to determine the surface area, pore
11 radius, and total pore volume of the samples. Inductively coupled plasma-optical emission
12 spectroscopy (ICP-OES; Perkin Elmer 4300 DV) was used to determine Fe and V ions leaching
13 in the supernatant solution sample.

14

15 **2.3. Photocatalytic experiments**

16 To investigate the optimum content of FeVO₄ in the ternary composite, the synthesized
17 xFV/Br sample (100 mg) was dispersed in aqueous solutions (200.0 mL) of organic dye
18 (methylene blue; MB and rhodamine B; RhB, 10 ppm) and a colorless organic compound
19 (salicylic acid; SA, 10 ppm). The MB, RhB and SA compounds with a purity of 99.0% were
20 purchased from Fluka, Riedel-de Haën and Sigma Aldrich, respectively. Prior to employing
21 light irradiation, the suspension was stirred in the dark for 30 min to reach an adsorption-
22 desorption equilibrium. The suspension was exposed to visible light generated from a 50 W
23 white light-emitting diode lamp (LED, YNL Model COB LED CHIP). At each given time
24 interval, the suspension was taken out and separated by centrifugation. The remaining
25 concentration of the organic compound was analyzed using a UV-vis spectrophotometer (UV-

1 vis, UV-1800 Shimadzu) by measuring the absorption intensity at its maximum absorption
2 wavelength ($\lambda_{\max} = 664, 554$ and 294 nm for MB, RhB and SA, respectively). A control
3 experiment was also carried out without adding the photocatalyst. The photodegradation
4 efficiency (%DE) was calculated using the following equation;

$$5 \quad \%DE = \frac{C_0 - C}{C_0} \times 100$$

6 where C_0 and C represent the concentrations of the target pollutants when the adsorption-
7 desorption equilibrium was achieved, and after being exposed to the light irradiation,
8 respectively. The photocatalytic reaction kinetic was investigated using the pseudo-first order
9 kinetic model as follows;

$$10 \quad \ln \frac{C_0}{C} = k_{\text{app}} t$$

11 where k_{app} represents the apparent pseudo-first order rate constant (min^{-1}).

12 The ternary $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ composite with an optimum content of FeVO_4 was
13 applied for the determination of the photoreduction of Cr(VI) ion in the $\text{K}_2\text{Cr}_2\text{O}_7$ solution
14 (200.0 mL, 20 and 30 ppm; Sigma-Aldrich, 99.0%). The suspension was stirred in the dark (30
15 min) to make sure that adsorption-desorption equilibrium was established. The remaining
16 concentration of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution was monitored using the diphenylcarbazide (DPC)
17 method in which the absorption intensity of the Cr(VI)-DPC complex was measured at 540
18 nm. The photoreduction efficiency (%RE) and the k_{app} value were also calculated in the same
19 way by using the photodegradation efficiency calculation. All the photocatalytic data are based
20 on the average values of three parallel experiments.

21 In addition, this photocatalyst was also applied in a mixed solution of $\text{K}_2\text{Cr}_2\text{O}_7$ (30 ppm)
22 and RhB (5, 10, or 20 ppm) to a total volume of 200.0 mL. Before treating the suspension with
23 the DPC method, an absorbance of 554 nm was measured to monitor the photodegradation of
24 RhB. For the accurate quantification of Cr(VI), the interference caused by the absorption of

1 RhB was eliminated by subtracting the absorbance at 540 nm of the suspension containing
2 Cr(VI) and RhB (the suspension before DPC reagent was added (Sigma-Aldrich, >99.0%))
3 from the absorbance at 540 nm of the Cr(VI)-DPC complex. A series of experiments were also
4 conducted by varying photocatalyst dosages and adjusting pH values with 1 M HNO₃ (Sigma-
5 Aldrich, 70.0%) or 1 M NH₄OH (QRëC™, 25%), in order to optimize the operation parameters.

6 Trapping experiments were carried out using 1 mM of various scavengers including
7 ascorbic acid (ASC; Merck, 99.0%) [11], ethylenediaminetetraacetic acid disodium salt
8 (EDTA-2Na; Sigma-Aldrich, 99.0%) [11], isopropanol (QRëC™, 99.7%) [38] and potassium
9 dichromate (K₂Cr₂O₇) [39]) to trap superoxide radicals (O₂^{•-}), holes (h⁺), hydroxyl radicals
10 (HO[•]) and photoexcited electrons (e⁻), respectively. The nitrotetrazolium blue (NBT)
11 transformation method [40] and the terephthalic acid photoluminescence (TA-PL) probing
12 technique [41] were also used to further confirm the detection of O₂^{•-} and HO[•] radicals
13 generated during the photocatalytic reaction.

14 The silver (Ag) photo-deposition experiment was carried out to further confirm the
15 charge transfer pathway in the ternary FeVO₄/Bi₄O₅Br₂/BiOBr heterojunction. The procedure
16 of this experiment is explained as follows. First, the photocatalyst (20 mg) was dispersed in
17 AgNO₃ solution (1 mM, 100.0 mL; Loba Chemie, 99.9%) under visible light irradiation for
18 360 min. Then, the photocatalyst was collected after Ag was photo-deposited was collected. It
19 was then washed several times with deionized water, and dried. The depositing of Ag on the
20 surface of the ternary heterostructure was then investigated by TEM.

21

22 **2.4. Electrochemical analyses**

23 All electrochemical measurements were carried out in a standard three electrode system
24 on a Metrohm Autolab Potentiostat/galvanostat (PGSTAT128N, Metrohm Siam Ltd.). The
25 measurement process utilized a working electrode as a photocatalyst coated on a fluorine-

1 doped tin oxide (FTO) coated sheet of glass, a counter electrode as a platinum (Pt) wire, a
2 reference electrode as Ag/AgCl (3.0 M KCl), and an electrolyte as 0.5 M Na₂SO₄ (pH ~ 6).
3 The electrochemical impedance spectra (EIS) were recorded under an alternating current (AC)
4 voltage at a bias potential of 1.5 V (vs. Ag/AgCl) with an amplitude of 0.05 V and a frequency
5 range of 0.01 to 10⁵ Hz. Mott-Schottky measurements were performed at a fixed frequency of
6 10 Hz and an AC amplitude of 10 mV. The transient photocurrent responses were recorded at
7 a fixed applied potential of 1.0 V (vs. Ag/AgCl) under visible light irradiation generated from
8 two 50 W LED lamps. To convert the Ag/AgCl (3.0 M KCl) scale to a normal hydrogen
9 electrode (NHE) scale (pH = 0), the following equation was applied;

$$10 \quad E_{\text{NHE}} = E_{\text{Ag/AgCl}} + E^{\circ}_{\text{Ag/AgCl (3.0 M KCl)}} = E_{\text{Ag/AgCl}} + 0.210 \text{ V (25 }^{\circ}\text{C)}.$$

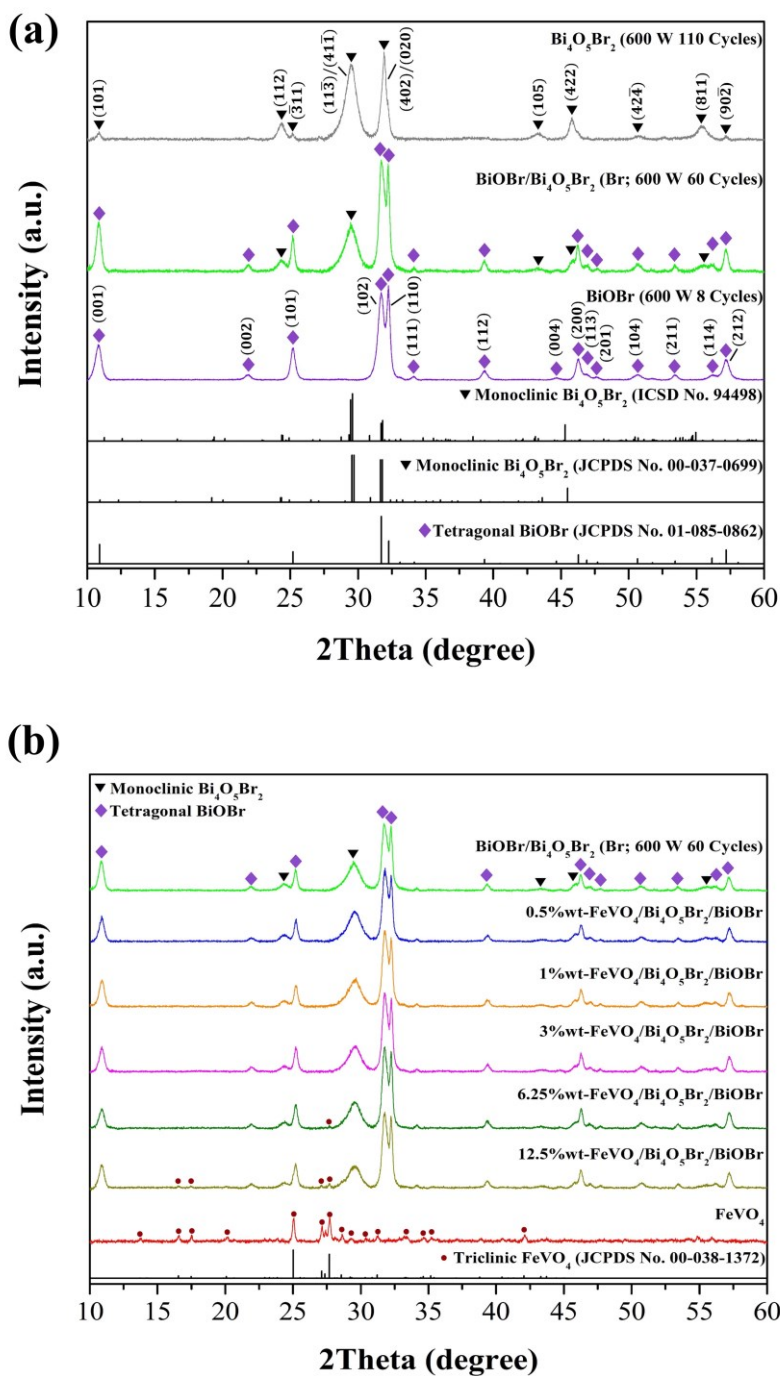
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12 **3. Results and Discussion**

13 **3.1. Structural characterization**

14 XRD patterns of the synthesized BiOBr, Bi₄O₅Br₂, and BiOBr/Bi₄O₅Br₂ powders are
15 illustrated in **Fig. 1(a)**. All detectable diffraction peaks of the BiOBr powder matched well with
16 the tetragonal phase of BiOBr (Joint Committee of Powder Diffraction Standards (JCPDS)
17 number 01-085-0862). The diffraction peaks of the Bi₄O₅Br₂ powder corresponded to the
18 monoclinic phase of Bi₄O₅Br₂ (JCPDS number 00-037-0699 and Inorganic Crystal Structure
19 Database (ICSD) number 94498). The XRD pattern of the binary BiOBr/Bi₄O₅Br₂ composite
20 was composed of the characteristic peaks of both tetragonal BiOBr and monoclinic Bi₄O₅Br₂
21 phases. The formation of bismuth-rich Bi₄O₅Br₂ could be a consequence of the raised
22 temperature in the reaction system that occurred during the microwave heating process. At a
23 given microwave power, increasing microwave irradiation cycles to 60 and 110 cycles resulted
24 in an increase in the reaction temperature [42], which could then enable the loss of bromide ion
25 in the BiOBr crystal.

1 XRD patterns of the ternary FeVO₄/Bi₄O₅Br₂/BiOBr composites in comparison with
2 FeVO₄ and binary BiOBr/Bi₄O₅Br₂ composite are presented in **Fig. 1(b)**. The diffraction
3 pattern of FeVO₄ is in good accordance with the triclinic FeVO₄ structure (JCPDS number 00-
4 038-1372). No impurity peaks were observed suggesting that BiOBr, Bi₄O₅Br₂,
5 BiOBr/Bi₄O₅Br₂ and FeVO₄ were successfully synthesized through the cyclic microwave
6 heating route. In cases of the ternary FeVO₄/Bi₄O₅Br₂/BiOBr composites with 0.5, 1 and 3%wt
7 of FeVO₄, the XRD patterns exhibited only the characteristic peaks of BiOBr and Bi₄O₅Br₂
8 owing to much lower contents of FeVO₄ as well as a lower diffraction intensity when compared
9 with those of BiOBr and Bi₄O₅Br₂. Upon adding more FeVO₄ (6.25 and 12.5%wt), the major
10 diffraction peaks of FeVO₄ at 27.1° and 27.7° indexing to (01 $\bar{2}$) and ($\bar{2}$ 20) planes became
11 detectable.

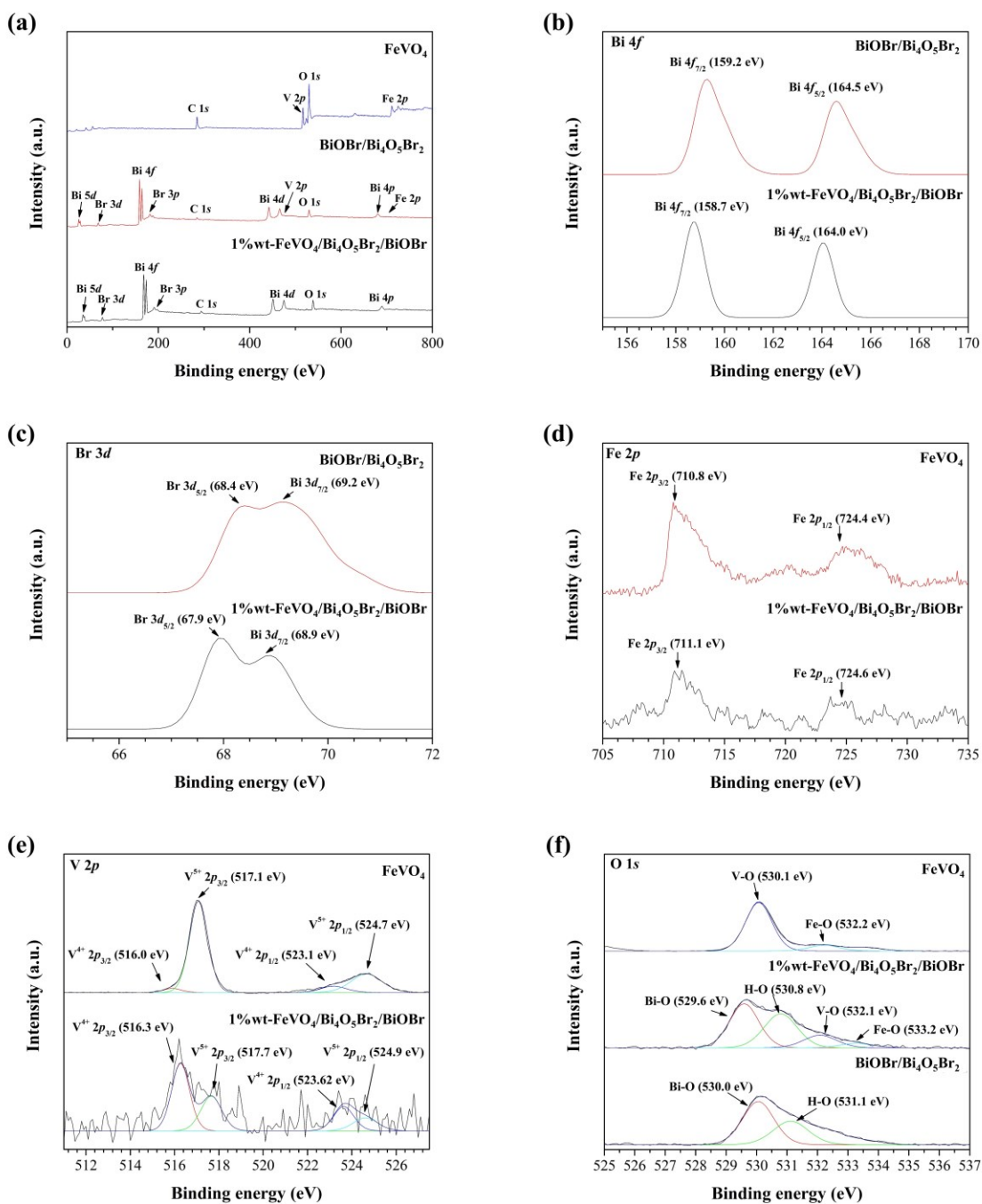


1
 2 **Fig. 1.** XRD patterns of (a) BiOBr, Bi₄O₅Br₂, and BiOBr/Bi₄O₅Br₂ powders synthesized using
 3 different microwave irradiation cycles, and (b) FeVO₄, BiOBr/Bi₄O₅Br₂, and
 4 FeVO₄/Bi₄O₅Br₂/BiOBr nanocomposites with different loading amounts of FeVO₄.

