



1	Synthesis of Ag/AgBr/Bi <sub>4</sub> O <sub>5</sub> Br <sub>2</sub> Plasmonic Heterojunction
2	Photocatalysts: Elevated Visible-light Photocatalytic Performance
3	and Z-scheme Mechanism
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20	ABSTRACT
21	The novel photocatalysts of Ag/AgBr/Bi <sub>4</sub> O <sub>5</sub> Br <sub>2</sub> layered microspheres (AAB-LMs)
22	were firstly constructed via the in-situ deposition and visible-light photoreduction
23	approach. Their compositions, structures, morphologies and optical properties were

were 28 and 3.4 times higher than those of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs towards degrading acid

characterized by various techniques. The photocatalytic efficiencies of AAB-LMs-10

orange II and aniline, respectively. The superior photocatalytic behavior of AAB-LMs

27 benefited from efficient separation and transfer of photo-generated charges, which was

28 mainly credited to the surface plasmon resonance effect of Ag nanoparticles and the

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synthetic interaction among Ag, AgBr and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>.  $\bullet$ O<sub>2</sub><sup>-</sup> and h<sup>+</sup> were characterized as the predominant photoactive species in this AAB-LMs-photocatalysis system. Moreover, due to the presence of radical species Br<sup>0</sup>, which was verified by the detection of bromoaniline and dibromoaniline during the photocatalytic degradation process of aniline, Z-scheme mechanism rather than the conventional heterojunction mode was more suitable to explain the enhanced photocatalytic performance of AAB-LMs.

8

## 9 Introduction

The rapid progression in the world economy and urbanization as well as people's 10 unfailing demand for energy storage enormously influence on global environment. 11 What is more, there is a serious water pollution resulting from various assortment of 12 toxic and harmful contaminants discharged into aqueous environment for uncontrolled 13 anthropogenic activities.<sup>[1-3]</sup> Herein, seeking an effective, clean and low-cost method to 14 reclaim the polluted water including wastewater has become a hotspot.<sup>[4-6]</sup> 15 16 Semiconductor based photocatalysis, one of the most promising advanced oxidation technologies, can effectively decompose some organic pollutants with structural 17 stability, high toxicity and anti-biodegradation.<sup>[7-9]</sup> Therefore, the exploration and 18 application of novel photocatalysts with high efficiency have been urgently needed. 19

20 During recent decades, visible-light-driven (VLD) photocatalysts have been a prospective candidate for their efficient light absorption in the full spectrum of solar 21 energy.<sup>[10-12]</sup> Bismuth oxybromide (BiOBr) exhibits commendable visible-light 22 photocatalytic performance with highly anisotropic layered structure and suitable band 23 gap ( $E_g = 2.7 \text{ eV}$ ).<sup>[13-14]</sup> Despite these advantages, the too positive conduction band 24 minimum (CBM) of BiOBr and high recombination of photo-induced charges still limit 25 its practical application.<sup>[15]</sup> The result of density functional theory (DFT) indicates that 26 the conduction band (CB) of BiOBr is mainly made up of Bi 6p orbits,<sup>[16]</sup> thus some 27 researchers have suggested that the CB position can be adjusted by increasing the 28 content of bismuth in BiOBr to improve the hybridization of CB and decrease its band 29

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gap, which is in favor of charge transfer and visible-light absorption of Bi-O-Br 1 semiconductor photocatalysts such as the construction of Bi<sub>5</sub>O<sub>7</sub>Br,<sup>[17]</sup> Bi<sub>3</sub>O<sub>4</sub>Br<sup>[18]</sup> and 2 Bi<sub>24</sub>O<sub>31</sub>Br<sub>10</sub>.<sup>[19]</sup> Among them, Di et al. reported that the photocatalytic efficiency of as-3 prepared Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> ultrathin nanosheets was 1.9 times higher than that of BiOBr 4 ultrathin nanosheets towards degrading ciprofloxacin.<sup>[20]</sup> Recently, our group have 5 successfully synthetized a novel Bi-rich Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> with enhanced visible-light 6 absorption in an ionic liquid-in-water (IL/W) system, in which the ionic liquid could be 7 8 served as bromine source, dispersing agent and template synchronously. The synthesized Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> layered microspheres (Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs) performed excellent 9 photocatalytic activities for the degradation of o-phenylphenol and norfloxacin than 10 those of BiOBr nanosheets.<sup>[15]</sup> All these reports sufficiently demonstrate that Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-11 LMs has an outstanding photocatalytic performance in the removal of environmental 12 pollutants. However, since the single-component semiconductor photocatalysts have 13 the lower light utilization efficiency and higher recombination rate of photo-generated 14 electron-hole pairs than that of composite ones, which economically restrict their 15 further practical application.<sup>[21-23]</sup> Therefore, the construction of heterojunction 16 photocatalysts has rewarded extra consideration due to their unique optical and 17 electronic properties such as reinforced photo-absorption and photo-induced charge 18 transfer. Among them, Z-scheme heterojunction photocatalysts have been 19 20 incrementally studied, in which the enhanced photo-absorption efficiency, high chargeseparation and strong redox capacity can be realized synchronously through the 21 formation of Z-scheme heterostructure.<sup>[11, 24]</sup> For example, Zou et al. have prepared that 22 the ameliorated photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>/Au/C-TiO<sub>2</sub> hollow spheres on H<sub>2</sub> 23 production could be attributed to the Z-scheme charge transfer mechanism.<sup>[25]</sup> Liu et al. 24 also have reported that the carbon cloth-supported MoS<sub>2</sub>/Ag<sub>2</sub>S/Ag<sub>3</sub>PO<sub>4</sub> performed 25 enhanced photocatalytic efficiency in the degradation of rhodamine B via the direct Z-26 scheme photocatalytic system.<sup>[26]</sup> These results manifest that Z-scheme mechanism is 27 in great significance to improve the photocatalytic activity of semiconductor in the fuel 28 29 production and water treatment. Nevertheless, constructing Z-scheme heterojunction

photocatalysts based on Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> to further improve the catalytic activity is yet to be
 reported.

