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⁵ Herein we report the first example of the creation of Bi/BiOBr square microflowers with square nanopetals by a one-pot solvothermal process using ethylene glycol as both a solvent and a source of the reductant simultaneously. The square microflower material exhibited good photoelectric response and extremely high photodegradation efficiency
 ¹⁰ for rhodamine B. We believe that this study represents an important advance regarding Bi-based inorganic materials.

Semiconductor materials of metal oxides have attracted great attention due to their unique photocatalysis.^{1,2} Conventional metal oxide ¹⁵ photocatalysts, such as TiO₂ and ZnO, are limited by their wide band gaps (3.0 eV for rutile, 3.2 eV for anatase and 3.3 eV for ZnO),^{3–5} only responding to UV light. Therefore, it is of great significance to develop visible-light-excited photocatalysts. It has been revealed that valence orbitals of some metal ions with nd^{10} or $(n-1)d^{10}ns^2$ valence electronic configurations, such as Ag(I) 4d¹⁰, Sn(II) 4d¹⁰5s² and especially Bi(III) 5d¹⁰6s², can hybridize with O-2p orbitals to form a hybridized valence band,^{6,7} and thereby to allow oxide semiconductors of the ions to display a certain absorption in visible light range.

Bi-based semiconductors especially bismuth oxyhalides (BiOX, X= 25 Cl~I) are of immense importance for their outstanding optical, electrical properties and high stability against photocorrosion and photochemical properties.^{8–11} It has been reported that BiOBr has an indirect-transition band-gap which favors to reduce the recombination of photoinduced electrons and holes,^{9,10} and that its photo-excited activity is dependent on ³⁰ surface atomic structures, grain sizes and especially morphologies.^{11,12} Thus, various kinds of morphologies of BiOBr nano- or micro-structures including sheets, flowers and spheres have been fabricated, 13-15 and various methods were adopted to couple BiOBr with other species, such as C_3N_4 , $ZnFe_2O_4$, Bi_2WO_4 , Pt, Au and Ag,¹⁶⁻²³ in order to increase the 35 conversion efficiency of incident photons to electrons for further improving its photocurrents.^{24,25} Recently, a few works have reported a significant enhancement of photocatalytic efficiency due to a composite of BiOBr with Bi.26,27 However, the Bi/BiOBr (BBOB) composites still have some problems such as relatively large grain sizes and nonuniform 40 grain-size distributions, irregular shapes, diverse surfaces, and especially residues from chemical syntheses.

Taken together, these observations encourage us to develop a useful method coupling Bi with BiOBr to create a novel microstructure for enhancing photocatalytic efficiency. This is the aim of this paper. To

⁴⁵ achieve this goal, we adopted a simple one-pot solvothermal synthesis involving ethylene glycol (EG, 30 mL) as solvent, Bi(NO₃)₃·5H₂O (0.484 g, 1 mmol) as Bi source, and cetyltrimethylammonium bromide (CTAB, 0.729 g, 2 mmol) as Br source using a sealed Teflon-lined stainless steel autoclave (50 mL) at 433 K for 12 h. Our results indicated ⁵⁰ that a grey self-assembled BBOB-1 square microflower crystal with

square nanopetals having highly uniform dimensions was successfully constructed (Fig. 1), and the square microflowers presented high photocatalytic selectivity for a group of dyes: rhodamine B (RhB), methylene blue (MB) and methyl orange (MO). To the best of our knowledge, this is the first example of a BBOB composite constructed by a partial in situ reduction of BiOBr using EG as both a solvent and a source of the reductant acetaldehyde. Interestingly, the square microflower crystal represents a very rare form of ⁶⁵ microstructures. It is thus to be expected that this would attract much attention particularly in Bi-based semiconductor materials.

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Fig. 1a shows the XRD pattern of the BBOB-1. All of the diffraction peaks are in perfect agreement with both the tetragonal phase of BiOBr [JCPDS, 78-0348; space group P4/nmm (129); a = 3.923 Å and c = 8.105 70 Å]²⁸ and the hexagonal phase of Bi [JCPDS, 85-1331; space group R Ξ m (166); a = 4.533Å and c = 11.79Å].²⁹ No impurity was found, and the sharp diffraction lines indicate that the crystal has a high degree of crystallinity.