5
 6 XPS spectra of FeVO₄, BiOBr/Bi₄O₅Br₂, and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr are shown
 7 in **Fig. 2.** The survey spectrum of FeVO₄/Bi₄O₅Br₂/BiOBr (**Fig. 2(a)**) indicated that the peaks

1 belonging to Bi, O, Br, Fe, and V elements were observed. **Fig. 2(b)** shows the high-resolution
2 spectrum of Bi 4*f* of the binary BiOBr/Bi₄O₅Br₂ composite. The binding energies of 159.2 and
3 164.5 eV were indexed to Bi 4*f*_{7/2} and Bi 4*f*_{5/2} peaks, respectively [20,23]. After being combined
4 with FeVO₄, these doublet peaks shifted to the lower values of 158.7 and 164.0 eV,
5 respectively. These Bi 4*f* signals further confirm that the oxidation state of the Bi element was
6 +3 [20,23]. **Fig. 2(c)** shows Br 3*d* of BiOBr/Bi₄O₅Br₂ and FeVO₄/Bi₄O₅Br₂/BiOBr. For the
7 binary BiOBr/Bi₄O₅Br₂ composite, two peaks at 68.4 and 69.2 eV corresponded to Br 3*d*_{5/2} and
8 Br 3*d*_{3/2}, respectively. For the ternary FeVO₄/Bi₄O₅Br₂/BiOBr composite, these Br 3*d* peaks
9 shifted to the lower binding energies of 67.9 and 68.9 eV. The presence of these Br 3*d* peaks
10 signify that the Br element adopted the -1 oxidation state [20,23]. The high-resolution
11 spectrum for Fe 2*p* in the ternary composite (**Fig. 2(d)**) revealed two main peaks of Fe 2*p*_{3/2}
12 and Fe 2*p*_{1/2} (711.1 and 724.60 eV, respectively) which were located at higher binding energies
13 than those of FeVO₄ (710.8 and 724.4 eV, respectively) [43–45]. The doublet signals of Fe 2*p*
14 confirm the +3 oxidation state of Fe [43]. As is shown in **Fig. 2(e)**, the splitting of V 2*p* peaks
15 in FeVO₄ was observed at binding energies of 517.7 and 524.7 eV, which were then assigned
16 to the V 2*p*_{3/2} and V 2*p*_{1/2} states of the V⁵⁺ species [43,44]. However, two sub-peaks that
17 corresponded to the V 2*p*_{3/2} and V 2*p*_{1/2} states of V with +4 oxidation state were observed at
18 binding energies of 516.0 and 523.1 eV [46], wherein, the V⁴⁺ specie arose from certain oxygen
19 vacancies [45]. These V 2*p* peaks shifted to the lower binding energies after FeVO₄ was
20 introduced into the binary BiOBr/Bi₄O₅Br₂ heterostructure. **Fig. 2(f)** reveals that there were
21 four O 1*s* peaks located at 529.6, 530.8, 532.1, and 533.2 eV implying four types of oxygen
22 species exist in the ternary composite. Furthermore, these peaks were attributed to the chemical
23 bonding of Bi–O [23], H–O in the adsorbed water on the material surface [45], V–O [45], and
24 Fe–O [45], respectively. As can be seen from the high-resolution XPS spectrum of
25 FeVO₄/Bi₄O₅Br₂/BiOBr in comparison to FeVO₄ and BiOBr/Bi₄O₅Br₂, there are noticeable

1 shifts in the binding energies of the XPS peaks. Changes in the binding energy values resulted
 2 from the formation of a ternary heterostructure system suggesting the presence of a strong
 3 chemical interaction between these materials. This interaction could be beneficial for charge
 4 transfer between these materials and reduce the recombination of the photoactivated charge
 5 carriers [24,47,48].



6

1 **Fig. 2.** XPS spectra of FeVO₄, BiOBr/Bi₄O₅Br₂ and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr: (a) survey
2 spectra and (b-f) high-resolution XPS spectra of Bi 4*f*, Br 2*p*, Fe 2*p*, V 2*p* and O 1*s*,
3 respectively.

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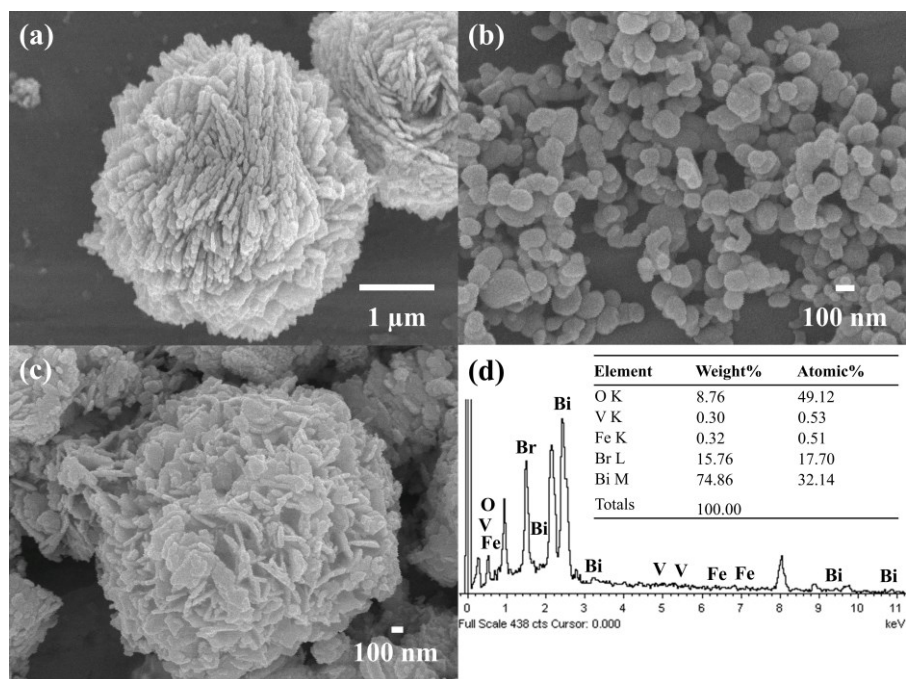
5 **3.2. Morphological investigation**

6 FESEM images of the BiOBr, Bi₄O₅Br₂, FeVO₄, BiOBr/Bi₄O₅Br₂, and 1%wt-
7 FeVO₄/Bi₄O₅Br₂/BiOBr powders are shown in **Fig. S1** and **Fig. 3(a)-(c)**. FESEM (**Fig. S1(a)**)
8 and TEM (**Fig. S2(a)**) images of BiOBr reveal a flower-like microsphere with an average
9 diameter of 3.9 μm that is built up of ellipsoid-like nanoparticles with an average vertical height
10 of 247 nm and an average width of 57 nm. EDS spectrum of BiOBr (**Fig. S1(c)**) presents the
11 existence of Bi, O and Br elements with an atomic ratio of 1.10:1.01:1.00, respectively, which
12 agrees with the stoichiometry of BiOBr. The FESEM (**Fig. S1(b)**) and TEM (**Fig. S2(b)**)
13 images of Bi₄O₅Br₂ show a flower-like micro-spherical structure that is comprised of densely
14 packed thin nanosheets. EDS spectrum of Bi₄O₅Br₂ (**Fig. S1(d)**) reveals the spectra of Bi, O
15 and Br elements with a molar ratio of Bi:Br at 2.03 confirming the formation of a bismuth-rich
16 compound. HRTEM images of BiOBr (inset of **Fig. S2(a)**) and Bi₄O₅Br₂ (inset of **Fig. S2(b)**)
17 reveal the crystal lattice fringes with *d*-spacings of 0.197 and 0.198 nm, which corresponded
18 to the (200) plane of tetragonal BiOBr and (422) plane of monoclinic Bi₄O₅Br₂, respectively.
19 These findings confirm the crystalline structure of both materials.

20 For the binary BiOBr/Bi₄O₅Br₂ composite, flower-like microspheres with an average
21 diameter of 3.8 μm were still observed (**Fig. 3(a)** and **Fig. S2(c)**). Morphologically, the flower-
22 like micro-spherical structure is likely to be in a transitional phase between BiOBr and
23 Bi₄O₅Br₂ as has been suggested by its moderately packed nanosheets. The combination of
24 BiOBr and Bi₄O₅Br₂ in the binary composite was confirmed by HRTEM (**Fig. S2(d)**). The
25 HRTEM image shows a distribution of nanoparticles with an average diameter of 13 nm on the

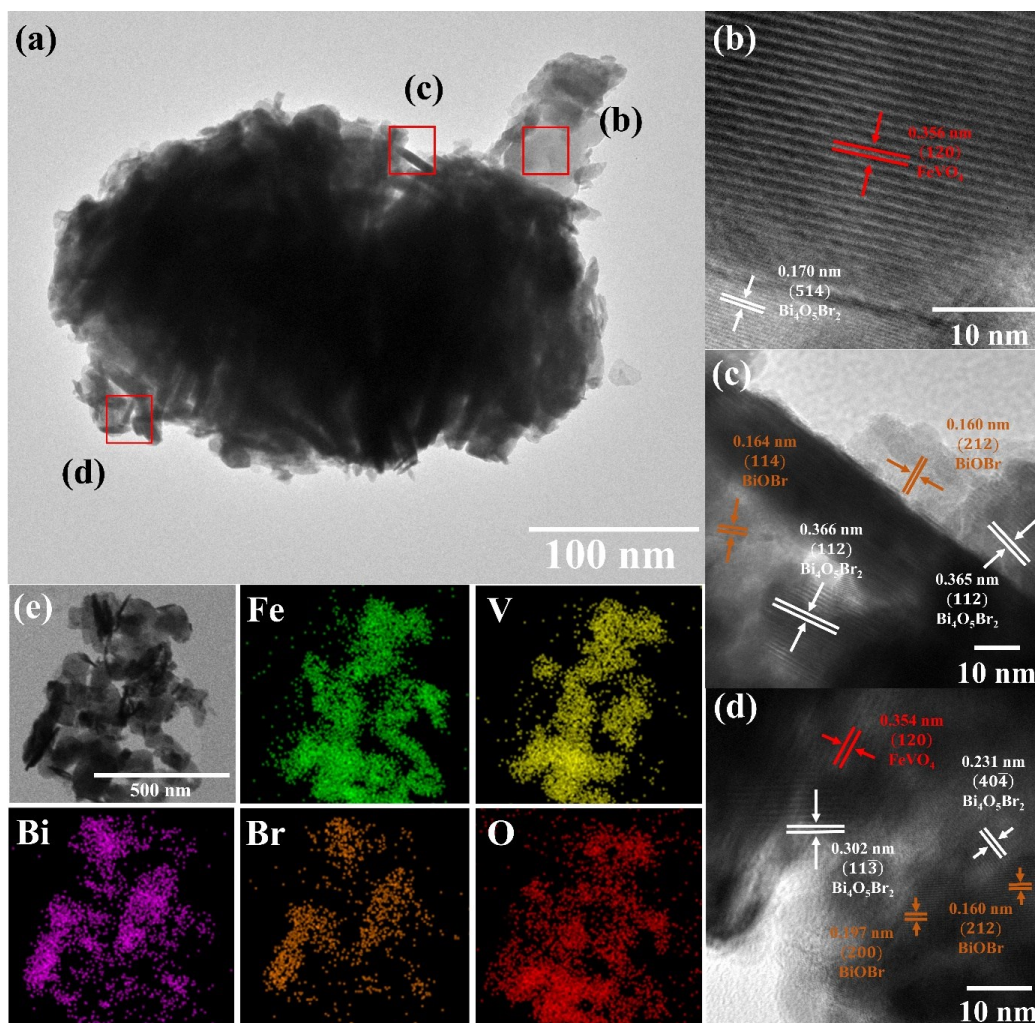
1 nanosheets. The nanoparticles revealed two lattice fringes of 0.279 and 0.359 nm that were
2 consistent with the (110) and (101) planes of BiOBr. The nanoplate showed lattice intervals
3 of 0.299 and 0.300 nm which corresponded to the (41 $\bar{1}$) plane of Bi₄O₅Br₂. For FeVO₄, a large
4 number of nanoparticles with an average diameter of about 100 nm were observed (**Fig. 3(b)**).
5 FESEM (**Fig. 3(c)**) and TEM (**Fig. 4(a)**) images of the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr
6 composite revealed that the FeVO₄ nanoparticles were anchored on the surface of the flower-
7 like BiOBr/Bi₄O₅Br₂ microspheres. The corresponding EDS spectrum demonstrated the
8 compositions of Fe, V, O, Bi, and Br elements (**Fig. 3(d)**). The actual weight percentages of
9 FeVO₄ and BiOBr/Bi₄O₅Br₂ in the composite were calculated to be 0.98 and 98.91,
10 respectively, which were close to those of the fabrication contents.

11 HRTEM image of the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr composite shown in **Fig.**
12 **4(b)** reveals lattice fringes with *d*-spacings of 0.356 and 0.170 nm which corresponded to the
13 (120) and (514) planes of FeVO₄ and Bi₄O₅Br₂, respectively. HRTEM image presented in
14 **Fig. 4(c)** reveals two sets of lattice fringes, for which the *d*-spacings of 0.164 and 0.160 nm
15 could be assigned to the (114) and (212) planes of BiOBr, while the *d*-spacings of 0.365 and
16 0.366 nm belonged to the (112) plane of monoclinic Bi₄O₅Br₂. Additionally, HRTEM image
17 presented in **Fig. 4(d)** reveals the lattice fringes of the FeVO₄, Bi₄O₅Br₂ and BiOBr phases in
18 the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr composite indicating the formation of intimate
19 contacts between these materials. Moreover, scanning TEM-EDS mapping on the ternary
20 composite was recorded to obtain more information with regard to elemental distribution. As
21 is shown in **Fig. 4(e)**, the ternary composite composed of Fe, V, Bi, Br, and O elements that
22 are homogeneously distributed in the ternary composite. These results clearly indicate the
23 coexistence of FeVO₄ and BiOBr/Bi₄O₅Br₂, as well as an intimate contact between the
24 component materials, confirming the presence of a ternary FeVO₄/Bi₄O₅Br₂/BiOBr
25 heterojunction.



1

2 **Fig. 3.** FESEM images of (a) BiOBr/Bi₄O₅Br₂, (b) FeVO₄, and (c) 1%wt-
 3 FeVO₄/Bi₄O₅Br₂/BiOBr. (d) EDS spectrum with elemental compositions of 1%wt-
 4 FeVO₄/Bi₄O₅Br₂/BiOBr.



1
 2 **Fig. 4.** (a) TEM image of the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr composite and (b-d)
 3 HRTEM images of FeVO₄ and BiOBr/Bi₄O₅Br₂ in the ternary composite. (e) Scanning TEM-
 4 EDS mapping of 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr.

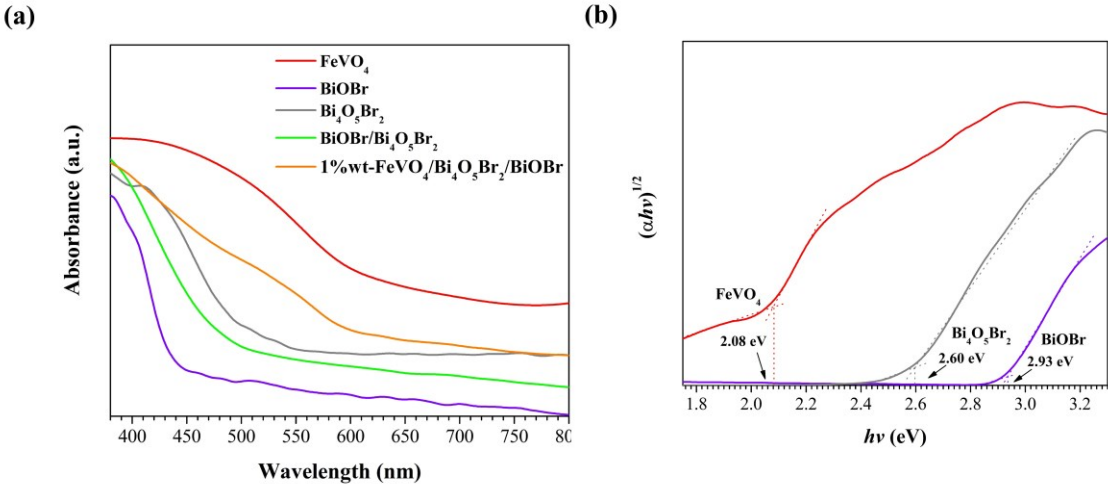
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 6 **3.3. Optical properties**

7 Optical properties of FeVO₄, BiOBr, Bi₄O₅Br₂, BiOBr/Bi₄O₅Br₂, and 1%wt-
 8 FeVO₄/Bi₄O₅Br₂/BiOBr were investigated by UV-vis DRS analysis. The binary
 9 BiOBr/Bi₄O₅Br₂ heterojunction exhibited an absorption edge at around 480 nm (**Fig. 5(a)**),
 10 which was in between those of BiOBr (440 nm) and Bi₄O₅Br₂ (500 nm). The coupling of
 11 FeVO₄ with the binary BiOBr/Bi₄O₅Br₂ heterostructure relatively enhanced the absorption
 12 ability in the visible light region. In addition, an absorption edge of 1%wt-

1 FeVO₄/Bi₄O₅Br₂/BiOBr was extended to a higher wavelength when compared to those of
 2 BiOBr, Bi₄O₅Br₂, and BiOBr/Bi₄O₅Br₂. The improved absorption capacity in the visible light
 3 region, after compositing FeVO₄ with BiOBr/Bi₄O₅Br₂, could improve the generation of charge
 4 carriers and consequently enhance photocatalytic activity. Moreover, the absorption spectrum
 5 of the ternary composite exhibited two absorption slopes at around 480 and 595 nm, which
 6 corresponded well with the absorption edges of the BiOBr/Bi₄O₅Br₂ and FeVO₄ parent
 7 materials. This indicated the coexistence of FeVO₄ and BiOBr/Bi₄O₅Br₂. The band gap energy
 8 (E_g) was determined from the Tauc equation [49] as follows;

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

9
 10 where α , h , ν , A , and E_g represent the absorption coefficient, Plank's constant, light frequency,
 11 constant, and the band gap energy of the materials, respectively. The n values depend upon
 12 characteristics of the optical transition of the semiconductor. For FeVO₄, BiOBr and Bi₄O₅Br₂,
 13 the n values were recorded at 4 for their indirect transition [20,50]. Thus, the corresponding E_g
 14 values of FeVO₄, BiOBr, and Bi₄O₅Br₂ were calculated to be 2.08, 2.93, and 2.60 eV,
 15 respectively.



16
 17 **Fig. 5.** (a) UV-vis DRS spectra of FeVO₄, BiOBr, Bi₄O₅Br₂, BiOBr/Bi₄O₅Br₂, and 1%wt-
 18 FeVO₄/Bi₄O₅Br₂/BiOBr. (b) Corresponding Tauc' plots of the single materials.