Lately, extensive concern has been focused on plasmonic photocatalysts, such as 3 Ag/AgX (X = Cl, Br, I), for their high visible-light photocatalytic performance.<sup>[27-28]</sup> 4 Because the conduction electrons of Ag oscillate coherently with the oscillating electric 5 field after exciting by the light, the generated surface plasmon resonance (SPR) effect 6 can further expand the light response of AgX to the visible-light region.<sup>[28]</sup> Although 7 8 the instability and photo-sensitivity of AgX under light irradiation hinder their commercialization, the construction of composite photocatalysts combined Ag/AgX 9 with other semiconductors was proposed to overcome these weaknesses and boost their 10 such as Ag/AgI/BiOI,  $^{\left[ 27\right] }$  Ag/AgBr/g-C\_3N\_4  $^{\left[ 29\right] }$ photocatalytic behavior, and 11 Ag/AgCl/TiO2.<sup>[30]</sup> Specifically, most of the ternary semiconductor photocatalysts 12 anchored with Ag/AgX have complex preparation process, and need to be added other 13 chemical reagents as the halogen source during the synthesis process.<sup>[31-33]</sup> Therefore, 14 anchoring Ag/AgBr particles on the surface of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> can overcome the complexity 15 16 of preparation, because Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> can serve as the template to offer bromine source for the formation of AgBr, and Ag<sup>0</sup> can also be generated simultaneously. The in-situ 17 growth of Ag/AgBr on Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> via photoreduction can accomplish tight coupling 18 between Ag/AgBr on Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>, which is of great significance for the separation and 19 20 transfer of photo-induced charge. On the other hand, the Br of AgBr can be oxidized by holes to produce Br<sup>0</sup>, which could act as a reactive radical species to participate in 21 the degradation process of pollutants.<sup>[33]</sup> All of these inspire that synthesizing 22 Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> plasmonic heterojunction photocatalysts can efficaciously improve 23 24 the visible-light photocatalytic efficiency.

In this study,  $Ag/AgBr/Bi_4O_5Br_2$  layered microspheres (AAB-LMs) with Zscheme heterostructure were firstly fabricated via a facile in-situ deposition and photoreduction approach. In the  $Bi_4O_5Br_2$  preparation, the ionic liquid 1-Octyl-3methylimidazolium bromide and the surfactant Triton X-100 were used as template and stabilizer, respectively. Furthermore, the  $Bi_4O_5Br_2$ -LMs could offer the bromine for the

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formation of AgBr, Ag<sup>+</sup> could be reduced to Ag<sup>0</sup> during the visible-light irradiation. The 1 2 obtained materials Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs with different photoreduction time of 10 min, 40 min, 90 min and 180 min were designated as AAB-LMs-10, AAB-LMs-40, 3 AAB-LMs-90 and AAB-LMs-180, respectively. The compositional, structural and 4 morphology characterization as well as optical properties of as-synthesized samples 5 were also analyzed. The photocatalytic proficiency of AAB-LMs was investigated via 6 7 the degradation of acid orange II (AO7), 4-tert-butylphenol (PTBP) and aniline under 8 visible-light. Moreover, the photocatalytic enhancement mechanism and structureactivity relationships of AAB-LMs were discussed in detail. At last, the conjectural 9 degradation pathways of aniline in this AAB-LMs-photocatalysis system were also 10 11 proposed.

12

# **13 Results and Discussion**

## 14 Compositional and Structural Information

XRD was utilized to characterize the crystalline structure of the samples, and the 15 16 resulting XRD patterns are shown in Figure 1. Clearly, the diffraction peaks of asprepared Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs were indexed to the monoclinic Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> (JCPDS Card No. 17 37-0699).<sup>[20]</sup> The diffraction peaks of AAB-LMs which located at 31.0°, 44.3°, 18 64.5° and 73.3° belonged to (200), (220), (400) and (420) facets of AgBr (JCPDS Card 19 No. 06-0438), respectively,  $^{[28, 34]}$  while the diffraction peaks at 44.3° and 64.4° were 20 attributed to the (200) and (220) facets of Ag<sup>0</sup> (JCPDS Card No. 65-2871), 21 respectively.<sup>[30]</sup> It is noticeable that although the diffraction peaks intensity of samples 22 performed much sharper by extending the photoreduction time, the peak of Ag $^0$  at 38.1 $^\circ$ 23 was not be detected, which might be due to the low content, small size and 24 homogeneous dispersion of Ag<sup>0.[28, 34]</sup> The mentioned XRD characterization 25 demonstrated that the crystallinities of the as-fabricated composites were getting better 26 gradually and Ag/AgBr had been successfully generated on the surface of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-27 LMs. Moreover, no diffraction peak of impurities in crystallographic measurement was 28 found, indicating that no new crystalline phase was formed during the whole 29

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1 preparation process and the crystalline phase structure of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs was not



2 changed after the introduction of Ag and AgBr.

3

Figure 1. XRD patterns of as-prepared materials treated with different visible-light
photoreduction time.

6

7 The elemental composition and chemical states of as-synthesized materials were characterized by XPS. Figure 2a depicts the survey scan spectrum of AAB-LMs-10, 8 9 demonstrating that the composite mainly consists of Bi (157.8 eV, 163.2 eV), O (530.8eV), Br (67.3 eV) and Ag (366.5 eV, 372.6 eV). The high-resolution spectra of 10 Bi 4f, O 1s, and Br 3d are shown in Figure 2b-d, respectively. Specifically, the binding 11 characteristic orbital energies of Bi 4f with peaks located at 157.7 eV and 163.1 eV 12 closely conformed to Bi  $4f_{7/2}$  and Bi  $4f_{5/2}$  of Bi ions with a valence of +3.<sup>[35]</sup> The broad 13 peaks at 528.6 eV and 531.0 eV were ascribed to O 1s of AAB-LMs-10, which was 14 mainly due to the lattice oxygen and the surface absorbed  $H_2O$  or hydroxyl group (-OH) 15 of the sample.<sup>[21]</sup> The characteristic peaks of 67.3 eV and 68.6 eV corresponded to the 16 Br 3d<sub>5/2</sub> and Br 3d<sub>3/2</sub>, indicating that Br ions presented a valence of -1. In order to further 17 verify the presence of Ag and AgBr, the high resolution XPS spectra of Ag 3d were 18 also conducted. As depicted in Figure S1, the characteristic peaks of Ag 3d were mainly 19