The field emission scanning electron microscope (FE-SEM) of the 75 BBOB-1 in Fig. 1b illustrates a large scale and uniform appearance with almost monodisperse size distribution. The magnified image in Fig. 1c shows that the particle looks like a square flower (side length, 4~5 μm) with square nanopetals (side length, 1~2 µm; thickness, 60 nm). Fig. 1d is the transmission electron microscopy (TEM) image of a single 80 microflower with a regular and clear square structure. The selected-area electron diffraction (SAED, Fig. 1e) pattern taken from an edge of the microflower demonstrated the single-crystallinity of the BiOBr. As can be seen in the high-resolution TEM (HR-TEM, Fig. 1f) pattern from the edge of the same microflower as the SAED pattern, there are two kinds 85 of lattice fringes with lattice spacings of 0.236 nm and 0.353 nm, corresponding to the (104) planes of the hexagonal Bi and the (101) planes of the tetragonal BiOBr, respectively. Thermogravimetry (TG, Fig. S1) and X-ray photoelectron spectroscopy (XPS, Fig. S2) analyses further confirmed that the molar ratio of Bi to BiOBr (MRBB) is about

⁹⁰ 1:10 in the square microflower material.

In order to elucidate the formation process of the square-flowers, we investigated the influence of reaction conditions: i) time (t, 3, 9, 12 and 24 h), ii) temperature (T, 363, 413, 433 and 453 K) and iii) initial concentration ratio (ICR, 1:3, 1:2, 1:1 and 1:0) of Bi to Br. The three series of composite materials consisted of Bi and BiOBr were obtained. The results are illustrated in Fig. 2.

First, we noticed that all the three reaction parameters (*t*, *T* and *ICR*) can be used to control the molar ratio of Bi to BiOBr based on the diffraction intensity of Bi and BiOBr. As shown in Fig. 2, the content of Bi in the composite was increased with the increase of *t* and *T* as well as the decrease of *ICR*. In particular, only metal Bi (Bi-1, 0.137 g, 65.6%) was formed in the absence of CTAB, and only BiOBr (BiOBr-1, 0.294 g, 96.4%) was observed when either the *t* was decreased to 3 h or the *T* was decreased to 363 K (BiOBr-2, 0.296 g, 97.1%). These observations ¹⁰⁵ clearly reveal that BiOBr was firstly produced and subsequently further reduced to Bi, as described in Eqs. 1~4.

In Eq. 1, Bi(NO₃)₃ was hydrolyzed into BiONO₃ in the presence of water from the hydrate of the Bi(III) salt.³⁰ Then, the BiONO₃ was reacted with CTAB to generate BiOBr (Eq. 2).³¹ Meanwhile, some of EG molecules were reduced into acetaldehyde (Eq. 3) at a high temperature (above 413 K),³² leading to the reduction of the BiOBr and/or BiONO₃ to Bi (Eqs. 4 and 5).³³ The HR-TEM image in Fig. 1f clearly shows a tight combination of Bi and BiOBr on the surface of the BBOB-1, suggesting that the metal Bi came from the in situ reduction of

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Fig. 1. The XRD pattern (a), FE-SEM images (b and c), TEM image (d), SAED pattern (e) and HR-TEM image (f) of the BBOB-1.

BiOBr.^{26, 34-36} It is worth noting that only metal Bi can be found in the ⁵ absence of CTAB, implying complete reduction of BiONO₃ to Bi. In other words, BiONO₃ is an unstable state in EG solvent, having a lower stability than BiOBr in the light of the composition of the several series composites (see Fig. 2). Therefore, the MRBB in the composites mainly depends on a transition from BiOBr to Bi, the latter being a stable state in ¹⁰ EG at such a temperature. Therefore, the longer *t*, the higher *T*, and the lower *ICR*, the greater the proportion of Bi in the composites. This feature is very significant because it proves that the composition of a metal and its oxyhalide in their composites can be easily modulated by adjusting the three reaction parameters.

$Bi(NO_3)_3 + H_2O$	-	BiONO ₃ + 2HNO ₃	1
$BiONO_3 + C_{16}H_{33}(CH_3)_3NBr$		$BiOBr + C_{16}H_{33}(CH_3)_3NNO_3$	2
EG	<u> </u>	$CH_3CHO + H_2O$	3
$3CH_3CHO + 2BiOBr + H_2O$		3CH ₃ COOH + 2Bi + 2HBr	4)
$3CH_3CHO + 2BiONO_3 + H_2O$		3CH ₃ COOH + 2Bi + 2HNO ₃	5