19

1 3.4. Photocatalytic degradation of organic pollutants

2 3.4.1. Effect of $FeVO_4$ content in ternary composites

3 Photocatalytic activities of the samples were evaluated by degrading RhB and MB dyes,
4 as well as colorless SA under visible light irradiation. For the photolysis tests (**Fig. S3**), the
5 self-photodegradation of these organic compounds was negligible. **Fig. S3(a)** shows that
6 BiOBr/ $Bi_4O_5Br_2$ completely degraded RhB within 180 min, while BiOBr and $Bi_4O_5Br_2$
7 degraded 63.5% and 90.3% of RhB, respectively. Similarly, BiOBr/ $Bi_4O_5Br_2$ exhibited higher
8 %DE (66.9%) than did BiOBr (40.9%) and $Bi_4O_5Br_2$ (54.7%) towards MB within 360 min
9 (**Fig. S3(b)**). The BiOBr and $Bi_4O_5Br_2$ photocatalysts exhibited lower degrees of SA
10 degradation with %DE of 22.7% and 30.5% relative to BiOBr/ $Bi_4O_5Br_2$ (45.6%). The k_{app}
11 values for the photodegradation of organic compounds by BiOBr/ $Bi_4O_5Br_2$ were about 2.2 and
12 1.5 times higher than those of BiOBr and $Bi_4O_5Br_2$, respectively (**Fig. S3(d)-(f)**). These results
13 imply the successfulness in the fabrication of binary BiOBr/ $Bi_4O_5Br_2$ heterostructure which
14 provided higher photocatalytic efficiencies than both BiOBr and $Bi_4O_5Br_2$.

15 **Fig. S4(a)-(c)** present the photocatalytic activities of $FeVO_4$, BiOBr/ $Bi_4O_5Br_2$, and
16 $FeVO_4/Bi_4O_5Br_2/BiOBr$ with different $FeVO_4$ contents for the degradation of RhB, MB, and
17 SA. The corresponding k_{app} values are presented in **Fig. S4(d)-(f)** and **Fig. S5**. As is shown in
18 **Fig. S4(a)**, there was almost no photodegradation of RhB in the presence of $FeVO_4$. On the
19 other hand, the ternary $FeVO_4/Bi_4O_5Br_2/BiOBr$ heterojunctions exhibited %DE of 93.2, 99.3,
20 88.9, 80.8 and 65.3 within 120 min with the $FeVO_4$ contents of 0.5, 1, 3, 6.25 and 12.5%wt,
21 respectively. It was found that 1%wt- $FeVO_4/Bi_4O_5Br_2/BiOBr$ exhibited the highest
22 photocatalytic activity with a k_{app} value of $3.44 \times 10^{-2} \text{ min}^{-1}$ (**Fig. S4(d)**). Additionally, this
23 ternary heterojunction exhibited the highest %DE (84.2% after 360 min) with a k_{app} value of
24 $0.53 \times 10^{-2} \text{ min}^{-1}$ for the MB photodegradation among the other photocatalysts (**Figs. S4(b)** and
25 (e)). Moreover, it exhibited improved photocatalytic efficiency and kinetic rate than those of

1 FeVO₄ and BiOBr/Bi₄O₅Br₂, which was attributed to increases in visible-light response and
2 more efficient charge segregation and transportation at the heterostructure interfaces. In
3 comparisons with our previous results [33,34], the k_{app} value for the RhB degradation by the
4 ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst ($3.44 \times 10^{-2} \text{ min}^{-1}$) was around 2.6 and 1.6
5 times higher than for the binary 6.25%wt-FeVO₄/Bi₇O₉I₃ ($1.30 \times 10^{-2} \text{ min}^{-1}$) and 6.25%wt-
6 FeVO₄/BiOCl ($2.15 \times 10^{-2} \text{ min}^{-1}$) photocatalysts, respectively. Moreover, in this research, the
7 photo-efficacy of FeVO₄/Bi₄O₅Br₂/BiOBr was maximized after only small amounts of FeVO₄
8 (1%wt) was introduced into the host materials. These findings suggest that the ternary
9 heterojunction could exhibit a significant performance by synergistic effect of the
10 multicomponent, which then gave rise to the extension of the light absorption range and the
11 efficient generation of the charge carriers.

12 We also tested the photocatalytic degradation of these dyes by using a commercial TiO₂
13 P25 photocatalyst (Degussa P25) under visible light irradiation. It is well known that P25
14 cannot be activated by visible light; however, in this work, 22.4% of RhB and 31.0% of MB
15 were degraded in the presence of P25 within 120 min and 360 min of visible light irradiation,
16 respectively. The degradation of these dyes in the presence of P25 could be attributed to the
17 photosensitization effect of these dyes. For the photocatalytic degradation of dye, an indirect
18 dye-sensitization process usually takes place in which the extra excited electrons from the
19 lowest unoccupied molecular orbital (LUMO) of the dye molecules are injected into the
20 conduction band of the semiconductor [51–53], facilitating the visible light sensitivity of P25
21 in the degradation of RhB and MB. Notably, RhB was significantly degraded by the ternary
22 heterojunctions when compared to the degradation of MB. This could be attributed to more
23 negative LUMO of RhB over that of MB which favored the transfer of the excited electrons
24 from the LUMO of RhB molecules to the conduction band of the materials [54,55].

1 To further clarify the contribution of the dye-sensitization process, the
2 photodegradation of colorless SA was also performed. **Figs. S4(c)** and (f) illustrate that P25
3 exhibited negligible photo-activity confirming that there was no occurrence of
4 photosensitization process in the photocatalysis of colorless SA [56]. Introducing 1%wt of
5 FeVO₄ into the binary BiOBr/Bi₄O₅Br₂ heterojunction could maximize the photocatalytic
6 activity of the ternary FeVO₄/Bi₄O₅Br₂/BiOBr heterojunction, where 12.5, 45.6 and 57.2% of
7 SA were degraded by FeVO₄, BiOBr/Bi₄O₅Br₂ and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr,
8 respectively.

9 It should be noted that the loading amount of FeVO₄ strongly affected the photocatalytic
10 activity. Further increases in FeVO₄ content led to a decrease in both %DE and k_{app} . This could
11 be ascribed to an excess amount of FeVO₄ nanoparticles, which may induce agglomeration and
12 cover the active surface of the flower-like BiOBr/Bi₄O₅Br₂ microstructures. These phenomena
13 resulted in the poor utilization of light, and thus a reduction in a generation of electron-hole
14 pairs [47,57,58]. The photocatalytic activity of the physical mixture of 1%wt of FeVO₄ and
15 BiOBr/Bi₄O₅Br₂ (denoted as PM) was also tested. The results indicate that it provided lower
16 %DE for RhB (91.9%,120 min), MB (52.3%, 360 min), and SA (26.3%, 360 min) than those
17 of BiOBr/Bi₄O₅Br₂ and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr. The results further indicate that the
18 formation of the ternary heterojunction by coupling FeVO₄ with binary BiOBr/Bi₄O₅Br₂
19 heterojunction could be responsible for the enhanced photocatalytic activity rather than the
20 physically mixing of these materials.

21 As reusability is an important factor for practical usages, RhB photodegradation by the
22 binary and ternary heterojunction photocatalysts were carried out in three-successive runs. As
23 is shown in **Fig. S6**, 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr exhibited no significant changes in the
24 photodegradation of RhB after three recycle reactions. However, a loss in photocatalytic
25 efficiency of RhB was detected for the binary BiOBr/Bi₄O₅Br₂ photocatalyst. This could have

1 arisen from the unremovable adsorbed RhB molecules on the photocatalyst's surface, lowering
2 the surface-active site of BiOBr/Bi₄O₅Br₂. Furthermore, it could have occurred because of the
3 reduction of Bi³⁺ by photoactivated electrons since the reduction potential of Bi(III)/Bi (0.308
4 V vs. NHE) is more positive than either CB of BiOBr (-0.032 V vs. NHE) or Bi₄O₅Br₂ (-0.15
5 V vs. NHE) [59].

6

7 *3.4.2. Effects of photocatalytic conditions on RhB degradation*

8 A series of photocatalytic experiments were carried out to evaluate the effects of RhB
9 initial concentration and photocatalyst dosage on RhB degradation, the results of which are
10 shown in **Figs. S7** and **S8**. At constant amounts of the photocatalyst (100 mg of 1%wt-
11 FeVO₄/Bi₄O₅Br₂/BiOBr), an increase in RhB concentration from 10 to 40 ppm led to a decrease
12 in the photocatalytic efficiency and degradation rate (**Fig. S7(a)** and (c)). These results may
13 have occurred because the reaction solution became more intensely colored as the initial dye
14 concentration was increased, shielding the light penetration to the photocatalyst's surface
15 [33,57]. Consequently, the generation of electron-hole pairs was decreased, limiting the
16 production of the active species that are responsible for photodegradation.

17 In the experiments, the photocatalyst dosage was varied from 50 to 250 mg and was
18 administered along with an RhB initial concentration of 10 ppm. RhB degradation increased
19 along with increases in the photocatalyst dosage at up to 200 mg (**Figs. S7(b)** and (d)). The
20 increase in RhB degradation could have been due to an increase in the available active sites on
21 the photocatalyst's surface. However, RhB degradation declined when 250 mg of photocatalyst
22 was used. This occurred because excessive amounts of the photocatalyst suspended in the
23 solution scattered the incident light, while the light penetration through the solution was
24 diminished. Consequently, there was a reduction in the number of active species produced
25 during the photocatalytic reaction [33,57].

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3.5. Photocatalytic Cr(VI) reduction and optimization of photocatalytic conditions

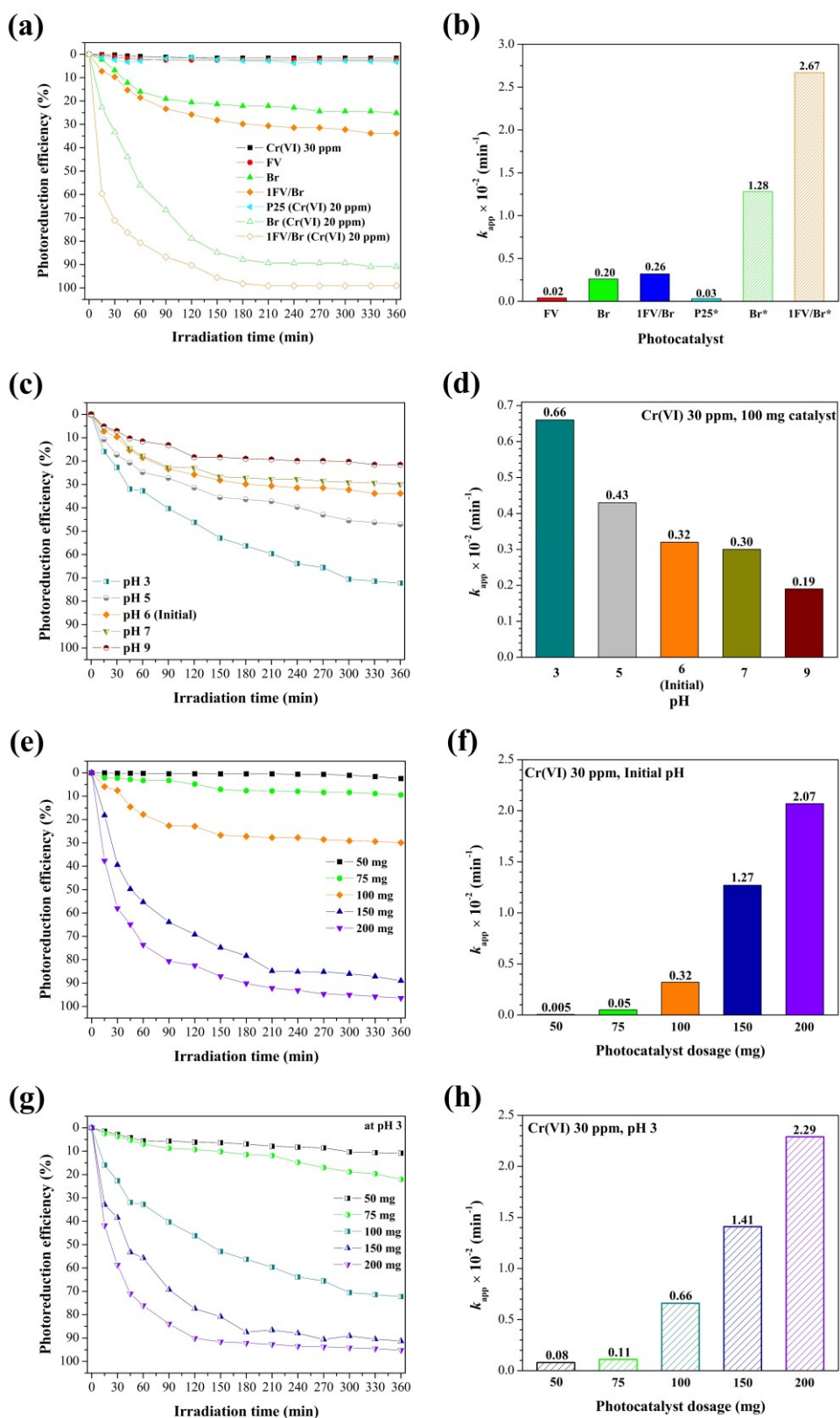
To study the feasibility of utilizing the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr heterojunction for photocatalytic reduction, 20 ppm of the Cr(VI) aqueous solution was used as a studied target. As is shown in **Fig. 6(a)**, both P25 and FeVO₄ exhibited almost no photocatalytic Cr(VI) photoreduction, whereas BiOBr/Bi₄O₅Br₂ reduced approximately 90% of Cr(VI). The 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst exhibited the highest photoreduction efficiency (%RE = 99.1) and the photoreduction rate was 2 times faster than that of BiOBr/Bi₄O₅Br₂. In addition, the kinetic rates (**Fig. 6(b)** and **Fig. S9(a)**) are in a good agreement with the photoreduction efficiencies.

The photoreduction efficiency of the Cr(VI) solution with a higher initial concentration (30 ppm) by 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr was further tested. As is shown in **Fig. 6(a)**, although 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr was capable of degrading only 33.9% of Cr(VI), it still provided higher efficiency than those of FeVO₄ (%RE = 2.5) and BiOBr/Bi₄O₅Br₂ (%RE = 25.2). The initial pH of the 30 ppm Cr(VI) solution was then adjusted from 6 (initial pH) to 3, 5, 7 and 9 in attempts to improve photoreduction activity, the results for which are shown in **Fig. 6(c)** and **(d)**. Photoreduction was significantly improved with %RE of 72.3 and 47.1 at pH values of 3 and 5, and k_{app} of 0.66×10^{-2} and $0.43 \times 10^{-2} \text{ min}^{-1}$, respectively. On the basis of the thermodynamic aspect, Cr(VI) ions exist in different ionic forms under different pH conditions. Under acidic condition, Cr(VI) ions in the HCrO₄⁻ and Cr₂O₇²⁻ forms are the dominant species, while CrO₄²⁻ is a dominant species under neutral and basic conditions [60,61]. The reduction potentials of the HCrO₄⁻/Cr³⁺ couple (1.35 V vs. NHE) and the Cr₂O₇²⁻/Cr³⁺ couple (1.33 V vs. NHE) are more positive than that of the CrO₄²⁻/Cr(OH)₃ couple (-0.13 V vs. NHE) [62]. As a result, the reduction of Cr(VI) to Cr(III) ions in the acidic solution became easier than in the neutral and basic solutions. Additionally, in the basic solution, the Cr(OH)₃ produced from the

1 reduction of Cr(VI) in the CrO_4^{2-} form could adsorb and block the active sites of the
2 photocatalyst, decreasing the photocatalytic activity [63,64].

3 Additionally, we also studied the effect of photocatalyst dosage on the Cr(VI)
4 photoreduction. The reaction was carried out by fixing the Cr(VI) concentration at 30 ppm
5 along with the initial pH value. **Fig. 6(e)** and (f) clearly show that an increase in the
6 photocatalyst dosage from 50 to 200 mg significantly improved the Cr(VI) photoreduction
7 efficiency and rate; %RE and k_{app} were distinctly enhanced to 96.0 and $2.07 \times 10^{-2} \text{ min}^{-1}$ when
8 using 200 mg of the photocatalyst. This outcome resulted by an increase in the active sites on
9 the photocatalyst's surface, wherein the generation of the active species involved in the
10 photocatalytic reaction increased. Notably, the effects of the solution's opacity and light
11 scattering occurred as a result of using large amounts of suspended photocatalyst powder on
12 the photocatalytic activity, which did not take place in the event of the Cr(VI) reduction. This
13 could have occurred because the color of the Cr(VI) solution was relatively transparent when
14 compared to that of the RhB solution.

15 Subsequently, we cross-studied the effects of the solution pH and photocatalyst dosage
16 in order to maximize the photocatalytic activity of the photocatalyst for a reduction of 30 ppm
17 Cr(VI). We investigated Cr(VI) reduction at the solution pH of 3 using different amounts of
18 the ternary 1%wt- $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ photocatalyst (50 to 200 mg). As is shown in **Fig.**
19 **6(g)**, by using 200 mg of the photocatalyst, %RE was around 96.2 which was nearly identical
20 to what we recorded when similar amounts of the photocatalyst were used without adjusting
21 pH (**Fig. 6(e)**). However, by considering the k_{app} values for these two conditions, Cr(VI)
22 photoreduction in the acidic environment ($k_{\text{app}} = 2.29 \times 10^{-2} \text{ min}^{-1}$) (**Fig. 6(h)**) was higher than
23 when the solution pH was not adjusted ($k_{\text{app}} = 2.07 \times 10^{-2} \text{ min}^{-1}$) (**Fig. 6(f)**). Therefore, under
24 the study conditions, it can be concluded that the photocatalytic Cr(VI) reduction activity could
25 be maximized by using 200 mg of the photocatalyst and decreasing the solution pH to 3.