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detected at 367.0 eV and 372.5 eV, corresponding to Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>, which could 1 be further divided into four peaks. 366.5 eV and 372.6 eV belonged to Ag<sup>+</sup> 3d<sub>5/2</sub> and 2 Ag<sup>+</sup>  $3d_{3/2}$  respectively, whereas 366.8eV and 373.1 eV ascribed to Ag<sup>0</sup>  $3d_{5/2}$  and Ag<sup>0</sup> 3 3d<sub>3/2</sub> respectively. The above observation further validated the existence of Ag with 4 different valences of as-prepared photocatalysts.<sup>[22]</sup> Moreover, comparing the 5 characteristic peaks belonging to the Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> of the AAB-LMs composites 6 7 treated with different photoreduction time (Figure S1), it is easy to find that the shift of 8 these peaks to the left or right occurred, which may be due to the various amount of 9 Ag/AgBr loaded on the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs or the different surrounding chemical 10 environment during the preparation process. In addition, the semi-quantitative analysis of the molar ratio of Ag to AgBr in the AAB-LMs was also performed using the XPS 11 12 spectra of Ag 3d peak area (Table 1). It indicates that the content of Ag on the surface 13 of the composites decreased with the extension of the photoreduction time of the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs. 14



16 Figure 2. The XPS spectra of (a) survey, (b) Bi 4f, (c) O 1s and (d) Br 3d for as-



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- 1 synthesized AAB-LMs-10 composite.
- 2

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Photocatalysts	Peak position (eV)	Peak area	Peak attribution	Ag/AgBr ratio
AAB-LMs-10	366.460	1988.220	$\mathrm{Ag}^{+}$	46.81%
	366.814	677.284	$\mathrm{Ag}^0$	
	372.585	948.771	$\mathrm{Ag}^{+}$	
	373.103	697.519	$\mathrm{Ag}^{0}$	
AAB-LMs-40	365.652	1826.777	$\mathrm{Ag}^{\scriptscriptstyle +}$	45.93%
	366.241	673.654	$\mathrm{Ag}^{0}$	
	371.684	1011.960	$\mathrm{Ag}^{+}$	
	372.079	630.225	$\mathrm{Ag}^{0}$	
AAB-LMs-90	366.260	924.560	$\mathrm{Ag}^{+}$	44.02%
	367.054	357.234	$\mathrm{Ag}^0$	
	372.377	646.096	$\mathrm{Ag}^{+}$	
	372.517	334.204	$\mathrm{Ag}^{0}$	
AAB-LMs-180	365.800	932.679	$\mathrm{Ag}^{+}$	34.93%
	366.405	448.519	$\mathrm{Ag}^{0}$	
	371.840	534.151	$\mathrm{Ag}^{+}$	
	372.663	63.849	$Ag^0$	

3 **Table 1** XPS Ag 3d peak area analysis of AAB-LMs with different photoreduction time.

4

# 5 Morphology and Textural Properties

The morphologies of the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and AAB-LMs samples were observed by SEM. 6 7 As shown in Figure 3a-e, Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs with rough surfaces maintained its integrity 8 without much morphological change after the Ag/AgBr particles anchored. Since the 9 microsphere was composed of many sheets stacked on top of each other, some extra pieces around the sphere could be found from the SEM images. Besides, many 10 nanoparticles could be obviously discovered on the outer surfaces of the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs 11 owing to the formation of Ag/AgBr particles (20-80 nm). Some of the Ag/AgBr 12 nanoparticles were deeply embedded or attached on the surface of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, 13 confirming the combination of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs with the Ag and AgBr. With respect to 14 the unembellished Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, the particle sizes were mainly about 2.2 µm, whereas 15 16 the average size of AAB-LMs gradually decreased in order by prolonging 17 photoreduction time: AAB-LMs-10 (~1.1  $\mu$ m) > AAB-LMs-40 (~0.9  $\mu$ m) > AAB-LMs-90 (~0.75  $\mu$ m)  $\approx$  AAB-LMs-180 (~0.76  $\mu$ m). Considering the bromine of AgBr mainly 18

came from Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and the exfoliation of the sheet structure of the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-1 LMs occurred on the surface, the decrease of particle size of the overall AAB-LMs 2 3 seemed reasonable, which was consistent with the increasing AgBr proportion of the AAB-LMs mentioned in the XPS characterization. The SEM-EDS line scan and 4 elemental mapping spectra were also recorded to gain insight of the surface element 5 6 composition and distribution of the as-fabricated materials. Figure 3f depicts the SEM-7 EDS spectrum of AAB-LMs-10, indicating that Bi, O, Br and Ag elements distributed 8 throughout the composite. Moreover, the SEM-EDS elemental mapping (Figure 4) 9 illustrates that all elements were uniformly distributed on the surface of the AAB-LMs-10 10. All characterizations disclosed that the Ag/AgBr particles had been successfully loaded during the photoreduction process. 11



12

13 Figure 3. The SEM images of the (a) Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, (b) AAB-LMs-10, (c) AAB-LMs-

- 14 40, (d) AAB-LMs-90 and (e) AAB-LMs-180 samples, and (f) SEM-EDS spectrum of
- 15 AAB-LMs-10 material.
- 16



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Figure 4. (a) SEM-EDS elemental mapping of AAB-LMs-10, (b) - (e) the EDS
elemental mapping of Bi, O, Br and Ag.