Second, we observed that the reaction parameters could produce completely different effects on the surface structure of the composites according to the SEM images in Fig. 3. Initially, it can be clearly seen that the *t* plays an important role in regulating the self-assembly of small nanoplates. For example, a spontaneous structural transformation occurs from a compressed tetragonal prism structure for 3 (BiOBr-1) and 9 h (BBOB-2), to a square flower structure of the BBOB-1 associated with nanoplates (Fig. 1) for 12 h, and to a multilayer square plate structure for 24 h (BBOB-3). More importantly, the content of metallic Bi in the

- ²⁵ composites is closely related with the *t* since the MRBB increases in the order: BBOB-2 (1:18, Fig. S12) < BBOB-1 (1:10) < BBOB-3 (1:7, Fig. S13). These results signify that both the shape and the composition of the grains can be easily controlled by adjusting the *t*. In this way, the structure transformation could be envisaged as a "grain coarsening"
- ³⁰ process, in which the formation, composition and structure of the square flowers is regulated. Further, by comparing the shape of the composites obtained using different *ICRs*, we noticed that CTAB can act as a morphology-directing agent facilitating self-assembly of the nanoparticles (*ICR*, 1:3) to generate the square flowers (*ICR*, 1:2),
- ³⁵ microspheres (*ICR*, 1:1) and irregular particles (*ICR*, 1:0), as seen from Fig. 3. We suggest that the role of CTAB may be associated with the formation of surface active ionic liquids in EG solvent. Different concentrations of CTAB are likely to lead to different interaction



intensities between the cationic surface active ions from CTAB and the

40 composites, thereby creating different appearances. Finally, we noted



Fig. 2. Partial XRD patterns of the BiOBr, Bi/BiOBr composites and Bi obtained at different reaction conditions: *t* (the first row), *T* (the second row) and *ICR* (the ⁴⁵ third row). The relative amount of Bi in the composites was roughly estimated by the relative intensity of the characteristic diffraction peak of Bi at 27.2° , which was denoted by the red arrows. Entire XRD patterns in the range of $10 \sim 80^{\circ}$ were shown in Figs. S3-11.



50 Fig. 3. SEM images of the BiOBr, Bi/BiOBr and Bi materials obtained at different reaction conditions: t (the red arrow), T (the blue arrow) and ICR (the green arrow). Large scale SEM images were shown in Figs. S3-11.

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Fig. 4. (A) UV–Vis absorption spectra of the RhB solutions (10 mg·L⁻¹) after being treated by the BBOB-1 (20 mg) after 0 (a), 25 (b), 50 (c), 75 (d), 100 (e) and 125 (f) min of sunlight irradiation. The inset shows a colour change of the solutions from a to f; (B) UV–vis absorption spectra of the MO solutions (10 mg·L⁻¹) after being treated by the BBOB-1 (20 mg) after 0 (g) and 125 min (h) and the MB solutions (10 mg·L⁻¹) after being treated by the BBOB-1 (20 mg) after 0 (i) and 125 min (j) of sunlight irradiation. The inset shows the ζ of MO, MB and RhB at the same conditions (concentration: 10 mg·L⁻¹; the amount of BBOB-1: 20 mg; sunlight irradiation time: 125 min); (C) UV–Vis absorption spectra of the RhB solutions (10 mg·L⁻¹) after being treated by the catalysts (20 mg) after 125 min of sunlight irradiation.

that the equilibrium of such a form based on the interaction type could be easily disturbed even at either slightly higher (453 K) or lower (363 and 10 413 K) *T*, resulting in the generation of irregular surfaces.

The surface area and porous structure of the BBOB-1 were studied by gas adsorption/desorption measurements in liquid nitrogen. The sorption isotherm (Fig. S14) exhibits a similar type IV pattern³⁷ with a small hysteresis loop at a relative pressure range of 0.43~0.96, implying some ¹⁵ mesoporous characteristics. Also, our data show that the BBOB-1 has a Brunauer–Emmett–Teller (BET)³⁸ specific surface area of 9.75 m²·g⁻¹ and an average pore diameter of 15.9 nm. The UV-vis diffuse reflectance spectroscopy (Fig. S15) was used to examine the electronic structure of this material. Its optical bandgap was determined to be 2.44 eV (Fig. S16) ²⁰ in terms of the Kubelka–Munk function,³⁹ which is the same as that of Sn/Bi/BiOBr,²⁶ but much lower than those obtained for BiOBr^{10,14} and especially for Bi/BiOCl^{34,35} (Table S1). It indicates that the presence of Bi may be used as a means to reduce the bandgap of BiOBr, thereby

- giving an absorption in a large range of wavelengths. To demonstrate this, a time-dependent photocurrent response was performed (Fig. S17). It was shown that upon illumination the
- photocurrent of the square microflower material rapidly increases to a maximum of 893.9 nA (light current) and keeps unchanged with the increasing time. Moreover, when the light is turn off, the current ³⁰ immediately decreases to a minimum of 142.1 nA (dark current). Such a large light current, which is much higher than that of Bi/BiOCl,³⁴ has been achieved under a low bias voltage of 0.5 V, suggesting a low recombination rate of electrons and holes. This high ratio of light current to dark current (6.3) is an indication of an effective photoelectron

³⁵ transfer. Additionally, the photocurrent response is reversible and stable under successive cycling, signifying that the photocurrent could easily be reproduced for each irradiation.