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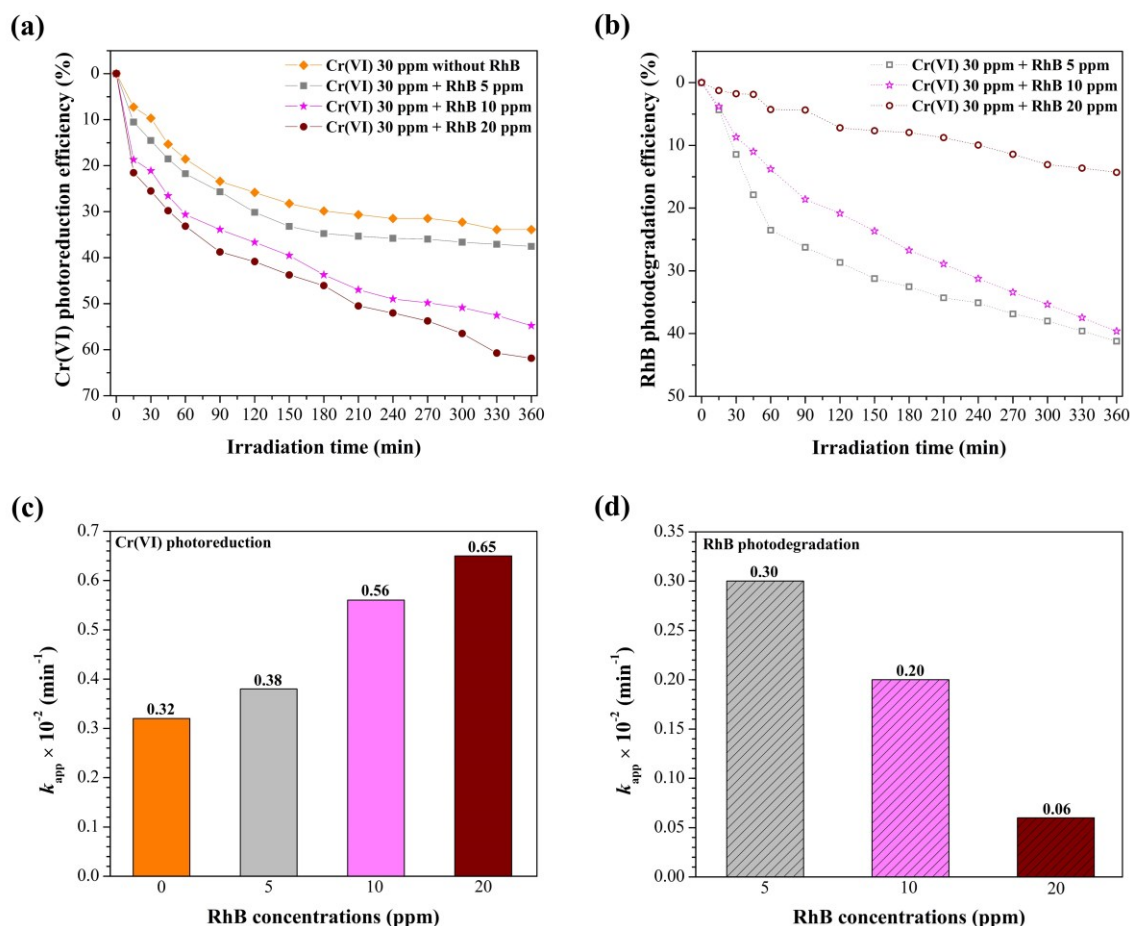
2 **Fig. 6.** (a-b) Effect of initial Cr(VI) concentration (20 ppm (signified with *) and 30 ppm) on
 3 photoreduction activity of the selected photocatalysts. Photoreduction efficiency and the
 4 corresponding kinetic rate of the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst were

1 affected by (c-d) the solution pH and photocatalyst dosage at (e-f) both the initial pH and (g-h)
2 pH 3 when using 30 ppm of Cr(VI).

3

4 **3.6. Simultaneous photocatalytic removal of Cr(VI) and RhB by FeVO₄/Bi₄O₅Br₂/BiOBr** 5 **in combined pollution system**

6 Since dyes and heavy metal ions often co-exist in wastewater, the simultaneous removal
7 effect of the Cr(VI) and RhB co-exist system in visible light-irradiated 1%wt-
8 FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst was investigated. By fixing the initial Cr(VI)
9 concentration (30 ppm) and photocatalyst dosage (100 mg), the concentration of the co-existing
10 RhB was varied (5, 10 and 20 ppm) to investigate the photo-efficacy of this ternary
11 photocatalyst in the Cr(VI)/RhB combined pollution system. The results presented in **Figs. 7**
12 **and S10. Fig. 7(a)** clearly shows that, in the presence of RhB, the photoreduction efficiency of
13 Cr(VI) was significantly promoted. The %RE increased from 33.9 to 37.5, 54.8 and 61.9 after
14 adding 5, 10 and 20 ppm of RhB, respectively. Under these circumstances, 41.2, 39.6, and
15 14.3% of RhB were also simultaneously degraded (**Fig. 7(b)**). RhB degradation was
16 remarkably decreased by 25.3% after the RhB concentration was increased from 10 to 20 ppm.
17 On the contrary, the photoreduction efficiency of Cr(VI) increased only by 7.1%. Additionally,
18 the k_{app} values for Cr(VI) reduction (**Fig. 7(c)**) were 0.56×10^{-2} and $0.65 \times 10^{-2} \text{ min}^{-1}$ for the
19 combined systems at 10 and 20 ppm RhB, respectively. In these systems, the k_{app} values (**Fig.**
20 **7(d)**) for RhB degradation were 0.20×10^{-2} and $0.06 \times 10^{-2} \text{ min}^{-1}$. By considering the
21 photoreduction of Cr(VI) and the photodegradation of RhB along with the k_{app} values, we
22 decided that an introduction of 10 ppm of RhB into the combined system would be sufficient
23 to greatly improve the photoreduction efficiency of Cr(VI) with a moderate RhB degradation
24 efficiency.

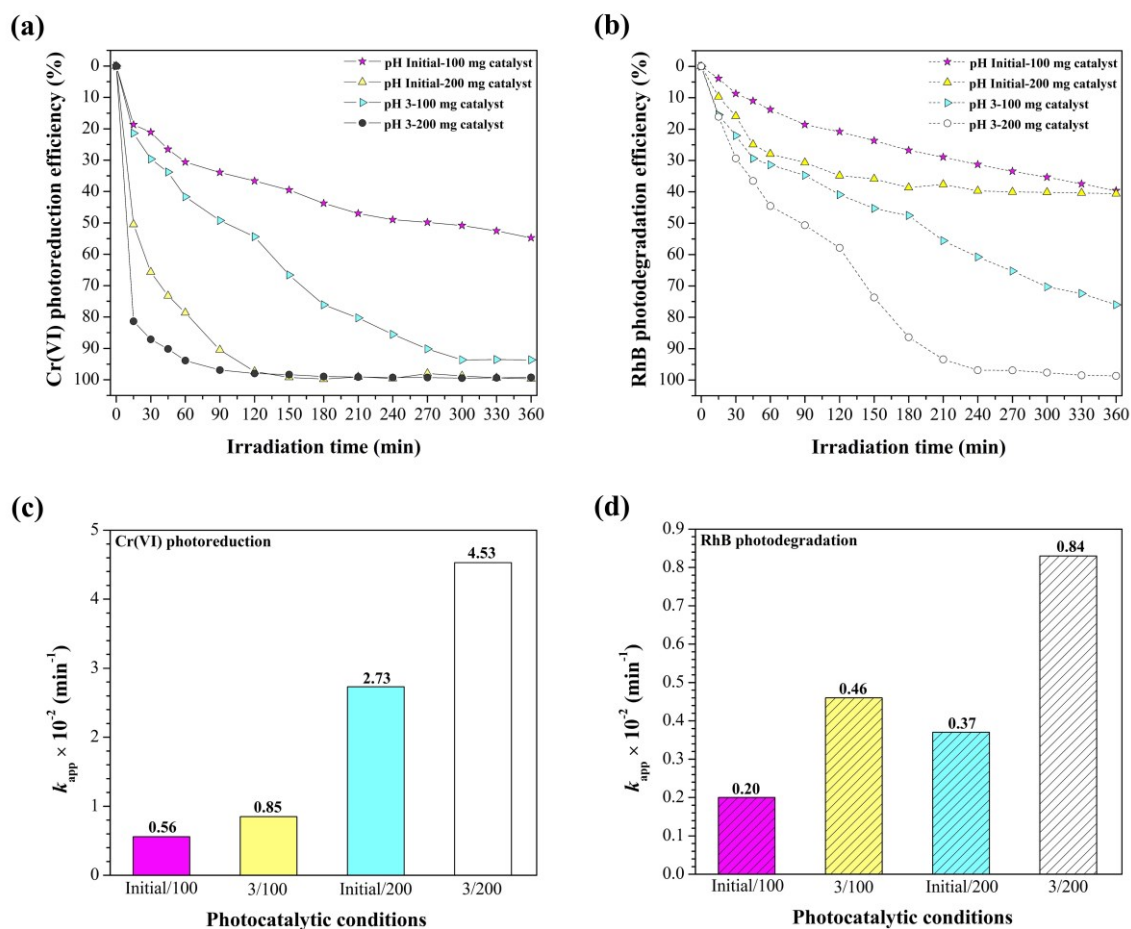


1
 2 **Fig. 7.** (a) Photoreduction of Cr(VI) and (b) photodegradation of RhB in the Cr(VI) and RhB
 3 co-exist system over the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst; the
 4 corresponding k_{app} values for (c) Cr(VI) photoreduction and (d) RhB photodegradation.

5
 6 As has been expressed in the previous section, the photoreduction Cr(VI) activity could
 7 be maximized by adjusting the pH of the solution to 3 and/or by increasing the photocatalyst
 8 dosage to 200 mg (**Fig. 6**). Thereby, we adjusted the pH value of the mixed Cr(VI) (30 ppm)
 9 and RhB (10 ppm) solution to 3 and/or employed 200 mg of the ternary photocatalyst with the
 10 aim of achieving the highest photoreduction Cr(VI) activity. The Cr(VI) photoreduction and
 11 RhB photodegradation efficiencies, along with the corresponding k_{app} values are summarized
 12 in **Table S1**. As can be seen in **Fig. 8(a)** and (c), at the initial pH of the mixed solution, the
 13 Cr(VI) photoreduction efficiencies increased from 54.8 to 99.7% when using 100 and 200 mg

1 of the photocatalyst, respectively, within 360 min. Similarly, at a pH value of 3 in the mixed
2 solution, with the use of 200 mg of the photocatalyst, the Cr(VI) reduction efficiency also
3 increased to 99.8%. Although, the Cr(VI) photoreduction efficiency for the latter condition was
4 comparable to that of the former condition, the kinetic rate was relatively faster ($k_{app} =$
5 $4.53 \times 10^{-2} \text{ min}^{-1}$ at pH of 3, and $2.73 \times 10^{-2} \text{ min}^{-1}$ at the initial pH) (**Fig. 8(c)**). These results
6 suggest that, under the latter condition, the photocatalyst was more effective in reducing Cr(VI)
7 in the combined pollutant system. Under this condition, Cr(VI) was completely reduced within
8 150 min of irradiation, while 98.2% of RhB was degraded within 360 min of irradiation (**Fig.**
9 **8(b)**). These results indicate that the presence of RhB in the combined pollutant system can
10 lead to an increment of photoreduction of Cr(VI) implying that RhB acts as an efficient
11 photosensitizer for the Cr(VI) reduction process. **Fig. S11** presents the photocatalytic data with
12 error bars that are based on the standard deviations of three parallel experiments. The small
13 standard deviation for each irradiated time interval reflects the accuracy of the sample data.

14 As is understood, the adsorption of dye molecules on a photocatalyst's surface is
15 required in a dye-sensitization process in order to inject electrons from LUMO of the excited
16 dye molecules to a conduction band of a semiconductor [35]. Typically, RhB exists in two
17 forms in an aqueous medium, the cationic (RhB^+) and zwitterion (RhB^\pm) forms, depending
18 upon the pH of the solution. The cationic form exists at pH values lower than the pKa of RhB
19 (3.7), while the zwitterion form exists at pH values higher than the pKa due to a deprotonation
20 of its carboxyl group [65]. Therefore, to elucidate the adsorption ability toward RhB molecules,
21 zeta potentials of 1%wt- $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ were measured at different pH values of the
22 solution. **Fig. S12** indicates that the zeta potentials varied from -12.8 to -22.4 mV. Thus, at a
23 pH value beyond 2, the photocatalyst's surface charge is negatively charged. As a result, it
24 could well adsorb RhB molecules in both forms via an electrostatic interaction, and
25 consequently, fulfill the dye-sensitization requirement.



1
 2 **Fig. 8.** (a) Photoreduction of Cr(VI) and (b) photodegradation of RhB in the coexistence over
 3 the 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst influenced by pH value and photocatalyst
 4 dosage; corresponding k_{app} values for (c) Cr(VI) photoreduction and (d) RhB photodegradation.

5
 6 To further clarify this point, an anionic dye (methyl orange, MO) was introduced into
 7 the combined pollution system instead of RhB. **Fig. S13(a)** shows that, in the Cr(VI)/MO
 8 combined system, Cr(VI) photoreduction was significantly suppressed. In terms of the
 9 adsorption ability, 21% of the RhB molecules were adsorbed by the 1%wt-
 10 FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst, whereas only 4% of MO were adsorbed. Therefore, the
 11 requirements of the dye-sensitization mechanism could not be fulfilled by MO. It should be
 12 noted that the adsorption percentages of Cr(VI) remain fairly constant by approximately 10%
 13 in both systems. Moreover, the Cr(VI) photoreduction efficiency in the Cr(VI)/MO combined

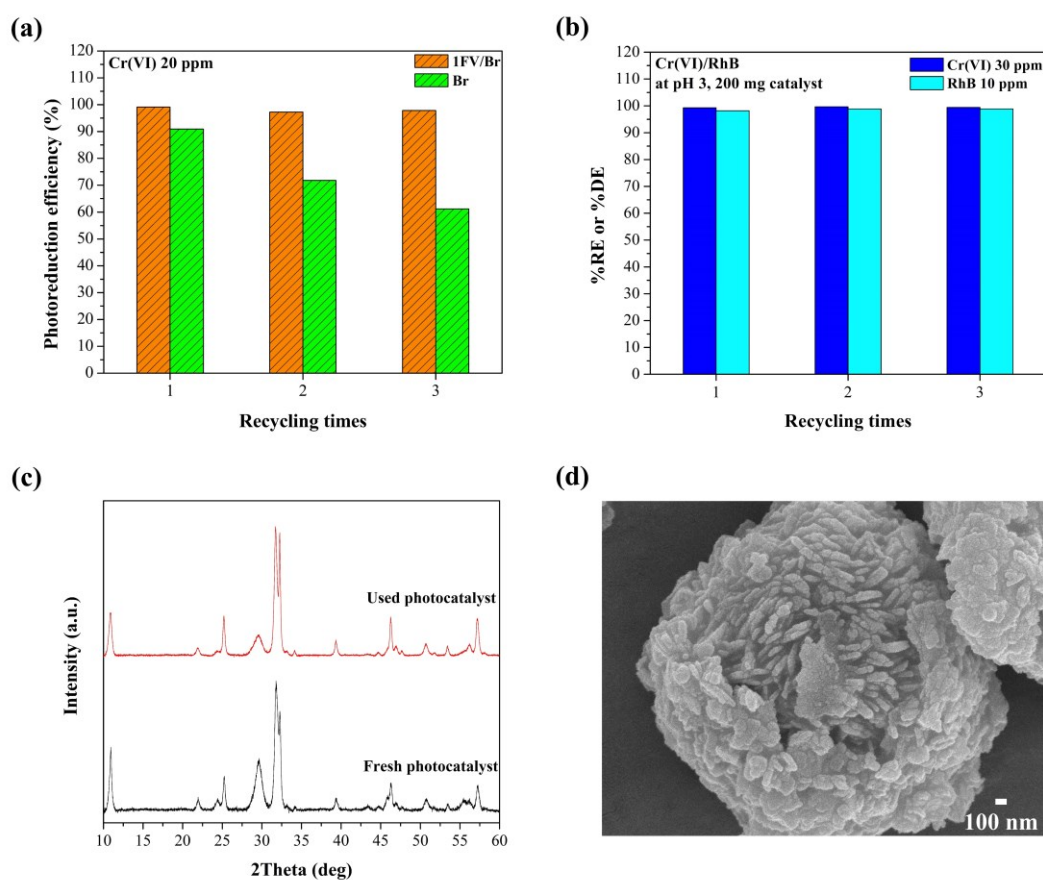
1 system was significantly lower than that of the Cr(VI) single pollutant system although the
2 levels of adsorption of Cr(VI) in these systems were similar. Remarkably, in the MO single
3 system, 60% and 32.7% of MO molecules were adsorbed and degraded by the ternary
4 photocatalyst, respectively, which were much higher than those of the Cr(VI)/MO combined
5 system (**Fig. S13(b)**). A lowering in the adsorption and degradation abilities towards MO and
6 the reduction ability of Cr(VI) in the coexistence could be elucidated by considering the UV–
7 vis absorption spectra of the Cr(VI) solution, along with the mixed solution of Cr(VI) and MO
8 remained after the photocatalytic process. As is shown in **Fig. S13(d)**, λ_{\max} of Cr(VI) in the
9 mixed Cr(VI) and MO solutions shifted from 352 nm to 374 nm. On the other hand, the shift
10 in λ_{\max} was not observed in the case of RhB (**Fig. S13(c)**). This finding implies that the presence
11 of MO in the combined system could induce the formation of a Cr(VI)-MO complex,
12 consequently decreasing free Cr(VI) ions and MO molecules that are available for the
13 photocatalytic reaction.