TEM can be used to obtain more microstructural information about the as-prepared 5 material. In Figure 5a, the as-synthesized AAB-LMs-10 mainly presents the 6 microsphere structure with a certain degree of hollowness and layered structure, and 7 this distinctive morphology is extremely cooperative throughout the whole 8 9 photocatalytic process because of the continuous diffraction and reflection of the absorbed light beam inside the material, thus further increasing the photon capture 10 rate.<sup>[15]</sup> Moreover, combined with the SEM characterization, convex granular structural 11 materials assembled on the surface of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs might be the Ag/AgBr particles. 12 To prove the conjecture further, high-resolution transmission electron microscopy 13 (HRTEM) analysis was carried out, which is shown in Figure 5b. The interplanar 14 spacing of 0.333 nm and 0.261 nm corresponded to the crystallographic plane of AgBr 15 (111)<sup>[36]</sup> and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs (220),<sup>[15]</sup> respectively. The lattice fringes with the spacing 16 of 0.236 nm referred to the cubic Ag (111) crystal plane,<sup>[28]</sup> which can be regarded as a 17 Z-scheme bridge to transfer the photo-induced electrons and holes. This 18 characterization adequately confirmed that metallic Ag and AgBr coexisted on the 19 surface of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and they tightly contacted each other, which could facilitate 20 21 the separation and transportation of photo-induced charges.



- Figure 5. (a) TEM and (b) HRTEM images of AAB-LMs-10.
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The BET surface area of the catalyst is also a non-negligible factor affecting its 4 photocatalytic activity. Figure 6 displays the N<sub>2</sub> adsorption-desorption isotherms and 5 BJH pore size distribution curves of the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and AAB-LMs-10. Both N<sub>2</sub> 6 7 adsorption-desorption isotherms exhibited the IV type isotherm, which was typical for 8 the mesoporous materials. The distinct hysteresis loops for both Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and AAB-LMs-10 in the relative pressure  $P/P_0$  range of 0.7 to 1.0 indicated that there was 9 the pore size distribution. The surface textural properties of as-prepared materials 10 11 obtained from BET characterization are listed in Table 2. It illustrates that all samples were filled with many mesopores. Moreover, compared to that of the uncovered 12 Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, a slight decrease in BET specific surface area of AAB-LMs with 13 prolonging the photoreduction time happened, which might owe to the increased 14 Ag/AgBr nanoparticles that entered the inner surface of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and occupied 15 their mesopores. This phenomenon was also accompanied by a reduction of the active 16 17 sites on the surface of AAB-LMs, leading to an attenuation in the catalytic performance of the photocatalyst. 18



Figure 6. N<sub>2</sub> adsorption-desorption isotherms and inset BJH pore size distribution
curves of (a) the unembellished Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and (b) the as-prepared AAB-LMs-10.

5 **Table 2** BET areas, pore size and volume of the as-prepared materials.

Photocatalyst	Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Pore size (nm)	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
Bi <sub>4</sub> O <sub>5</sub> Br <sub>2</sub> -LMs	35.5395	18.0511	0.132271
AAB-LMs-10	32.6872	16.992	0.134203
AAB-LMs-40	30.8193	9.2379	0.063651
AAB-LMs-90	28.943	17.7095	0.120520
AAB-LMs-180	28.907	16.6258	0.115338
 AAD-LWIS-100	20.907	10.0258	0.115558

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# 7 **Optical Absorption Properties**

DRS has been regarded as a constructive characterization due to its sensitive 8 9 identification of the existence of metal ion coordinating in semiconductors, and the 10 DRS results could illustrate the spectral characteristics of the samples under light.<sup>[37]</sup> After depositing Ag/AgBr nanoparticles, the color of the AAB-LMs composite changed 11 from the light yellow of the pristine Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs to brown, showing that the optical 12 properties of AAB-LMs had been changed. As revealed in Figure 7, the uncovered 13 Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs had strong absorption at 480 nm, which mainly derived from the 14 intrinsic band gap absorption. As for the AAB-LMs, there was a continuous absorption 15 in the wavelength range 200-800 nm and a noticeable bulge located at 550 nm, which 16 17 were the evidence of more significant enhancement in light absorption bands than pure 18 Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs. All of these oddities resulted from the synergistic effects among Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, Ag and AgBr,<sup>[38]</sup> the SPR effect of Ag nanoparticles<sup>[39]</sup> and the 19

involvement of isolated energy levels in the band gap of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs,<sup>[40]</sup> which demonstrated that the as-fabricated AAB-LMs possessed high effectiveness and wide application as a VLD photocatalyst.<sup>[41]</sup> Since the photocatalytic behavior of semiconductors can be greatly affected by their light absorption performance, the extending of light absorption edges possibly worked out the boosted visible-light photocatalytic behavior of AAB-LMs.



7

8 Figure 7. UV-vis diffuse reflection spectra of the as-fabricated materials.

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It is well-known that the light absorption performance of the semiconductor is 10 strongly linked to its energy band structure for the intrinsic transition.<sup>[42]</sup> The smaller 11 the band gap energy  $(E_g)$ , the higher the utilization rate of light. The  $E_g$  of as-prepared 12 sample is calculated by  $\alpha hv = A (hv - E_g)^{n/2}$ , where  $\alpha$ , h, v and A are the absorption 13 14 coefficient, Planck's constant, light frequency and a constant, respectively. As for the AgBr and Bi-O-Br, both of values of n are 4,<sup>[27]</sup> and their indirect band structures allow 15 the excited electrons of valence band (VB) transport to the conduction band (CB) of the 16 semiconductor through a certain k-space distance, which effectively suppresses the 17 combination of photo-induced electron-hole pairs and improves their photocatalytic 18 behavior.<sup>[13-14]</sup> The calculated Egs of as-prepared samples are displayed in Figure S2, 19

which were 2.40 eV, 2.33 eV, 2.35eV, 2.36 eV and 2.22 eV for Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, AABLMs-10, AAB-LMs-40, AAB-LMs-90 and AAB-LMs-180, respectively. Although
there were slight differences between the values of E<sub>g</sub>s of AAB-LMs, all of them were
lower than that of the pure Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, demonstrating that the loading of Ag/AgBr
nanoparticles was conductive to generate more photo-induced electron-hole pairs under
visible-light irradiation, thus improving their photocatalytic activities.<sup>[35]</sup>