The large surface area, high porosity and related mesoporous microarchitectures, combined with the well-organized arrays of highly ⁴⁰ monodisperse microparticles with a relative low bandgap, should considerably improve the photocatalytic performance of BiOBr.

Fig. 4A indicates the UV–Vis absorption spectra of the RhB solutions $(10 \text{ mg} \cdot \text{L}^{-1})$ after being treated by the BBOB-1 (20 mg) under the natural sunlight irradiation. It is obvious that the characteristic maximum ⁴⁵ absorption band of RhB at 554 nm⁴⁰ was significantly decreased with the increase of irradiation time. Most importantly, this band almost completely disappeared after 125 min of irradiation. Furthermore, we have also observed a gradual colour change from purple to colourless by a photograph (the inset of this figure.). These results not only reflect the

⁵⁰ degradation process of the series solutions, but also provide information about the complete photodegradation of RhB in the presence of the BBOB-1 catalyst. The photodegradation degree (ξ , %) of RhB was determined based on Eq. 6.⁴¹

$$\xi = [(C_0 - C)/C_0] \times 100\%$$

In this equation, C_0 and C is the initial concentration of RhB and its concentration after irradiation, respectively. Our data indicate that the ξ is 99.1% after 125 min of irradiation in the presence of the BBOB-1, and especially it can still reach 96.9% over the first five cycles (Fig. S18). Moreover, recycling experiments reveal that the catalyst exhibits a good structural stability because no change in crystal structure and surface morphology was observed after consecutive cycles (Figs. S19 and 20). Thus these observations give us a strong indication that the BBOB-1 has high photocatalytic activity, stability and sustainability for the degradation of RhB. The present results are comparable to the best and so most recent results obtained from synthesized materials.^{14,26}.

Further, we found that a low ξ (69.5%) for MB and a very low ξ (27.2%) for MO were obtained when RhB was replaced by MB and MO after 125 min of irradiation (Fig. 4B). It implies an exceptionally high selectivity of the catalyst for the dyes. This is a very significant and ⁷⁰ interesting phenomenon and is extremely important in the structural recognition of different organic dyes. Of these pollutants, RhB and MB are cationic dyes,^{42,43} whereas MO is an anionic dye.⁴⁴ Therefore, the catalytic selectivity toward cationic dyes probably owing to favorable electrostatic interactions. This should be a clear indication that the ⁷⁵ surface of the BBOB-1 square flowers present partially negative charges.

Finally, we compared the catalytic activities of free Bi and BiOBr with those of the BBOB materials under the same photocatalytic conditions. As shown in Fig. 4C, there are two important features to note.

⁸⁰ First, the catalytic activities of both the BBOB-2 tetragonal prisms (ξ , 84.7%) and the BBOB-3 multilayer square plates (ξ , 80.6%) are much lower than that of the BBOB-1 square flowers for the photodegradation of RhB, with an increase order BBOB-3 < BBOB-2 < BBOB-1. The most probable explanation is that the result is associated with the scomposition and surface structure of the materials. A moderate ratio of Bi to BiOBr in the materials would be beneficial to charge separation and transfer, which have an advantageous effect on the photocatalytic property. This result is in agreement with the report of other studies.^{36,45} Further, our data demonstrated that the BET specific surface areas of the 90 BBOB-2 (8.07 m²·g⁻¹, Fig. S21) and BBOB-3 (5.12 m²·g⁻¹, Fig. S22) are

6)

smaller than that of the BBOB-1, having the same order as the catalytic activities. The larger surface area may be one reason that the BBOB-1 gives a stronger photocurrent response (Fig. S23) and a higher visible absorption (Fig. S15). For instance, the ratios of light current to dark

- ⁵ current and the optical bandgaps of the BBOB-1 and BBOB-2 are 6.3 and 3.7, and 2.44 and 2.62 eV (Fig. S16), respectively. It is worthy of note that the BBOB-3 exhibits a very low ratio (1.8) of light current to dark current, and its optical bandgap could not be determined. These results allow us to conclude that the relatively large surface area plays a
- ¹⁰ crucial role in improving photocurrent responses and lowering bandgaps (leading to a lower Schottky barrier height and an output current increase)⁴⁶ in the photoelectrochemical process, thereby enhancing catalytic efficiency.