14 In addition to the MO dye, SA was introduced to the combined pollution system instead
15 of RhB. **Fig. S14(a)** shows that 5 ppm of SA did not improve Cr(VI) photoreduction, which
16 could be ascribed to the competitive adsorption of SA (34.5%). However, a slight incremental
17 increase in the Cr(VI) photoreduction efficiency to 40% was observed by adding 10 ppm of
18 SA. Despite the lack of sensitization ability of SA, it could act as a hole scavenger which
19 consequently reduced electron-hole pair recombination, and thus, facilitated Cr(VI)
20 photoreduction efficiency. However, the incremental increase in the Cr(VI) photo-efficiency
21 by SA in the Cr(VI)/SA combined system was not as significant as it was for RhB, suggesting
22 the significance of the dye-sensitization mechanism that was induced by the RhB molecules.

23 The reusability of the ternary photocatalyst for the photoreduction of Cr(VI) (20 ppm)
24 over the binary and ternary heterojunction photocatalysts were evaluated. As is shown in **Fig.**
25 **9(a)**, the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst maintained high photoreduction

1 efficiency towards Cr(VI) without a significant decrease in photo-efficiency after three
2 successive runs, while the binary BiOBr/Bi₄O₅Br₂ photocatalyst exhibited a significant loss in
3 photo-efficiency. The loss in recyclability of the binary photocatalyst could be arisen from
4 unremovable adsorbed Cr(VI) ions on its surface, and the reduction of Bi³⁺ ions by
5 photoactivated electrons as has been discussed in the previous section. Similarly, the reusability
6 and stability of the ternary heterojunction photocatalyst for the photocatalytic removal of
7 Cr(VI) and RhB in the Cr(VI)/RhB combined pollutant system were also investigated under
8 conditions including 30 ppm Cr(VI)/10 ppm RhB, solution pH of 3, and 200 mg of the
9 photocatalyst. As is shown in **Fig. 9(b)**, 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr exhibited no significant
10 changes in the removal of RhB and Cr(VI) after the three-recycling test. The XRD patterns
11 (**Fig. 9(c)**) and FESEM image (**Fig. 9(d)**) indicate that 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr
12 maintained its crystalline structure and three-dimensional flower-like structure. Moreover, as
13 was determined by ICP-OES analysis, Fe and V ions were not detected in the supernatant
14 solution. These results prove that the ternary heterojunction photocatalyst is reusable and stable
15 against photocorrosion and chemical corrosion. Its reusability and stability towards Cr(VI)
16 reduction and RhB degradation were probably due to the migration of photoactivated electrons
17 from the binary BiOBr/Bi₄O₅Br₂ heterojunction to FeVO₄ through the intimate interfacial
18 contact between BiOBr/Bi₄O₅Br₂ and FeVO₄. This could be beneficial in preventing the
19 reduction of Bi³⁺ ions in the ternary heterojunction. The photocatalytic removal of Cr(VI) and
20 RhB in the coexisting system by 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr, when compared with the
21 outcomes of previously published reports, are summarized and shown in **Table S2**. Differences
22 in the efficiency could have been caused by variations in the photocatalytic conditions such as
23 type and power of the light source, pH solution, catalyst dosage, and type of catalyst. However,
24 the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr photocatalyst exhibited better photo-activity under
25 the same photocatalytic conditions than that of the single and binary photocatalysts, P25, and

1 even the counterpart photocatalysts (6.25%wt-FeVO₄/Bi₇O₉I₃ [33] and 6.25%wt-
 2 FeVO₄/BiOCl [34]).



3
 4 **Fig. 9.** Cyclic runs of (a) photoreduction of 20 ppm Cr(VI) in a single pollutant system over
 5 BiOBr/Bi₄O₅Br₂ (Br) and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr (1FV/Br) samples, (b)
 6 photodegradation of RhB and photoreduction of Cr(VI) in the Cr(VI)/RhB combined pollution
 7 system under conditions including 30 ppm Cr(VI)/10 ppm RhB, solution pH of 3, and 200 mg
 8 of photocatalyst over 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr. (c) XRD patterns before and after
 9 recycling experiments towards Cr(VI) and (d) the corresponding FESEM image of 1%wt-
 10 FeVO₄/Bi₄O₅Br₂/BiOBr after the three-recycling test.

11

12 3.7. Discussion on enhanced photocatalytic activity

13 The charge carrier separation properties of the heterojunction photocatalysts in
 14 comparison to the single photocatalysts were determined by PL. Generally, a PL emission

1 signal arises from the recombination of charge carriers in a semiconductor. A lower PL
2 emission intensity indicates a lower electron-hole pair recombination which facilitates a
3 photocatalytic reaction [66]. The PL spectra of BiOBr, Bi₄O₅Br₂, BiOBr/Bi₄O₅Br₂ and 1%wt-
4 FeVO₄/Bi₄O₅Br₂/BiOBr are presented in **Fig. 10(a)**. It can be seen that 1%wt-
5 FeVO₄/Bi₄O₅Br₂/BiOBr emitted the lowest PL emission intensity in comparison to the single
6 BiOBr and Bi₄O₅Br₂, and binary BiOBr/Bi₄O₅Br₂ materials. This result suggests that the
7 fabrication of the ternary heterojunction can effectively reduce electron-hole recombination,
8 which is essential in the enhancement of photocatalytic activity.

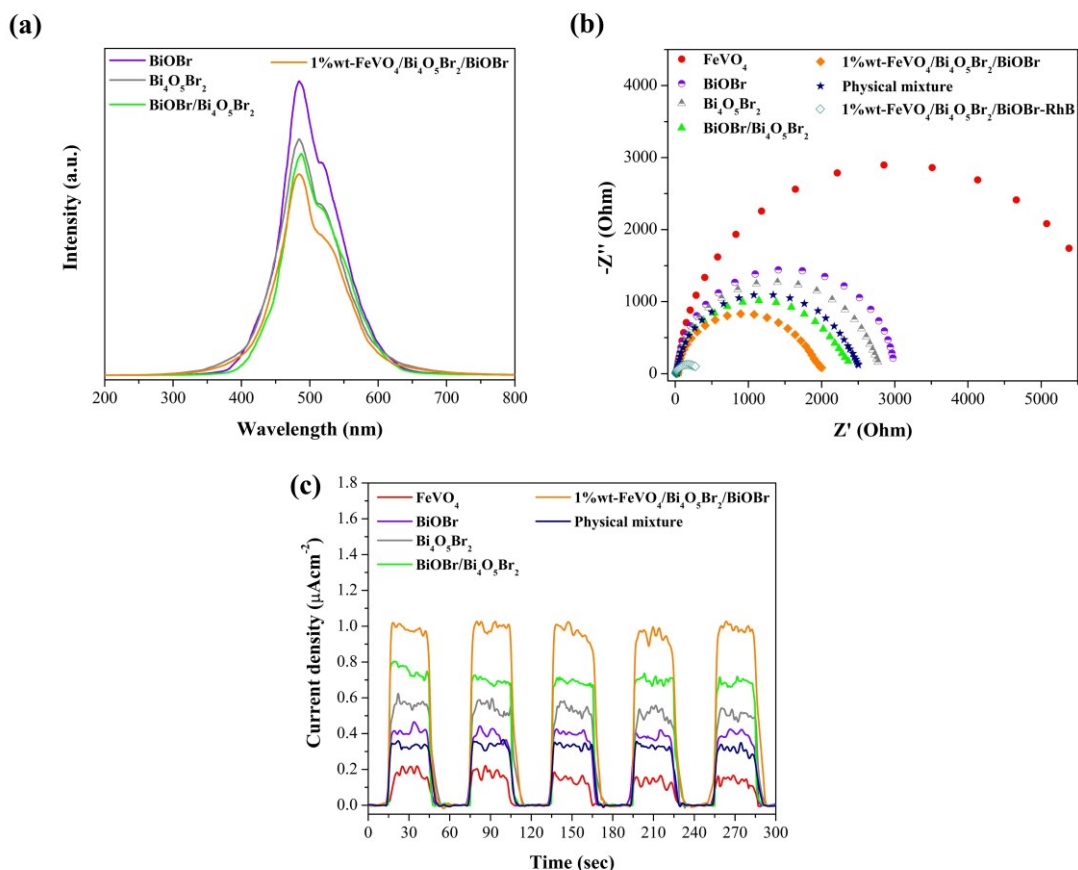
9 EIS was used to determine the charge transfer resistance of the materials [66,67]. A
10 smaller arc radius in the EIS Nyquist plot indicated a lower charge transfer resistance at the
11 interface between the electrode and the electrolyte solution, implying a better migration of the
12 charge carrier. As is shown in **Fig. 10(b)**, the arc radius of the ternary 1%wt-
13 FeVO₄/Bi₄O₅Br₂/BiOBr electrode exhibited the smallest among the single and binary
14 electrodes. This result implies the highest level of effective charge transfer efficiency, and
15 therefore, a large number of charge carriers took part in the photocatalytic reactions [67–69].
16 The arc radius of this electrode was also smaller than that of the physical mixture electrode,
17 implying that the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr heterostructure was formed by a
18 chemical interaction. Moreover, the arc radius of the physical mixture electrode was larger
19 than that of the binary BiOBr/Bi₄O₅Br₂ electrode, signifying the successfulness in the
20 formation of the ternary heterostructure. The 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr/RhB film on the
21 FTO glass was also fabricated and then analyzed to clarify the sensitization role of RhB in the
22 enhancement of the photocatalytic activity. The arc radius of the 1%wt-
23 FeVO₄/Bi₄O₅Br₂/BiOBr/RhB film was significantly smaller than that of 1%wt-
24 FeVO₄/Bi₄O₅Br₂/BiOBr, confirming that RhB indeed promoted the transportation of charge

1 carriers in the ternary 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr system [70], which resulted in
2 remarkably enhanced photocatalytic activity.

3 **Fig. 10(c)** shows the transient photocurrent responses of the FeVO₄, BiOBr, Bi₄O₅Br₂,
4 BiOBr/Bi₄O₅Br₂, 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr and physical mixture electrodes. The
5 photocurrent responses of the BiOBr/Bi₄O₅Br₂ and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr electrodes
6 were enhanced by comparison with that of the other electrodes. The 1%wt-
7 FeVO₄/Bi₄O₅Br₂/BiOBr electrode exhibited the largest photocurrent density, indicating that it
8 had a high ability to generate and transfer photoactivated charge carriers. In combining the PL,
9 EIS, and photocurrent responses results, the interfacial charge transfer efficiency in 1%wt-
10 FeVO₄/Bi₄O₅Br₂/BiOBr was greatly enhanced when compared with BiOBr/Bi₄O₅Br₂, which is
11 occurred as a result of the formation of multi-heterojunctions.

12 The N₂ adsorption-desorption isotherms and pore size distributions of the FeVO₄,
13 BiOBr/Bi₄O₅Br₂, and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr samples are shown in **Fig. S15**. The
14 BiOBr/Bi₄O₅Br₂ and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr samples exhibited type-IV isotherms with
15 the hysteresis loops in the range of 0.45-1.0 P/P₀, which is known to be a characteristic of slit-
16 like mesopores that are formed by plate-like particles [26]. In addition, the pore size
17 distribution curves reveal that the BiOBr/Bi₄O₅Br₂ and 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr had
18 mesopores with pore diameters in the range of 18–22 nm and the pore volume of the
19 BiOBr/Bi₄O₅Br₂ was the highest. The BET surface area of FeVO₄, BiOBr/Bi₄O₅Br₂ and 1%wt-
20 FeVO₄/Bi₄O₅Br₂/BiOBr were 19.8, 46.8, and 42.3 m²g⁻¹ with total pore volumes of 0.0415,
21 0.3340, and 0.2367 cm³g⁻¹, respectively. The slightly decreases in the surface area and total
22 pore volume of 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr could be due to the deposition of FeVO₄
23 nanoparticles on the BiOBr/Bi₄O₅Br₂ surface, decreasing the number of cavities on the surface
24 of BiOBr/Bi₄O₅Br₂ microspheres as observed in the FESEM image (**Fig. 3**). However, 1%wt-
25 FeVO₄/Bi₄O₅Br₂/BiOBr exhibited the highest photocatalytic activity, suggesting that the

1 surface area and pore volume were not the main factor enhancing its photocatalytic
 2 performance. Therefore, the enhanced photocatalytic activity of the ternary 1%wt-
 3 $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ heterojunction could be ascribed to its improved optical and
 4 electrochemical properties upon coupling $\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ with FeVO_4 .



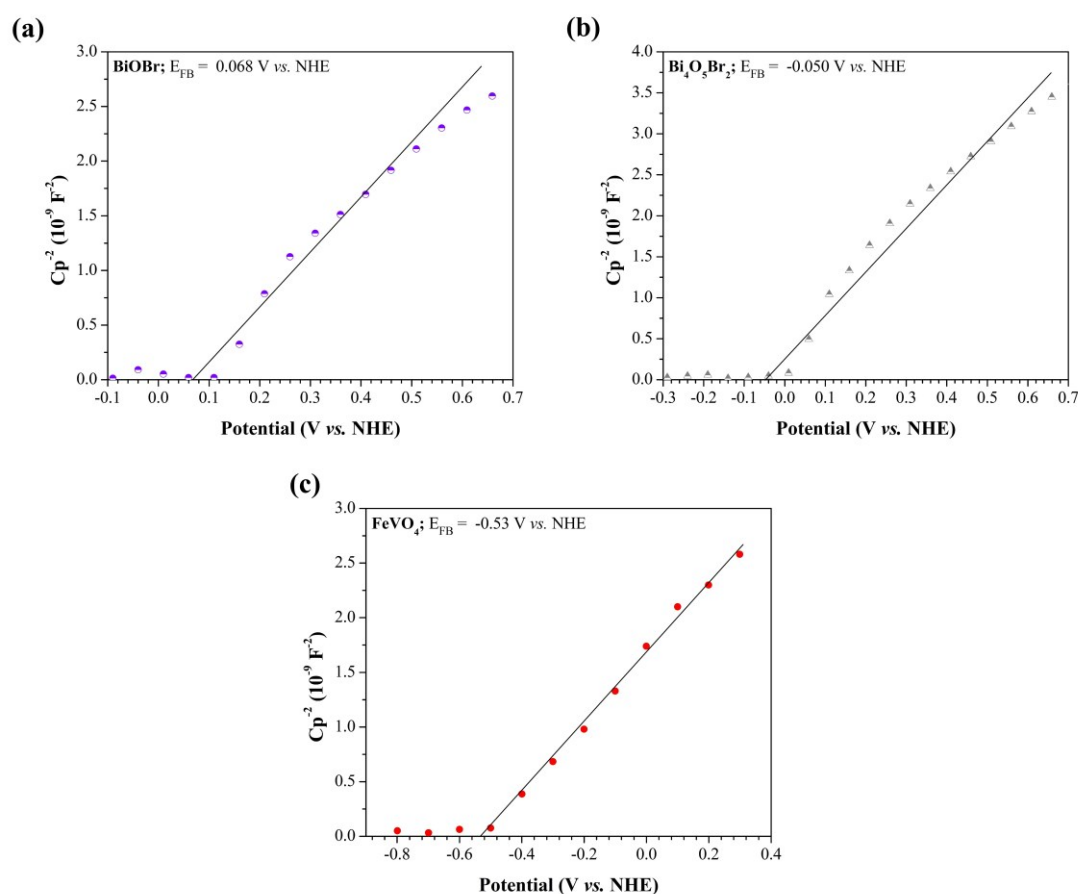
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 6 **Fig. 10.** (a) PL emission spectra, (b) EIS Nyquist plots and (c) photocurrent responses of the
 7 photocatalyst samples.

8

9 **3.8. Charge transfer and photocatalytic mechanisms**

10 Mott-Schottky measurements were performed to determine band potentials and the
 11 electrically conductive nature of the single materials. As illustrated in **Fig. 11**, positive slopes
 12 were observed for the BiOBr , $\text{Bi}_4\text{O}_5\text{Br}_2$ and FeVO_4 electrodes indicating that these materials
 13 are an n-type semiconductor [71,72]. The flat band potentials (E_{FB}) were 0.068, -0.050, and -

1 0.53 V (vs. NHE, pH = 0) for BiOBr, Bi₄O₅Br₂ and FeVO₄, respectively. Generally, E_{FB} of the
 2 n-type semiconductor was approximately -0.1 below its conduction band potential (E_{CB})
 3 [71,73]. Thereby, E_{CB} of BiOBr, Bi₄O₅Br₂ and FeVO₄ could be determined as -0.032, -0.15,
 4 and -0.63 V (vs. NHE, pH = 0), respectively. According to the Tauc' plots shown in **Fig. 5(b)**,
 5 the valence band potentials (E_{VB}) of BiOBr, Bi₄O₅Br₂, and FeVO₄ were 2.898, 2.45, and 1.45
 6 V (vs. NHE, pH = 0), respectively.