7 Photoelectrochemical measurements mainly includes Electrochemical Impedance Spectroscopy (EIS) and photocurrent analysis in this study. EIS can investigate the 8 transfer impedance of photo-generated charge and the relationship between charge 9 transfer and recombination. The radius of the arc of the EIS spectrum can indirectly 10 reflect the reaction rate happening on the surface of the electrode. The smaller diameter 11 12 of the semicircle assigned to charge transfer impedance, the lower recombination rates of photo-induced charge, indicating that the semiconductor has a better photocatalytic 13 activity.<sup>[35]</sup> In Figure 8a, the measured diameter of AAB-LMs-10 was significantly 14 smaller than that of the uncovered Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, affirming AAB-LMs-10 had a lower 15 16 charge transfer resistance and a more effective separation of photo-induced electronhole pairs. This was mainly attributed to the deposition of Ag/AgBr, which could 17 enhance the separation and transfer of electron-hole pairs of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs. To gain 18 further insight into the improved photocatalytic behavior, the instantaneous 19 photocurrent responses of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and AAB-LMs-10 were studied. The intensity 20 of photocurrent could indirectly represent the charge transfer ability of the 21 semiconductor under light.<sup>[21]</sup> As depicted in Figure 8b, the as-prepared samples had a 22 fast and reproducible photocurrent response under light irradiation, and the maximum 23 24 photocurrent density of the sample after treated with photoreduction process (AAB-LMs-10) was observably better than that of the pure Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs. It indicated that 25 AAB-LMs-10 had a lower recombination rate of the photo-generated electron-hole 26 pairs and an excellent photocatalytic property. Both photoelectrochemical 27 characterization illustrated that the loading of Ag/AgBr as well as the synthetic 28 29 interaction of Ag, AgBr and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs had a positive effect to promote the

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1 separation and transfer of photo-generated charge.

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Figure 8. (a) EIS spectra and (b) photocurrent response of the pure Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and
AAB-LMs-10.

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# 6 **Photocatalytic Performance**

The potential photocatalytic activity of the as-fabricated materials should be reflected 7 8 from the degradation performance of refractory organics pollutants, which is significant 9 for the environmental restoration and protection. In this study, it was mainly evaluated 10 by degradation of AO7, PTBP and aniline under visible-light irradiation. AO7, an anionic azo dye, has been widely used in the textile industry but hardly biodegraded.<sup>[43]</sup> 11 Besides, Ember et al. reported that AO7 did not deactivate or form precipitates over a 12 long reaction time (several days) even in bicarbonate buffer solutions containing 13 oxidants with high concentrations.<sup>[44]</sup> In this study, the concentration of AO7 was 14 indirectly detected by a UV-vis. spectrophotometer at 484 nm. The visible-light 15 photocatalytic degradation efficiency ( $\eta$ ) was reckoned with  $\eta = (1 - C_t / C_0) \times 100\%$ , 16 17 in which C<sub>t</sub> and C<sub>0</sub> are the equilibrium concentration of target pollutant at illumination 18 time t and initial time, respectively. As a comparison, the photodegradation of AO7 without any catalyst (Figure 9a) was performed, and the corresponding results declared 19 20 that AO7 itself rarely degraded with visible-light illumination alone. With respect to the degradation rates of AO7 with adding diverse as-synthesized photocatalysts, the 21 22 photocatalytic efficiencies of the as-fabricated AAB-LMs were dramatically higher than that of the pristine Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, in which AAB-LMs-10 performed the highest 23

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photocatalytic performance with the degradation efficiency of about 95 % in 60 min. 1 Compared with the reported CdS/TiO<sub>2</sub> photocatalyst, which only degraded 40 % AO7 2 within 35 min under the visible-light illumination,<sup>[45]</sup> the AAB-LMs had an eminent 3 visible-light photocatalytic activity in the removal of AO7. Interestingly, the catalytic 4 behavior reduced with the increment of loading amount of Ag/AgBr, manifesting that 5 although the surface silver nanoparticles (Ag NPs) promoted the separation and 6 migration of photo-induced charge, the presence of excessive AgBr might cover the 7 8 active sites on the surface of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and the reduction of surface area of the 9 sample could also inhibit the light absorption. Herein the degradation rate of AO7 with adding AAB-LMs-40, AAB-LMs-90 and AAB-LMs-180 as the photocatalysts 10 decreased gradually. In order to determine the optimal photoreduction time for the 11 12 preparation of AAB-LMs composites from the practical application view, photodegrading PTBP over different as-synthesized photocatalysts was also 13 comparatively performed under visible-light irradiation (Figure S3). Surprisingly, the 14 visible-light catalytic activity of AAB-LMs to the degradation of PTBP was opposite to 15 16 that of AO7, which AAB-LMs-180 showed the best catalytic activity by the little margin among the series of AAB-LMs. Although AAB-LMs had completely different 17 catalytic efficiency on different pollutants, the small disparity did not affect the fact that 18 AAB-LMs had splendid visible-light catalytic activity compared with BiOBr, Ag/AgBr, 19 20 Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-plate and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs. Therefore, combining the structural and morphological characterizations and photocatalytic activities of AAB-LMs, 10 min was 21 considered as the optimal photoreduction time during the preparation process of AAB-22 LMs, which not only saved energy consumed during the whole experimental process 23 24 but also reduced the whole preparation time of the composite photocatalyst. In addition, 25 the photodegradation process of AO7 also abided by the pseudo-first-order reaction and the first-order rate constant ( $k_{app}$ ) could be obtained by fitting the equation (-In ( $C_t / C_0$ ) 26 =  $k_{app}t$ , where  $C_t$ ,  $C_0$  and t represent the equilibrium concentration of the reaction 27 28 solution at instantaneous and initial time, and the visible-light irradiation time, 29 respectively). While Figure 9c plots the kinetic curves for AO7 photodegradation over

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as-fabricated catalysts, Figure 9e displays the values of k<sub>app</sub> for different photocatalytic
degradation systems. Specifically, AAB-LMs-10 (0.04298 min<sup>-1</sup>) had the highest value
of k<sub>app</sub>, which was nearly 28 times larger than that of the unembellished Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs
(0.0015 min<sup>-1</sup>). The above facts disclosed that Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs coupling with Ag/AgBr
could efficiently facilitate the separation of photo-generated electron-hole pairs, thereby
enhancing the photocatalytic efficiency of the composite AAB-LMs.