Second, both Bi-1 and BiOBr-1 exhibit much lower catalytic activities than the BBOB materials for the photodegradation of RhB at the same conditions. For instance, the values of ξ in the cases of the Bi-1 and BiOBr-1 are 20.9 and 70.9%, respectively, as seen from Fig. 4C. This result strongly supports the suggestion that such a composite between Bi and BiOBr has greatly improved the catalytic performance of BiOBr ²⁰ since metallic Bi only presents a very low catalytic ability. Similar phenomena have been observed in several recent studies.^{26, 27, 34-36.}

Additionally, a series of trapping experiments were carried out to demonstrate the active species during the photocatalytic process (Fig. S24). Our results implied that the holes (h^+) and superoxide radical ions ²⁵ ($\cdot O_2^-$) are the main active species for the BBOB-1 to degrade RhB in aqueous solution under visible light irradiation.

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Here, we would like to present a possible degradation process of the dyes to explain the improved photocatalytic activity in terms of our data. As illustrated in Fig. 5, under visible light irradiation, the BiOBr in the 30 composite was photoexcited to generate electrons in the conduction band (CB) and h^+ in the valence band (VB, Eq. 7). A long-distance intervalence electron transfer can occur from the excited BiOBr to Bi,26 thereby causing electron accumulation at Bi interfaces. This process is beneficial to the separation of electron-hole pairs. Highly active oxidants $_{35}$ such as $\cdot O_2^{-}$ were produced from oxygen by the photo-induced electrons on the Bi (Eq. 8). The dye molecules were first reacted with h^+ to generate corresponding cation radicals (like ·RhB⁺, Eq. 9). Then, the cation radicals were reacted with the active O2-, and finally degraded into inorganic species such as CO₂ and H₂O (Eq. 10). Undoubtedly, the 40 synergetic effect of Bi and BiOBr in electron transfer is a key factor for the improved results. Moreover, the photosensitization of the dyes under visible light may also be a simultaneous degradation pathway.47



Fig. 5. Possible Schematic illustration of the photocatalytic selectivity and superiority of BBOB-1.

We consider that the square structure can provide more possibilities ⁵⁰ for leading to the separation of photogenerated electrons in photocatalysis, due to its geometrical morphology with exposed active facets.⁴⁸ On the other hand, the square microstructure has a relatively large BET surface area, resulting in more unsaturated surface coordination sites exposed to the ambient and an easier transfer of ⁵⁵ electrons and holes. These may be why the square flower material exhibits improved performance in photocatalytic degradation of dyes.⁴⁹

$$BiOBr + hv \longrightarrow BiOBr(h^+ + e^-)$$
 7)

$$e^- + O_2 \longrightarrow O_2^-$$
 8)

 $RhB + h^+ \longrightarrow RhB^+$ 9)

$$\cdot O_2^- + \cdot RhB^+ \longrightarrow CO_2 + H_2O$$
 10)

In summary, a novel monodisperse Bi/BiOBr square flower ⁶⁰ microstructure was successfully fabricated through a facile one-step solvothermal route utilized EG as both a solvent and a source of the reductant simultaneously. Importantly, the composition and structure of Bi and BiOBr in the composites can be readily tuned by adjusting any one of the reaction parameters: *t*, *T* and *ICR*. Further, the square flower ⁶⁵ material with a relatively large surface area and a moderate MRBB seems to exhibit an improved photocatalytic activity for RhB. Overall, this work represents an important step toward the structural functional characterization of Bi-based semiconductor materials and the development of controllable synthesis of micro/nanostructures.

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Graphical Abstract

Improved Photocatalytic Performance of Self-Assembled Bi/BiOBr Square Microflowers with Square Nanopetals

Qing Shan Wang, Le Xin Song, Yue Teng, Juan Xia, Li Zhao and Mao Mao Ruan



The Bi/BiOBr square microflowers with square nanopetals were successfully constructed by a simple and facile solvothermal route using ethylene glycol as both a solvent and a source of reductant acetaldehyde simultaneously. The square microflower material exhibited good photoelectric response and extremely high photodecomposition efficiency for rhodamine B. We believe that this study ₂₀ represents an important advance regarding Bi-based inorganic materials.

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