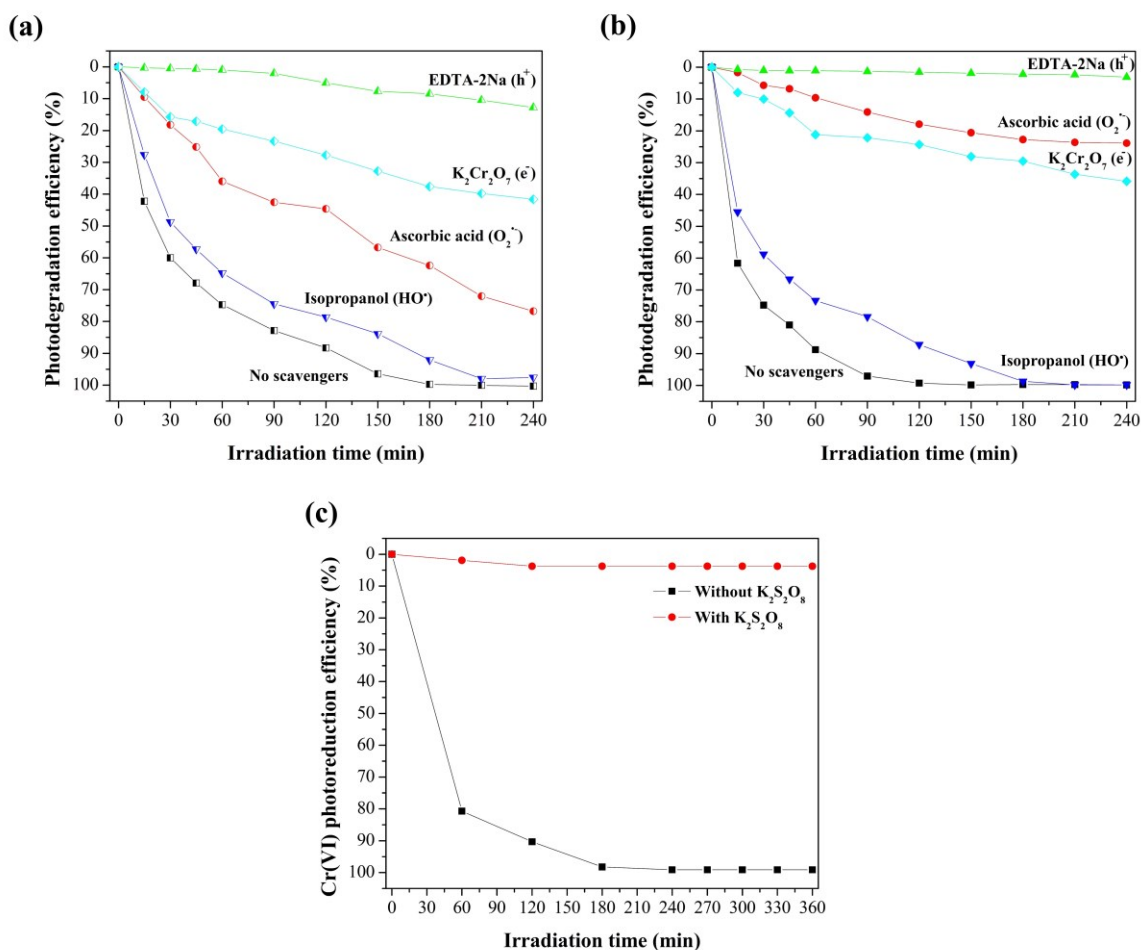
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 8 **Fig. 11.** Mott-Schottky plots of (a) BiOBr, (b) Bi₄O₅Br₂ and (c) FeVO₄.

9
 10 In order to fully realize the photocatalytic mechanism, the active species generated
 11 during the photocatalytic RhB degradation process were identified by trapping experiments.
 12 **Fig. 12(a)** shows the effect of different scavengers on RhB photodegradation over the binary
 13 BiOBr/Bi₄O₅Br₂ heterojunction photocatalyst. The photodegradation efficiency of RhB

1 significantly decreased with the addition of EDTA-2Na or $K_2Cr_2O_7$ demonstrating that h^+ and
2 e^- are mainly responsible for RhB degradation. The photodegradation efficiency moderately
3 decreased by 30% in the presence of ASC, implying that $O_2^{\bullet-}$ was also one of the active species
4 involved in the photocatalytic reaction; however, it was not determined to be a main active
5 specie. On the contrary, the degradation efficiency changed slightly after adding isopropanol,
6 implying that HO^\bullet was not involved in the photocatalytic reaction.

7 The main active species responsible for the photocatalytic degradation of RhB over the
8 ternary 1%wt- $FeVO_4/Bi_4O_5Br_2/BiOBr$ heterojunction photocatalyst was also identified by a
9 series of trapping experiments that employed the same approach. As is presented in **Fig. 12(b)**,
10 the photodegradation of RhB was completely inhibited in the presence of EDTA-2Na,
11 demonstrating that h^+ was the main active specie. Similarly, the photodegradation efficiencies
12 remarkably decreased after adding ASC and $K_2Cr_2O_7$, suggesting the importance of both $O_2^{\bullet-}$
13 and e^- for RhB degradation. In the presence of isopropanol, a negligible change in photo-
14 efficiency was observed. This would indicate that HO^\bullet was almost negligibly active specie in
15 the reaction. The generation of HO^\bullet radicals was verified using the TA-PL probing technique
16 by employing terephthalic acid ($5.00 \times 10^{-4} \text{ mol L}^{-1}$) as a molecular probe. Accordingly, the
17 terephthalic acid reacted with HO^\bullet and generated 2-hydroxyterephthalic acid (TAOH) which
18 emitted an intense fluorescence at 425 nm with an excitation wavelength of 315 nm. The
19 intensity of TAOH was proportional to the amount of HO^\bullet produced. **Fig. S16** reveals that the
20 emission intensities of TAOH were very low, and the peak intensities of TAOH at prolonged
21 reaction times were just a little bit higher. This supports the understanding that a small amount
22 of HO^\bullet radicals were produced during the photocatalytic process, which agrees well with the
23 trapping experimental result. For the Cr(VI) photoreduction over 1%wt-
24 $FeVO_4/Bi_4O_5Br_2/BiOBr$ (**Fig. 12(c)**), the introduction of $K_2S_2O_8$ resulted in a complete

1 termination of the reaction indicating that photoactivated electrons were essential for Cr(VI)
 2 photoreduction [74].

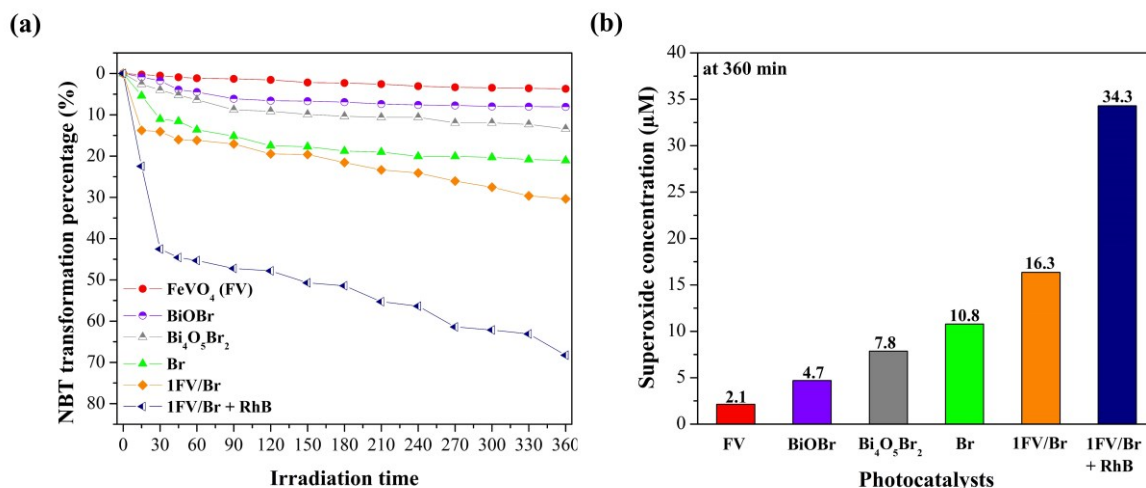


3
 4 **Fig. 12.** Effect of scavengers on the photodegradation of RhB by (a) BiOBr/Bi₄O₅Br₂ and (b)
 5 1%wt-FeVO₄/Bi₄O₅Br₂/BiOBr, and (c) the photoreduction of Cr(VI) (20 ppm) by 1%wt-
 6 FeVO₄/Bi₄O₅Br₂/BiOBr under the solution pH of 3.

7
 8 As shown in **Fig. 12**, the role of O₂⁻ was more predominant in the ternary
 9 FeVO₄/Bi₄O₅Br₂/BiOBr heterojunction system relative to the binary BiOBr/Bi₄O₅Br₂
 10 heterojunction system. This would suggest that a larger number of O₂⁻ radicals were involved
 11 in the RhB degradation process over the ternary heterojunction. The amount of O₂⁻ generated
 12 from the photocatalyst during the photocatalytic reaction was thereby quantitatively
 13 determined using the nitrotetrazolium blue (NBT) transformation method [40]. By employing

1 nitrotetrazolium blue chloride ($1.25 \times 10^{-5} \text{ mol L}^{-1}$) as a molecular probe, the generated $\text{O}_2^{\bullet-}$
2 radicals reacted with NBT with a reaction molar ratio of 1:4 to form the formazan derivative
3 in the aqueous solution [29]. When the monitoring of this reaction was accomplished with the
4 use of the UV-vis spectrophotometer, the transformation percentage of NBT could be
5 calculated from a decrease in the absorption intensity of the NBT supernatant solutions at λ_{max}
6 of 265 nm. This decrease in intensity would indicate the presence of a higher degree of NBT
7 transformation, which correlated to an increase in the generated $\text{O}_2^{\bullet-}$ radicals. **Fig. 13(a)** and
8 **Fig. S17** clearly show that the single BiOBr photocatalyst exhibited lower NBT transformation
9 percentage (8.1%) than that of $\text{Bi}_4\text{O}_5\text{Br}_2$ (13.4%). This would suggest that electrons in CB of
10 BiOBr have lower reduction potential to reduce dissolved O_2 to $\text{O}_2^{\bullet-}$. For the binary
11 BiOBr/ $\text{Bi}_4\text{O}_5\text{Br}_2$ photocatalyst, the transformation percentage of NBT was higher (21.1%) than
12 in the single photocatalysts. This suggests a higher amount of $\text{O}_2^{\bullet-}$ was produced during the
13 photocatalysis. Among the other photocatalysts, 1%wt- $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ provided the
14 greatest NBT transformation percentage (30.4%). The amounts of generated $\text{O}_2^{\bullet-}$ radicals,
15 calculated from the NBT transformation experiments, were 2.1, 4.7, 7.8, 10.8, and 16.3 μmol
16 L^{-1} for FeVO_4 , BiOBr, $\text{Bi}_4\text{O}_5\text{Br}_2$, BiOBr/ $\text{Bi}_4\text{O}_5\text{Br}_2$, and 1%wt- $\text{FeVO}_4/\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$,
17 respectively (**Fig. 13(b)**). The higher $\text{O}_2^{\bullet-}$ production efficiency of the binary and ternary
18 heterojunction photocatalysts indicated improved segregation and migration processes of the
19 charge carriers between the interface of the constituent semiconductors in the heterojunctions.
20 Interestingly, the addition of RhB in the reaction system greatly improved both the NBT
21 transformation percentage (30.4%) and the $\text{O}_2^{\bullet-}$ yield ($34.3 \mu\text{molL}^{-1}$). This result further
22 supports the essential role of RhB as a photosensitizer during the photocatalytic reaction. In
23 addition, RhB could capture photogenerated holes [75–77], decreasing the overall
24 recombination of electron-hole pair in the ternary heterostructure and improving the charge
25 transfer efficiency [78]. Consequently, a large number of electrons could be photogenerated

1 and react to the dissolved O_2 in the solution to yield $O_2^{\bullet-}$ during the photocatalysis. The
2 impressive increase in the production of reactive $O_2^{\bullet-}$ resulted in an outperforming
3 photocatalytic process.



4
5 **Fig. 13.** (a) NBT transformation percentage and (b) concentration of $O_2^{\bullet-}$ radicals generated
6 after 360 min of visible light irradiation over the single, binary, and ternary photocatalysts.

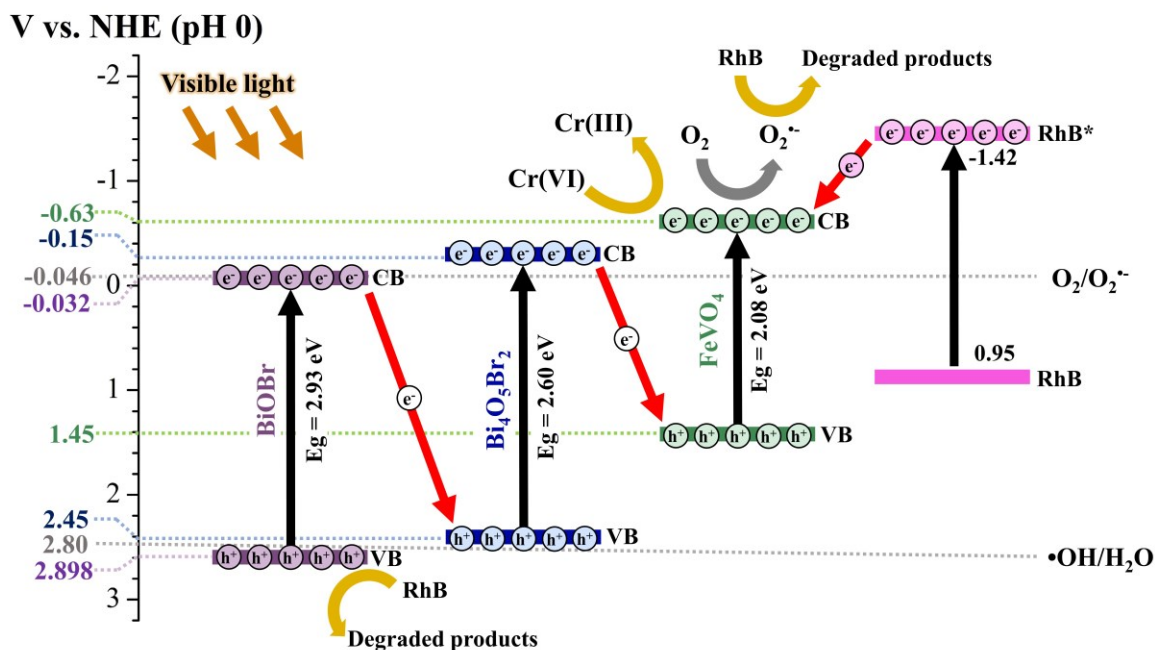
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8 According to the results from the Mott-Schottky plots, active species trapping
9 experiments, and the NBT transformation experiment, two possible charge transfer pathways
10 over the binary BiOBr/Bi₄O₅Br₂ heterojunction photocatalyst have been proposed in the first
11 step. As has been illustrated in **Scheme S1**, the band potentials of BiOBr and Bi₄O₅Br₂ were
12 aligned in a staggered manner, driving the migration of the charge carrier that was proceeded
13 via the conventional type-II (**Scheme S1(a)**) or direct Z-scheme (**Scheme S1(b)**) mechanisms.
14 Under visible light irradiation, both BiOBr and Bi₄O₅Br₂ were excited to yield electrons and
15 holes on their CB and VB. In the conventional type-II mechanism, the excited electrons
16 transferred from CB of Bi₄O₅Br₂ (-0.15 V vs. NHE) to CB of BiOBr (-0.032 V vs. NHE) while
17 holes transfer from VB of BiOBr (2.898 V vs. NHE) to VB of Bi₄O₅Br₂ (2.45 V vs. NHE). This
18 charge transfer pathway resulted in low reducibility and oxidizability of the binary
19 BiOBr/Bi₄O₅Br₂ heterojunction. Furthermore, the potential of the accumulated electrons on CB

1 of BiOBr were at a lower band position than the reduction potential of $O_2/O_2^{\bullet-}$ (-0.046 V vs.
2 NHE). Hence, these electrons could not reduce O_2 to $O_2^{\bullet-}$ radicals, which is contrary to the
3 results from the active species trapping and NBT transformation experiments. For the direct Z-
4 scheme mechanism, the photoactivated electrons at CB of BiOBr were transferred to combine
5 with holes in VB of $Bi_4O_5Br_2$, thus preserving a strong reducibility of electrons accumulated
6 in CB of $Bi_4O_5Br_2$, and thereby decreasing the probability of electron-hole pair recombination
7 within the constituent photocatalysts. As a result, the strong reducing electrons in CB of
8 $Bi_4O_5Br_2$ could react with O_2 to produce $O_2^{\bullet-}$. In the meantime, the strong oxidizing holes that
9 remained in VB of BiOBr could directly degrade RhB molecules [79,80].

10 After introducing $FeVO_4$ into the binary BiOBr/ $Bi_4O_5Br_2$ heterostructure, the ternary
11 $FeVO_4/Bi_4O_5Br_2/BiOBr$ heterostructure was constructed. The charge transfer pathway in the
12 ternary heterojunction system could then be proposed by the same approach as the binary
13 BiOBr/ $Bi_4O_5Br_2$ heterostructure system. As is shown in **Scheme S2**, $FeVO_4$ was also activated
14 by visible light, generating electrons and holes at its CB and VB, respectively. The electrons
15 accumulated at CB of $Bi_4O_5Br_2$ in the binary BiOBr/ $Bi_4O_5Br_2$ heterostructure could migrate to
16 VB of $FeVO_4$ through the Z-scheme charge transfer process. With regard to this mechanism,
17 the photoactivated electrons in CB of $FeVO_4$ (-0.63 V vs. NHE) possessed the highest reduction
18 potential when compared with BiOBr (-0.032 V vs. NHE) and $Bi_4O_5Br_2$ (-0.15 V vs. NHE). As
19 a result, remarkably higher amounts of $O_2^{\bullet-}$ were generated as was proven by the active species
20 trapping (**Fig. 12**) and NBT transformation (**Fig. 13**) experiments. Thus, the charge transfer in
21 the ternary $FeVO_4/BiOBr/Bi_4O_5Br_2$ heterostructure was proposed to be a double Z-scheme
22 mechanism.