7 Aniline is one of the most vital intermediates and raw materials in the manufacture 8 of dyes, pesticides, pharmaceutical sulfa medicines and anti-explosive agent of gasoline.<sup>[46-47]</sup> Moreover, as one of the 129 priority contaminants (U.S Environmental 9 Protection Agency, U.S.EPA), aniline can even destroy the ecological balance of the 10 aquatic system and endanger the growth and survival of aquatic organisms after being 11 discharged into the environment.<sup>[48-49]</sup> Therefore, it is imperative to explore an efficient 12 and green way to remove aniline from the environment. With respect to the 13 photocatalytic degradation of aniline, the catalytic efficiencies of the as-fabricated 14 BiOBr, Ag/AgBr, Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-plate, Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and AAB-LMs were carried out in 15 16 this study. As depicted in Figure 9b, the photocatalytic degradation capability of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs (27.7 %) was better than that of BiOBr (18.2 %) and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-plate 17 (22.4 %), which revealed that the Bi-rich Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs had more salient visible-light 18 catalytic activity, and might mainly attribute to the 3D-monodisperse layered 19 20 microsphere structures and the presence of ionic liquid acted as the dispersing agent as well as TX-100 served as stabilizer.<sup>[15]</sup> Interestingly, the degradation rate of aniline with 21 22 adding Ag/AgBr (43.2 %) as the photocatalyst was higher than that of as-prepared single-phase photocatalysts but lower than that of the AAB-LMs-10 composite (about 23 24 70 %), demonstrating that the deposition of Ag/AgBr had a positive influence to boost 25 the photocatalytic efficiency of the composite. Moreover, the photodegradation of aniline with adding different as-fabricated catalysts was also investigated by fitting the 26 obtained data in  $-In (C_t / C_0) = k_{app}t$ . The kinetic curves and the values of  $k_{app}$  for 27 degrading aniline are displayed in Figure 9d and Figure 9f, respectively. The data 28 29 showed that the photocatalytic degradation process of aniline corresponded to the

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1 pseudo-first-order kinetics and the value of  $k_{app}$  obtained from AAB-LMs was much

- 2 higher than those from other as-prepared catalysts, which further ensured that the AAB-
- 3 LMs possessed higher photocatalytic activity.

In general, the photocatalytic efficiency of as-prepared AAB-LMs for degrading 4 AO7 was markedly stronger than that of aniline under visible-light irradiation, which 5 was mainly because the  $\pi$ -conjugated molecular structure of aniline gave it stable and 6 inert electronic structure.<sup>[38]</sup> As for the commendable photocatalytic degradation of 7 AO7 over AAB-LMs, the self-photosensitization mechanism of dye molecules 8 interacted with AAB-LMs photocatalyst should not be ignored.<sup>[50]</sup> The AO7 molecules 9 adsorbed on the AAB-LMs could absorb visible-light to generate a singlet and/or a 10 triplet state of AO7, in which the former was more reactive than the latter. After that, 11 the electrons generated from excited state AO7 molecules could transport to the surface 12 of AAB-LMs and react with adsorbed oxygen to form active species  $(\bullet O_2^{-})$ , which was 13 beneficial to improve the photodegradation efficiency of AO7.<sup>[41, 51]</sup> Therefore, 14 combined with the above photocatalytic degradation performance of AO7, PTBP and 15 16 aniline, the synergetic effect among Ag, AgBr and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs was conductive to boost the visible-light catalytic activity of the composite. All in all, the as-prepared 17 AAB-LMs composite photocatalyst had prominent photocatalytic performance and 18 bright application prospect in the removal of environmental pollutants. 19



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Figure 9. Photocatalytic degradation, pseudo-first-order kinetics curves and k<sub>app</sub> of (a,
c, e) AO7 (10 mg/L) and (b, d, f) aniline (16 mg/L) with adding different as-prepared
photocatalysts under visible-light irradiation.

6 It is well-known that the recyclability and stability of catalyst are also imperative 7 for its long-time existence and repeated use in terms of practical applications.<sup>[1]</sup> To 8 verify the recyclability of as-synthesized AAB-LMs, repeatedly photocatalytic 9 degradation experiments of AO7 under the same reaction condition were designed and

carried out. In Figure 10a, the photocatalytic proficiency of AAB-LMs-10 for degrading 1 AO7 still maintained high even after four consecutive cycles. Furthermore, the stability 2 of AAB-LMs was also characterized by XRD, XPS and SEM measurements. As 3 depicted in Figure 10b, the crystalline structure of AAB-LMs-10 used before and after 4 four photocatalytic degradation circles had hardly changed, and their position of the 5 6 peaks still corresponded well to the standard characteristic peaks of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> (JCPDS 7 No. 37-0699), Ag (JCPDS No.65-2871) and AgBr (JCPDS No.06-0438). High-8 resolution XPS spectra of the used AAB-LMs (Figure S4a-e) demonstrated that 9 although these corresponding characteristic peaks shifted slightly to the left, which may be ascribed to the change of the chemical environment, its composition and valence 10 states of elements had not changed. Moreover, the morphology of AAB-LMs (Figure 11 12 S4f) after the photodegradation still kept the complete spherical structure with some nanoparticles embedded or attached on their surface. These described consequences 13 indicated that the as-prepared AAB-LMs-10 behaved favorable reusability and 14 structural stability and had a potentially practical application. 15



Figure 10. (a) Recycling runs of as-prepared AAB-LMs-10 for AO7 (10 mg/L) degradation in the photocatalytic reaction process, (b) XRD patterns of as-prepared AAB-LMs-10 before and after photocatalytic degradation reaction under visible-light irradiation.

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### 22 Photocatalytic Mechanism Insight

23 For better understanding the potential photocatalytic mechanism of the as-prepared

AAB-LMs, the photocatalytic degradation experiments of aniline over AAB-LMs-10 1 with adding diverse radical scavengers were conducted. Specifically, isopropanol (IPA), 2 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), potassium dichromate 3 (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), and ammonium oxalate (AO) were selected to serve as scavengers for 4 hydroxyl radical (•OH), superoxide radical (•O<sub>2</sub><sup>-</sup>), electrons (e<sup>-</sup>) and hole (h<sup>+</sup>), 5 respectively.<sup>[52-53]</sup> As shown in Figure S5, the photocatalytic efficiency of AAB-LMs-6 10 dropped significantly with the presence of TEMPOL and AO, indicating that  $\cdot O_2^{-1}$ 7 8 and h<sup>+</sup> were the primary active species in this photocatalysis system. Since photoinduced electrons (e<sup>-</sup>) can be captured by the surface adsorbed  $O_2$  of catalysts to 9 generate  $\cdot O_2^-$ , the addition of  $K_2Cr_2O_7$  could also suppress the photocatalytic 10 proficiency of AAB-LMs-10, thereby inhibiting the degradation of aniline. However, 11 the degradation rate of aniline was not affected by the addition of IPA, indicating that 12 •OH played a minor role in this photocatalytic degradation process. 13

The dominant radical species of the AAB-LMs-photocatalysis system was further 14 verified by EPR (Figure 11). No distinct characteristic peak was found in the dark, 15 16 indicating that the light irradiation was indispensable for the generation of active species. Besides, the characteristic peaks of DMPO- $\cdot$ O<sub>2</sub><sup>-</sup> were observed in both the 17 AAB-LMs-10 and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs methanol dispersion, while no obvious characteristic 18 peak belonging to DMPO-•OH was observed in either EPR spectra of AAB-LMs-10 or 19 20 that of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs in aqueous dispersion under visible-light illumination. Therefore,  $\cdot O_2^-$  but not  $\cdot OH$  was the predominant radical species in the AAB-LMs-photocatalytic 21 degradation system, which was in well agreement with the conclusion drawn from the 22 23 quenching experiments.





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The degradation pathway of aniline in this AAB-LMs-photocatalysis system was 6 deduced based on the theoretical calculation and the gas chromatography-mass 7 spectrometer (GC-MS) data of degradation products. The detailed analytical methods 8 9 of GC-MS and frontier electron densities (FEDs) analysis of aniline can be found in the Supplementary Material. Table S1 lists the formulas of identified relevant degradation 10 intermediates of aniline as well as their retention times and chemical structures, and 11 Figure S7 displays the resulting GC-MS chromatograms detected with different 12 degradation time of the aniline in the AAB-LMs-photocatalysis system. In the figure, 13 the relative abundance of characteristic peak belonging to aniline (retention time (RT) 14 = 5.47 min) was sharply reduced during the photocatalytic degradation process, 15 16 demonstrating that aniline was degraded in the AAB-LMs-photocatalysis system. The 17 main photocatalytic degradation routes are as follows (Figure 12). (1) Aniline was attacked by the active species ( $\bullet O_2^-$  and  $h^+$ ) to produce phenol, which was conductive 18 to increase the absorbance, and then further to convert into hydroquinone (G); (2) The 19 excited imino radicals could be attacked by  $\bullet O_2^-$  and  $h^+$  to form nitrophenols (B), and 20 then generated hydroquinone (G); (3) Due to the presence of AgBr in the AAB-LMs-21 photocatalysis system, the strong oxidizing agent Br<sup>0</sup> might be generated during the 22

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photocatalytic process. Therefore, aniline underwent the ortho, meta and para 1 substitution reactions with Br<sup>0</sup> to form bromoaniline (C) and dibromoaniline (D), which 2 was also an important phenomenon to illustrate the generation and participation of  $Br^{0}$ . 3 Subsequently, these intermediates were converted to hydroquinone (G) with the attack 4 of  $\bullet O_2^-$  and h<sup>+</sup>. After that, the resulting hydroquinone could be attacked to form 5 benzoquinone (H), which was accompanied by the aromatic ring-opening reaction to 6 produce a series of low-toxic small molecule organic compounds (I, J, K and L). These 7 degradation routes and the presence of Br<sup>0</sup> were verified by the gradually decreased 8 9 characteristic peaks of bromoaniline (RT=11.26 min) and dibromoaniline (RT=19.09 min) as well as the enhanced peaks of hydroquinone (RT=18.50 min) and benzoquinone 10 (RT=23.11 min) with the extended photocatalytic degradation time, which were also 11 12 depicted in Figure S7; (4) The intermediates (E) and (F) were mainly produced by the combination of aniline radicals excited by the active species and aniline or phenol 13 radicals, which could be in turn cleaved into some small molecular organics (I, J, K and 14 L). In conclusion, the generation and disappearance of bromoaniline and 15 16 dibromoaniline during the photocatalytic degradation process were mainly attributed to the fact that aniline was attacked by the active species Br<sup>0</sup> generated from the AgBr in 17 the AAB-LMs. Besides, considering the deamination efficiency of aniline was faster 18 than the aromatic ring-opening rate in the first 30 min,<sup>[54]</sup> the aromatic ring-NH<sub>2</sub> bond 19 20 of aniline was broken preferentially, followed by a ring-opening reaction. Since the benzene ring could not be directly oxidized to small molecular organics for its strong 21 stability, it was converted to a benzoquinone. Moreover, the presence of phenolic 22 compounds was mainly because the lone pair of electrons on the nitrogen atom together 23 24 with the benzene ring formed a delocalized large  $\pi$  bond (P- $\pi$  conjugate) after the hydrogen atom on the benzene ring was replaced by -NH<sub>2</sub>. 25





Figure 12. Possible photocatalytic degradation pathways of aniline on the as-prepared
AAB-LMs under visible-light illumination.