23 The silver (Ag) photo-deposition experiment was carried out to confirm the double Z-
24 scheme charge transfer pathway, where the photoactivated electrons were left in CB of $FeVO_4$.
25 HRTEM image of the $FeVO_4$ nanoparticles in the ternary 1%wt- $FeVO_4/Bi_4O_5Br_2/BiOBr$

1 heterostructure (**Fig. S18**) indicates that there were Ag nanoparticles with a lattice fringe of
2 0.231 nm, which corresponded to (111) plane of Ag that was deposited on the surface of
3 FeVO₄. This result indicated that the reduction of Ag⁺ under visible light irradiation occurred
4 on the surface of FeVO₄ rather than on the surface of BiOBr/Bi₄O₅Br₂ nanoparticles.
5 Furthermore, the sensitization mechanism triggered by RhB was found to be involved in the
6 charge transfer process. After irradiation by visible light, RhB molecules were also brought to
7 an excited states (RhB*). The excited electrons in the LUMO of RhB* (-1.42 V vs. NHE) could
8 be injected into CB of FeVO₄ with a higher favorability than either BiOBr or Bi₄O₅Br₂. This
9 was due to the more negative E_{CB} value of FeVO₄ [81]. The RhB photosensitization resulted in
10 an accumulation of electrons in CB of FeVO₄ which favored O₂^{•-} generation (**Scheme S2**).
11 According to the above discussion, a photocatalytic mechanism for the simultaneous Cr(VI)
12 reduction and RhB degradation in the Cr(VI)/RhB combined pollutant system over the ternary
13 heterojunction photocatalyst is presented in **Scheme 1**. RhB molecules not only act as an
14 efficient photosensitizer to increase electron concentrations injected into the ternary
15 heterojunction during photocatalytic reaction but they also act as a hole capturing agent [75–
16 77] by consuming the photocatalytically generated holes in VB of BiOBr. As a result, the
17 production of photoactivated electrons, which are essential for Cr(VI) photoreduction, is
18 further improved to promote the photoreduction of Cr(VI).



1
2 **Scheme 1.** Proposed charge transfer and photocatalytic mechanisms for simultaneous removal
3 of Cr(VI) and RhB in the Cr(VI) and RhB co-exist system over the ternary
4 FeVO₄/Bi₄O₅Br₂/BiOBr heterojunction photocatalyst.

6 4. Conclusion

7 Novel FeVO₄/Bi₄O₅Br₂/BiOBr ternary heterostructures with different FeVO₄ contents
8 were successfully synthesized by the facial one-step microwave irradiation method, followed
9 by the wet-impregnation process. Among other synthesized photocatalysts, 1%wt-
10 FeVO₄/Bi₄O₅Br₂/BiOBr displayed the maximum photocatalytic activity toward degrading
11 rhodamine B (RhB), methylene blue (MB) and salicylic acid (SA), and reducing hexavalent
12 chromium (Cr(VI)) with the removal rates of approximately 20, 5, 8, and 89 times higher than
13 those of commercial TiO₂ P25, respectively. In the Cr(VI)/RhB combined pollutant system,
14 the presence of RhB molecules synergically increased the Cr(VI) photoreduction efficiency
15 through the RhB-sensitization and photogenerated hole consuming processes. This would in
16 turn increase electron concentrations in the ternary heterojunction system and O₂^{•-} radicals, as
17 evidenced by the trapping experiments, electron-impedance spectroscopy and nitrotetrazolium

1 blue transformation studies. The adsorption abilities of the dyes on the surface of the ternary
2 photocatalyst with negatively charged zeta potential was required to initiate dye-sensitization.
3 In comparison with the single and binary photocatalysts, the boosted photocatalytic activity
4 and long-term photostability in the acidic conditions of the ternary heterojunction photocatalyst
5 were attributed to the improved visible light absorption, and the highly efficient segregation
6 and migration of the charge carriers through the double Z-scheme mechanism. These outcomes
7 resulted from the intimate interfacial contact between the three different semiconductor phases.
8 Practical applications of the ternary heterojunction photocatalysts in real wastewater containing
9 both Cr(VI) and RhB, as well as common inorganic anions existing in polluted water, require
10 further studies. However, this research has produced the promising directions to remediate
11 organic substances and heavy metal-contaminated water.

12

13 **Credit author statement**

14 **Auttaphon Chachvalvutikul:** Conceptualization; Methodology; Formal analysis;
15 Investigation; Writing - Original draft; Writing - review & editing; Visualization. **Tawanwit**
16 **Luangwanta:** Formal analysis; Investigation. **Sulawan Kaowphong:** Conceptualization;
17 Methodology; Validation; Investigation; Resources; Writing - original draft; Writing - review
18 & editing; Visualization; Supervision; Project administration; Funding acquisition.

19

20 **Declaration of interests**

21 The authors declare that there are no conflicts of interest.

22

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2 **References**

- 3 [1] X. Liu, H. Pang, X. Liu, Q. Li, N. Zhang, L. Mao, M. Qiu, B. Hu, H. Yang, X. Wang,
4 Orderly Porous Covalent Organic Frameworks-based Materials : Superior Adsorbents
5 for Pollutants Removal from Aqueous Solutions, *Innov.* 2 (2021) 100076.
6 <https://doi.org/10.1016/j.xinn.2021.100076>.
- 7 [2] X. Liu, R. Ma, L. Zhuang, B. Hu, J. Chen, X. Liu, Recent developments of doped g-
8 C₃N₄ photocatalysts for the degradation of organic pollutants, *Crit. Rev. Environ. Sci.*
9 *Technol.* 51 (2021) 751–790. <https://doi.org/10.1080/10643389.2020.1734433>.
- 10 [3] M. Hao, M. Qiu, H. Yang, B. Hu, X. Wang, Recent advances on preparation and
11 environmental applications of MOF-derived carbons in catalysis, *Sci. Total Environ.*
12 760 (2021) 143333. <https://doi.org/10.1016/j.scitotenv.2020.143333>.
- 13 [4] S. Dong, J. Feng, M. Fan, Y. Pi, L. Hu, X. Han, M. Liu, J. Sun, J. Sun, Recent
14 developments in heterogeneous photocatalytic water treatment using visible light-
15 responsive photocatalysts: A review, *RSC Adv.* 5 (2015) 14610–14630.
16 <https://doi.org/10.1039/c4ra13734e>.
- 17 [5] A. Hernández-Ramírez, I. Medina-Ramírez, *Photocatalytic Semiconductors*, Springer,
18 Switzerland, 2015. <https://doi.org/10.1007/978-3-319-10999-2>.
- 19 [6] J. Di, J. Xia, H. Li, S. Guo, S. Dai, Bismuth oxyhalide layered materials for energy and
20 environmental applications, *Nano Energy.* 41 (2017) 172–192.
21 <https://doi.org/10.1016/j.nanoen.2017.09.008>.
- 22 [7] Z. Liu, J. Niu, P. Feng, Y. Zhu, Solvothermal synthesis of Bi₂₄O₃₁Cl_xBr_{10-x} solid
23 solutions with enhanced visible light photocatalytic property, *Ceram. Int.* 41 (2015)
24 4608–4615. <https://doi.org/10.1016/j.ceramint.2014.12.004>.
- 25 [8] A.M. Ganose, M. Cuff, K.T. Butler, A. Walsh, D.O. Scanlon, Interplay of Orbital and

- 1 Relativistic Effects in Bismuth Oxyhalides: BiOF, BiOCl, BiOBr, and BiOI, *Chem.*
2 *Mater.* 28 (2016) 1980–1984. <https://doi.org/10.1021/acs.chemmater.6b00349>.
- 3 [9] L. Yao, H. Yang, Z. Chen, M. Qiu, B. Hu, X. Wang, Bismuth oxychloride-based
4 materials for the removal of organic pollutants in wastewater, *Chemosphere.* 273 (2021)
5 128576. <https://doi.org/10.1016/j.chemosphere.2020.128576>.
- 6 [10] L. Chen, R. Huang, M. Xiong, Q. Yuan, J. He, J. Jia, M.Y. Yao, S.L. Luo, C.T. Au, S.F.
7 Yin, Room-temperature synthesis of flower-like BiOX (X=Cl, Br, I) hierarchical
8 structures and their visible-light photocatalytic activity, *Inorg. Chem.* 52 (2013) 11118–
9 11125. <https://doi.org/10.1021/ic401349j>.
- 10 [11] J. Lv, Q. Hu, C. Cao, Y. Zhao, Modulation of valence band maximum edge and
11 photocatalytic activity of BiOX by incorporation of halides, *Chemosphere.* 191 (2018)
12 427–437. <https://doi.org/10.1016/j.chemosphere.2017.09.149>.
- 13 [12] H. An, D.U. Yi, T.M. Wang, C. Wang, W. Hao, J. Zhang, Photocatalytic properties of
14 BiOX (X = Cl, Br, and I), *Rare Met.* 27 (2008) 243–250. [https://doi.org/10.1016/S1001-](https://doi.org/10.1016/S1001-0521(08)60123-0)
15 [0521\(08\)60123-0](https://doi.org/10.1016/S1001-0521(08)60123-0).
- 16 [13] I.D. Sharma, G.K. Tripathi, V.K. Sharma, S.N. Tripathi, R. Kurchania, C. Kant, A.K.
17 Sharma, K.K. Saini, One-pot synthesis of three bismuth oxyhalides (BiOCl, BiOBr,
18 BiOI) and their photocatalytic properties in three different exposure conditions, *Cogent*
19 *Chem.* 1 (2015) 1–15. <https://doi.org/10.1080/23312009.2015.1076371>.
- 20 [14] D. Kato, K. Hongo, R. Maezono, M. Higashi, H. Kunioku, M. Yabuuchi, H. Suzuki, H.
21 Okajima, C. Zhong, K. Nakano, R. Abe, H. Kageyama, Valence Band Engineering of
22 Layered Bismuth Oxyhalides toward Stable Visible-Light Water Splitting: Madelung
23 Site Potential Analysis, *J. Am. Chem. Soc.* 139 (2017) 18725–18731.
24 <https://doi.org/10.1021/jacs.7b11497>.
- 25 [15] X. Jin, L. Ye, H. Xie, G. Chen, Bismuth-rich bismuth oxyhalides for environmental and

- 1 energy photocatalysis, *Coord. Chem. Rev.* 349 (2017).
2 <https://doi.org/10.1016/j.ccr.2017.08.010>.
- 3 [16] G. Wu, Y. Zhao, Y. Li, B. Souvanhthong, H. Ma, J. Zhao, Facile aqueous synthesis of
4 $\text{Bi}_4\text{O}_5\text{Br}_2$ nanosheets for improved visible-light photocatalytic activity, *Ceram. Int.* 44
5 (2018) 5392–5401. <https://doi.org/10.1016/j.ceramint.2017.12.168>.
- 6 [17] X. Zhang, P. Yang, B. Yang, Y. Bai, W. Liu, K. Zhang, Synthesis of the composite
7 catalyst $\text{Bi}_4\text{O}_5\text{Br}_2/\text{BiOBr}$ for the improved photocatalytic degradation of oilfield
8 produced wastewater, *J. Mater. Sci. Mater. Electron.* 30 (2019) 17276–17287.
9 <https://doi.org/10.1007/s10854-019-02074-6>.
- 10 [18] R. Li, F. Xie, J. Liu, Y. Wang, Y. Wang, X. Zhang, C. Fan, Synthesis of $\text{Bi}_4\text{O}_5\text{Br}_2$ from
11 reorganization of BiOBr and its excellent visible light photocatalytic activity, *Dalt.*
12 *Trans.* 45 (2016) 9182–9186. <https://doi.org/10.1039/c6dt00997b>.
- 13 [19] J. Xu, Y.G. Mao, T. Liu, Y. Peng, Synthesis of a novel one-dimensional BiOBr -
14 $\text{Bi}_4\text{O}_5\text{Br}_2$ heterostructure with a high quality interface and its enhanced visible-light
15 photocatalytic activity, *CrystEngComm.* 20 (2018) 2292–2298.
16 <https://doi.org/10.1039/c8ce00157j>.
- 17 [20] X. Su, D. Wu, Facile construction of the phase junction of BiOBr and $\text{Bi}_4\text{O}_5\text{Br}_2$
18 nanoplates for ciprofloxacin photodegradation, *Mater. Sci. Semicond. Process.* 80
19 (2018) 123–130. <https://doi.org/10.1016/j.mssp.2018.02.034>.
- 20 [21] X. Jin, C. Lv, X. Zhou, H. Xie, S. Sun, Y. Liu, Q. Meng, G. Chen, A bismuth rich hollow
21 $\text{Bi}_4\text{O}_5\text{Br}_2$ photocatalyst enables dramatic CO_2 reduction activity, *Nano Energy.* 64
22 (2019) 103955. <https://doi.org/10.1016/j.nanoen.2019.103955>.
- 23 [22] J. Zhao, M. Ji, J. Di, Y. Ge, P. Zhang, J. Xia, H. Li, Synthesis of $\text{g-C}_3\text{N}_4/\text{Bi}_4\text{O}_5\text{Br}_2$ via
24 reactable ionic liquid and its cooperation effect for the enhanced photocatalytic behavior
25 towards ciprofloxacin degradation, *J. Photochem. Photobiol. A Chem.* 347 (2017) 168–

- 1 176. <https://doi.org/10.1016/j.jphotochem.2017.07.023>.
- 2 [23] P. Li, W. Cao, Y. Zhu, Q. Teng, L. Peng, C. Jiang, C. Feng, Y. Wang, NaOH-induced
3 formation of 3D flower-sphere BiOBr/Bi₄O₅Br₂ with proper-oxygen vacancies via in-
4 situ self-template phase transformation method for antibiotic photodegradation, *Sci.*
5 *Total Environ.* 715 (2020) 136809. <https://doi.org/10.1016/j.scitotenv.2020.136809>.
- 6 [24] J. Xu, Y.G. Mao, T. Liu, Y. Peng, Synthesis of a novel one-dimensional BiOBr-
7 Bi₄O₅Br₂ heterostructure with a high quality interface and its enhanced visible-light
8 photocatalytic activity, *CrystEngComm.* 20 (2018) 2292–2298.
9 <https://doi.org/10.1039/c8ce00157j>.
- 10 [25] M. Li, Y. Cui, Y. Jin, H. Li, Facile hydrolysis synthesis of Bi₄O₅Br₂ photocatalyst with
11 excellent visible light photocatalytic performance for the degradation of resorcinol, *RSC*
12 *Adv.* 6 (2016) 47545–47551. <https://doi.org/10.1039/c6ra07386g>.
- 13 [26] C. Zheng, G. He, X. Xiao, M. Lu, H. Zhong, X. Zuo, J. Nan, Selective photocatalytic
14 oxidation of benzyl alcohol into benzaldehyde with high selectivity and conversion ratio
15 over Bi₄O₅Br₂ nanoflakes under blue LED irradiation, *Appl. Catal. B Environ.* 205
16 (2017) 201–210. <https://doi.org/10.1016/j.apcatb.2016.12.026>.
- 17 [27] Y. Bai, T. Chen, P. Wang, L. Wang, L. Ye, Bismuth-rich Bi₄O₅X₂ (X = Br, and I)
18 nanosheets with dominant {1 0 1} facets exposure for photocatalytic H₂ evolution,
19 *Chem. Eng. J.* 304 (2016) 454–460. <https://doi.org/10.1016/j.cej.2016.06.100>.
- 20 [28] Y. Bai, P. Yang, L. Wang, B. Yang, H. Xie, Y. Zhou, L. Ye, Ultrathin Bi₄O₅Br₂
21 nanosheets for selective photocatalytic CO₂ conversion into CO, *Chem. Eng. J.* 360
22 (2019) 473–482. <https://doi.org/10.1016/j.cej.2018.12.008>.
- 23 [29] D. Majhi, K. Das, A. Mishra, R. Dhiman, B.G. Mishra, One pot synthesis of
24 CdS/BiOBr/Bi₂O₂CO₃: A novel ternary double Z-scheme heterostructure photocatalyst
25 for efficient degradation of atrazine, *Appl. Catal. B Environ.* 260 (2020) 118222.

- 1 <https://doi.org/10.1016/j.apcatb.2019.118222>.
- 2 [30] S. Heidari, M. Haghighi, M. Shabani, Sunlight-activated BiOCl/BiOBr–Bi₂₄O₃₁Br₁₀
3 photocatalyst for the removal of pharmaceutical compounds, *J. Clean. Prod.* 259 (2020)
4 120679. <https://doi.org/10.1016/j.jclepro.2020.120679>.
- 5 [31] Y. Yu, P. Ju, D. Zhang, X. Han, X. Yin, L. Zheng, C. Sun, Peroxidase-like activity of
6 FeVO₄ nanobelts and its analytical application for optical detection of hydrogen
7 peroxide, *Sensors Actuators B Chem.* 233 (2016) 162–172.
8 <https://doi.org/10.1016/j.snb.2016.04.041>.
- 9 [32] B. Ozturk, G.S. Pozan Soylu, Synthesis of surfactant-assisted FeVO₄ nanostructure:
10 Characterization and photocatalytic degradation of phenol, *J. Mol. Catal. A Chem.* 398
11 (2015) 65–71. <https://doi.org/10.1016/j.molcata.2014.11.013>.
- 12 [33] A. Chachvalvutikul, J. Jakmunee, S. Thongtem, S. Kittiwachana, S. Kaowphong, Novel
13 FeVO₄/Bi₇O₉I₃ nanocomposite with enhanced photocatalytic dye degradation and
14 photoelectrochemical properties, *Appl. Surf. Sci.* 475 (2019) 175–184.
15 <https://doi.org/10.1016/j.apsusc.2018.12.214>.
- 16 [34] A. Chachvalvutikul, S. Kaowphong, Direct Z-scheme FeVO₄/BiOCl heterojunction as a
17 highly efficient visible-light-driven photocatalyst for photocatalytic dye degradation and
18 Cr(VI) reduction, *Nanotechnology.* 31 (2020). [https://doi.org/10.1088/1361-](https://doi.org/10.1088/1361-6528/ab61d1)
19 [6528/ab61d1](https://doi.org/10.1088/1361-6528/ab61d1).
- 20 [35] Q. Wang, X. Chen, K. Yu, Y. Zhang, Y. Cong, Synergistic photosensitized removal of
21 Cr(VI) and Rhodamine B dye on amorphous TiO₂ under visible light irradiation, *J.*
22 *Hazard. Mater.* 246–247 (2013) 135–144.
23 <https://doi.org/10.1016/j.jhazmat.2012.12.017>.
- 24 [36] F. Hashemzadeh, A. Gaffarinejad, R. Rahimi, Porous p-NiO/n-Nb₂O₅ nanocomposites
25 prepared by an EISA route with enhanced photocatalytic activity in simultaneous Cr(VI)

- 1 reduction and methyl orange decolorization under visible light irradiation, *J. Hazard.*
2 *Mater.* 286 (2015) 64–74. <https://doi.org/10.1016/j.jhazmat.2014.12.038>.
- 3 [37] L. Huang, Q. Chan, X. Wu, H. Wang, Y. Liu, The simultaneous photocatalytic
4 degradation of phenol and reduction of Cr (VI) by TiO₂/CNTs, *J. Ind. Eng. Chem.* 18
5 (2012) 574–580. <https://doi.org/10.1016/j.jiec.2011.11.060>.
- 6 [38] J. Xu, L. Li, C. Guo, Y. Zhang, S. Wang, Removal of benzotriazole from solution by
7 BiOBr photocatalysis under simulated solar irradiation, *Chem. Eng. J.* 221 (2013) 230–
8 237. <https://doi.org/10.1016/j.cej.2013.01.081>.
- 9 [39] X. Li, C. Niu, D. Huang, X. Wang, X. Zhang, G. Zeng, Q. Niu, Preparation of
10 magnetically separable Fe₃O₄/BiOI nanocomposites and its visible photocatalytic
11 activity, *Appl. Surf. Sci.* 286 (2013) 40–46.
12 <https://doi.org/10.1016/j.apsusc.2013.08.139>.
- 13 [40] A. Chachvalvutikul, T. Luangwanta, S. Pattison, G.J. Hutchings, S. Kaowphong,
14 Enhanced photocatalytic degradation of organic pollutants and hydrogen production by
15 a visible light–responsive Bi₂WO₆/ZnIn₂S₄ heterojunction, *Appl. Surf. Sci.* 544 (2020)
16 148885. <https://doi.org/10.1016/j.apsusc.2020.148885>.
- 17 [41] C. Zeng, Y. Hu, H. Huang, BiOBr_{0.75}I_{0.25}/BiOIO₃ as a Novel Heterojunctional
18 Photocatalyst with Superior Visible-Light-Driven Photocatalytic Activity in Removing
19 Diverse Industrial Pollutants, *ACS Sustain. Chem. Eng.* 5 (2017) 3897–3905.
20 <https://doi.org/10.1021/acssuschemeng.6b03066>.
- 21 [42] N. Chumha, T. Thongtem, S. Thongtem, S. Kittiwachana, S. Kaowphong, Effect of
22 different polyol solvents on the synthesis of CuInS₂ nanoparticles by cyclic microwave
23 irradiation, *J. Ceram. Process. Res.* 18 (2017) 871–874.
- 24 [43] S. Samanta, R. Srivastava, Thermal catalysis vs. photocatalysis: A case study with
25 FeVO₄/g-C₃N₄ nanocomposites for the efficient activation of aromatic and benzylic C–

- 1 H bonds to oxygenated products, *Appl. Catal. B Environ.* 218 (2017) 621–636.
2 <https://doi.org/10.1016/j.apcatb.2017.06.043>.
- 3 [44] Q. Nong, M. Cui, H. Lin, L. Zhao, Y. He, Fabrication, characterization and
4 photocatalytic activity of g-C₃N₄ coupled with FeVO₄ nanorod, *RSC Adv.* 5 (2015)
5 27933–27939. <https://doi.org/10.1039/C5RA01484K>.
- 6 [45] X. She, Z. Zhang, M. Baek, K. Yong, Elevated photoelectrochemical activity of
7 FeVO₄/ZnFe₂O₄/ZnO branch-structures via slag assisted-synthesis, *RSC Adv.* 7 (2017)
8 16787–16794. <https://doi.org/10.1039/C7RA00812K>.
- 9 [46] X. Liu, G. Xie, C. Huang, Q. Xu, Y. Zhang, Y. Luo, A facile method for preparing VO₂
10 nanobelts, *Mater. Lett.* 62 (2008) 1878–1880.
11 <https://doi.org/10.1016/j.matlet.2007.10.022>.
- 12 [47] J. Gao, Y. Gao, Z. Sui, Z. Dong, S. Wang, D. Zou, Hydrothermal synthesis of
13 BiOBr/FeWO₄ composite photocatalysts and their photocatalytic degradation of
14 doxycycline, *J. Alloys Compd.* 732 (2018) 43–51.
15 <https://doi.org/10.1016/j.jallcom.2017.10.092>.
- 16 [48] Y. Yang, J. Wu, T. Xiao, Z. Tang, J. Shen, H. Li, Y. Zhou, Z. Zou, Urchin-like
17 hierarchical CoZnAl-LDH/RGO/g-C₃N₄ hybrid as a Z-scheme photocatalyst for
18 efficient and selective CO₂ reduction, *Appl. Catal. B Environ.* 255 (2019) 117771.
19 <https://doi.org/10.1016/j.apcatb.2019.117771>.
- 20 [49] S.R. Zhu, M.K. Wu, W.N. Zhao, F.Y. Yi, K. Tao, L. Han, Fabrication of
21 heterostructured BiOBr/Bi₂₄O₃₁Br₁₀/TiO₂ photocatalyst by pyrolysis of MOF composite
22 for dye degradation, *J. Solid State Chem.* 255 (2017) 17–26.
23 <https://doi.org/10.1016/j.jssc.2017.07.038>.
- 24 [50] K.W. Bladh, M.C. Nichols, M. Data, P. Each, K.W. Bladh, R.A. Bideaux, E. Anthony-
25 morton, G. Barbara, J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols,

- 1 Handbook of Mineralogy Crystal Data, Mineral Data Publishing, Virginia, USA, 2010.
- 2 [51] Shahid-ul-Islam, *Advanced Materials for Wastewater Treatment*, 1st ed., Scrivener
3 Publishing, Beverly, Massachusetts, 2017. <https://doi.org/10.1002/9781119407805>.
- 4 [52] G. Wu, Y. Zhao, Y. Li, H. Ma, J. Zhao, pH-dependent synthesis of iodine-deficient
5 bismuth oxyiodide microstructures: Visible-light photocatalytic activity, *J. Colloid
6 Interface Sci.* 510 (2018) 228–236. <https://doi.org/10.1016/j.jcis.2017.09.053>.
- 7 [53] C.Y. Wang, X. Zhang, H. Bin Qiu, W.K. Wang, G.X. Huang, J. Jiang, H.Q. Yu,
8 Photocatalytic degradation of bisphenol A by oxygen-rich and highly visible-light
9 responsive Bi₁₂O₁₇Cl₂ nanobelts, *Appl. Catal. B Environ.* 200 (2017) 659–665.
10 <https://doi.org/10.1016/j.apcatb.2016.07.054>.
- 11 [54] G. Ji, H. Shen, J. Zhang, A.A. Al-Saadi, X. Chang, M.A. Ali, Q. Zhou, M. Du, Y. Liu,
12 M.A. Gondal, Photodegradation of Rhodamine B over unexcited semiconductor
13 compounds of BiOCl and BiOBr, *J. Colloid Interface Sci.* 377 (2012) 291–298.
14 <https://doi.org/10.1016/j.jcis.2012.03.021>.
- 15 [55] Y.Y. Lee, J.H. Moon, Y.S. Choi, G.O. Park, M. Jin, L.Y. Jin, D. Li, J.Y. Lee, S.U. Son,
16 J.M. Kim, Visible-Light Driven Photocatalytic Degradation of Organic Dyes over
17 Ordered Mesoporous Cd_xZn_{1-x}S Materials, *J. Phys. Chem. C.* 121 (2017) 5137–5144.
18 <https://doi.org/10.1021/acs.jpcc.7b00038>.
- 19 [56] J. Jiang, K. Zhao, X. Xiao, L. Zhang, Synthesis and facet-dependent photoreactivity of
20 BiOCl single-crystalline nanosheets, *J. Am. Chem. Soc.* 134 (2012) 4473–4476.
21 <https://doi.org/10.1021/ja210484t>.
- 22 [57] W. Cui, W. An, L. Liu, J. Hu, Y. Liang, Synthesis of CdS/BiOBr composite and its
23 enhanced photocatalytic degradation for Rhodamine B, *Appl. Surf. Sci.* 319 (2014) 298–
24 305. <https://doi.org/10.1016/j.apsusc.2014.05.179>.
- 25 [58] Z. Cui, M. Si, Z. Zheng, L. Mi, W. Fa, H. Jia, Preparation and characterization of

- 1 Ag₃PO₄/BiOI composites with enhanced visible light driven photocatalytic
2 performance, *Catal. Commun.* 42 (2013) 121–124.
3 <https://doi.org/10.1016/j.catcom.2013.08.011>.
- 4 [59] C. Zhao, Z. Wang, X. Li, X. Yi, H. Chu, X. Chen, C.C. Wang, Facile fabrication of
5 BUC-21/Bi₂₄O₃₁Br₁₀ composites for enhanced photocatalytic Cr(VI) reduction under
6 white light, *Chem. Eng. J.* (2019) 123431. <https://doi.org/10.1016/j.cej.2019.123431>.
- 7 [60] A.D. Bokare, W. Choi, Chromate-Induced Activation of Hydrogen Peroxide for
8 Oxidative Degradation of Aqueous Organic Pollutants, *Environ. Sci. Technol.* 44 (2010)
9 7232–7237. <https://doi.org/10.1021/es903930h>.
- 10 [61] N. Unceta, F. Séby, J. Malherbe, O.F.X. Donard, Chromium speciation in solid matrices
11 and regulation: A review, *Anal. Bioanal. Chem.* 397 (2010) 1097–1111.
12 <https://doi.org/10.1007/s00216-009-3417-1>.
- 13 [62] Q. Wang, X. Shi, E. Liu, J.C. Crittenden, X. Ma, Y. Zhang, Y. Cong, Facile synthesis
14 of AgI/BiOI-Bi₂O₃ multi-heterojunctions with high visible light activity for Cr(VI)
15 reduction, *J. Hazard. Mater.* 317 (2016) 8–16.
16 <https://doi.org/10.1016/j.jhazmat.2016.05.044>.
- 17 [63] H. Xu, Z. Wu, M. Ding, X. Gao, Microwave-assisted synthesis of flower-like BN/BiOCl
18 composites for photocatalytic Cr(VI) reduction upon visible-light irradiation, *Mater.*
19 *Des.* 114 (2017) 129–138. <https://doi.org/10.1016/j.matdes.2016.10.057>.
- 20 [64] J. Qu, D. Chen, N. Li, Q. Xu, H. Li, J. He, J. Lu, Coral-inspired nanoscale design of
21 porous SnS₂ for photocatalytic reduction and removal of aqueous Cr(VI), *Appl. Catal.*
22 *B Environ.* 207 (2017) 404–411. <https://doi.org/10.1016/j.apcatb.2017.02.050>.
- 23 [65] S. Merouani, O. Hamdaoui, F. Saoudi, M. Chiha, Sonochemical degradation of
24 Rhodamine B in aqueous phase : Effects of additives, *Chem. Eng. J.* 158 (2010) 550–
25 557. <https://doi.org/10.1016/j.cej.2010.01.048>.

- 1 [66] H. Yu, B. Huang, H. Wang, X. Yuan, L. Jiang, Z. Wu, J. Zhang, G. Zeng, Facile
2 construction of novel direct solid-state Z-scheme AgI/BiOBr photocatalysts for highly
3 effective removal of ciprofloxacin under visible light exposure: Mineralization
4 efficiency and mechanisms, *J. Colloid Interface Sci.* 522 (2018) 82–94.
5 <https://doi.org/10.1016/j.jcis.2018.03.056>.
- 6 [67] S.R. Zhu, Q. Qi, W.N. Zhao, Y. Fang, L. Han, Enhanced photocatalytic activity in hybrid
7 composite combined BiOBr nanosheets and Bi₂S₃ nanoparticles, *J. Phys. Chem. Solids.*
8 121 (2018) 163–171. <https://doi.org/10.1016/j.jpcs.2018.05.023>.
- 9 [68] M. Jiang, Y. Shi, J. Huang, L. Wang, H. She, J. Tong, B. Su, Q. Wang, Synthesis of
10 Flowerlike g-C₃N₄/BiOBr with Enhanced Visible Light Photocatalytic Activity for Dye
11 Degradation, *Eur. J. Inorg. Chem.* 2018 (2018) 1834–1841.
12 <https://doi.org/10.1002/ejic.201800110>.
- 13 [69] S. Wang, X. Yang, X. Zhang, X. Ding, Z. Yang, K. Dai, H. Chen, A plate-on-plate
14 sandwiched Z-scheme heterojunction photocatalyst: BiOBr-Bi₂MoO₆ with enhanced
15 photocatalytic performance, *Appl. Surf. Sci.* 391 (2017) 194–201.
16 <https://doi.org/10.1016/j.apsusc.2016.07.070>.
- 17 [70] S. Guo, W. Yang, L. You, J. Li, J. Chen, K. Zhou, Simultaneous reduction of Cr(VI)
18 and degradation of tetracycline hydrochloride by a novel iron-modified rectorite
19 composite through heterogeneous photo-Fenton processes, *Chem. Eng. J.* 393 (2020)
20 124758. <https://doi.org/10.1016/j.cej.2020.124758>.
- 21 [71] C. Wang, X. Zhang, H. Qiu, G. Huang, H. Yu, Bi₂₄O₃₁Br₁₀ nanosheets with controllable
22 thickness for visible – light – driven catalytic degradation of tetracycline hydrochloride,
23 *Appl. Catal. B Environ.* 205 (2017) 615–623.
24 <https://doi.org/10.1016/j.apcatb.2017.01.015>.
- 25 [72] S. Lia, G. Zhu, Y. Jia, L. Pan, J. Nie, F. Rao, J. Gao, F. Zhang, C. Li, TiO₂ with exposed

- 1 (001) facets/Bi₄O₅Br₂ nanosheets heterojunction with enhanced photocatalytic for NO
2 removal, *Nanotechnology*. 31 (2020) 254002. [https://doi.org/10.1088/1361-](https://doi.org/10.1088/1361-6528/ab7583)
3 [6528/ab7583](https://doi.org/10.1088/1361-6528/ab7583).
- 4 [73] C. Zeng, Y. Hu, Y. Guo, T. Zhang, F. Dong, X. Du, Y. Zhang, H. Huang, Achieving
5 tunable photocatalytic activity enhancement by elaborately engineering composition-
6 adjustable polynary heterojunctions photocatalysts, *Appl. Catal. B Environ.* 194 (2016)
7 62–73. <https://doi.org/10.1016/j.apcatb.2016.04.036>.
- 8 [74] J. Yu, S. Zhuang, X. Xu, W. Zhu, B. Feng, J. Hu, Photogenerated electron reservoir in
9 hetero-p-n CuO-ZnO nanocomposite device for visible-light-driven photocatalytic
10 reduction of aqueous Cr(vi), *J. Mater. Chem. A*. 3 (2015) 1199–1207.
11 <https://doi.org/10.1039/c4ta04526b>.
- 12 [75] Z. Fang, Q. Li, L. Su, J. Chen, K.C. Chou, X. Hou, Efficient synergy of photocatalysis
13 and adsorption of hexavalent chromium and rhodamine B over Al₄SiC₄/rGO hybrid
14 photocatalyst under visible-light irradiation, *Appl. Catal. B Environ.* 241 (2019) 548–
15 560. <https://doi.org/10.1016/j.apcatb.2018.09.074>.
- 16 [76] Y. Guo, C. Li, Y. Guo, X. Wang, X. Li, Ultrasonic-assisted synthesis of mesoporous g-
17 C₃N₄/Na-bentonite composites and its application for efficient photocatalytic
18 simultaneous removal of Cr(VI) and RhB, *Colloids Surfaces A Physicochem. Eng. Asp.*
19 578 (2019) 123624. <https://doi.org/10.1016/j.colsurfa.2019.123624>.
- 20 [77] M. Qiu, Z. Liu, S. Wang, B. Hu, The photocatalytic reduction of U(VI) into U(IV) by
21 ZIF-8/g-C₃N₄ composites at visible light, *Environ. Res.* (2020) 110349.
22 <https://doi.org/10.1016/j.envres.2020.110349>.
- 23 [78] H. Wang, H. Guo, N. Zhang, Z. Chen, B. Hu, X. Wang, Enhanced Photoreduction of
24 U(VI) on C₃N₄ by Cr(VI) and Bisphenol A: ESR, XPS, and EXAFS Investigation,
25 *Environ. Sci. Technol.* 53 (2019) 6454–6461. <https://doi.org/10.1021/acs.est.8b06913>.

- 1 [79] A. Chachvalvutikul, W. Pudkon, T. Luangwanta, T. Thongtem, S. Thongtem, S.
2 Kittiwachana, S. Kaowphong, Enhanced photocatalytic degradation of methylene blue
3 by a direct Z-scheme Bi₂S₃/ZnIn₂S₄ photocatalyst, Mater. Res. Bull. 111 (2019) 53–60.
4 <https://doi.org/10.1016/j.materresbull.2018.10.034>.
- 5 [80] F. Qiu, W. Li, F. Wang, H. Li, X. Liu, J. Sun, In-situ synthesis of novel Z-scheme
6 SnS₂/BiOBr photocatalysts with superior photocatalytic efficiency under visible light, J.
7 Colloid Interface Sci. 493 (2017) 1–9. <https://doi.org/10.1016/j.jcis.2016.12.066>.
- 8 [81] Y.L. Min, K. Zhang, Y.C. Chen, Y.G. Zhang, Synthesis of novel visible light responding
9 vanadate/TiO₂ heterostructure photocatalysts for application of organic pollutants,
10 Chem. Eng. J. 175 (2011) 76–83. <https://doi.org/10.1016/j.cej.2011.09.042>.
- 11