In order to analyze the elevated photocatalytic capability of AAB-LMs from the 5 6 theoretical viewpoint, the relationships between the atomic structure and electronic structures of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> and AgBr were analyzed by using Density Function Theory 7 (DFT). The corresponding data are depicted in Figure 13. For Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>, the CB was 8 primarily dominated by Bi 6p orbit, while the VB was basically composed of Bi 6s, O 9 10 2p, Br 4p, Br 4s and O 2s orbits. Owing to the formed large hybrid electron density of O atoms with vicinal Bi and Br atoms enhanced the electrostatic attraction between 11 nuclear and electrons, all of atoms in the VB were hybrid together very well, so it was 12 hard for electrons in the VB to be excited. On the other hand, since the low hybridization 13 14 of Bi atoms with close Br atoms in the CB was in favor of the decrease of electrostatic attraction between nuclear and electrons, electrons could readily transfer to the surface 15 of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>, which availably facilitated the separation of electron-hole pairs. Compared 16 with Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>, the CB of AgBr was mainly made up of Br 4s and Ag 5s orbits, while 17 18 the VB consisted of Br 4p and Ag 4d orbits. Considering the lower hybrid electron density of Ag atoms with nearby Br atoms in the VB, the electrons of VB could be 19 effortlessly excited. Nevertheless, because Ag atoms with nearby Br atoms had the 20 24 / 35

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higher hybridization in the CB of AgBr, the migration of electrons of CB mostly 1 occurred inside of the AgBr, resulting in a higher recombination of electron-hole pairs. 2 3 Therefore, the hybrid electron density in the VB of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> would decline after the generation of the new composite system (AAB-LMs), which was conductive to the 4 migration of electrons in the VB to the CB of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> and the VB of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> to the 5 6 Ag. Moreover, since Ag might perform as the electron collector for its SPR effect and 7 a Z-scheme bridge, its presence could also reduce the hybridization in the CB of AgBr, 8 which made for the transfer of electrons from the CB of AgBr to the Ag and improved 9 the separation of electron-hole pairs. In summary, the successful preparation of AAB-LMs could efficaciously suppress the recombination of electron-hole pairs, thereby 10 enhancing the photocatalytic performance. 11

12 The conjectural mechanism for the robust stability and photocatalytic property of as-prepared AAB-LMs could be concluded based on the above-mentioned 13 characterizations and theoretical calculation. In detail, visible-light driven (VLD) 14 photocatalysts AgBr<sup>[27]</sup> and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs<sup>[20]</sup> could be effectively excited by the 15 16 visible-light to produce electron-hole pairs. As described in Figure 13e, AgBr adhered to the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs by a typical heterojunction mode, so that their matching band 17 potentials, in which the conduction band edge ( $E_{CB}$ ) of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs ( $E_{CB} = -1.21$ 18 eV<sup>[15]</sup> was more negative than that of AgBr (E<sub>CB</sub> = -0.45 eV),<sup>[55]</sup> were favorable to the 19 transportation of photo-excited charges between them. Under visible-light irradiation, 20 the excited electrons could migrate away from the VB to CB of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and 21 22 immediately be trapped by the CB of AgBr, while the photo-generated holes on the VB of AgBr would transfer to that of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs. Therefore, the effective separation of 23 24 photo-induced electron-hole pairs of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs could be achieved. However, the Ag<sup>+</sup> of AgBr would be reduced to Ag via the electrons gathered on the CB of AgBr, and 25 the resulting photo-corrosion of AgBr would cause the unsteadiness of the AAB-LMs, 26 which was contrary to the results of our recyclability and stability experiments results 27 and even the DFT analysis. Furthermore, since the h<sup>+</sup> in the VB of AgBr could react 28 with Br<sup>-</sup> to produce Br<sup>0</sup>, which might be reduced to Br<sup>-</sup> again during the oxidation of 29

organic pollutants, the faster transportation of  $h^+$  from the CB of AgBr to that of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs would have a negative impact on the production of Br<sup>0</sup> and the stability of AAB-LMs to some extent. Therefore, the conventional heterojunction mode between AgBr and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs was not suitable to illustrate the enhanced photoactivity and photostability of as-synthesized AAB-LMs.

Furthermore, a novel Z-scheme mechanism via Ag NPs as a bridge was more 6 7 appropriate to explain the separation and transfer of photo-induced charges in the AAB-8 LMs-photocatalysis system (Figure 13f). When AAB-LMs was excited by visible-light, the photo-induced electrons of AgBr could more likely transfer to the Ag NPs through 9 the Schottky barrier and react with h<sup>+</sup> migrated from the VB of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, which 10 further facilitated the efficacious separation of photo-induced charges of AgBr and 11 Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs. Moreover, the potential barrier witnessed by the gathered electrons at 12 the interface of the junction could not only make electrons back into the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, 13 which promoted the formation of  $\bullet O_2^-,$  but also reflect holes back into AgBr, so 14 promising the production of Br<sup>0.[24, 56]</sup> On the other hand, the migration of electrons on 15 the CB of the AgBr could also effectively avoid the reduction of Ag<sup>+</sup> and guarantee the 16 stability of AAB-LMs. Considering the reduction potential of O<sub>2</sub>/•O<sub>2</sub><sup>-</sup> was -0.33 eV, the 17 photo-induced electrons of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs could reduce the surface adsorbed oxygen to 18 produce active species  $\cdot O_2^-$  during the photocatalytic process. On the other hand, 19 20 compared with the reduction potentials of •OH/H<sub>2</sub>O (2.27 eV) and •OH/OH<sup>-</sup> (2.38 eV), the  $h^+$  in the VB of AgBr did not have enough oxidation ability to generate •OH 21 as the active species for this AAB-LMs-photocatalysis system.<sup>[21]</sup> Concomitantly, the 22 Br<sup>-</sup> of AgBr could be oxidized to Br<sup>0</sup> by h<sup>+</sup>. As the reactive radical species, Br<sup>0</sup> would 23 24 be reduced to Br<sup>-</sup> again by the oxidation of organic pollutants, which was verified by the photocatalytic degradation process of aniline over AAB-LMs mentioned before. 25 Meanwhile, free Br<sup>-</sup> recombined with Ag<sup>+</sup> to form AgBr, thus guaranteeing the stability 26 of the whole material.<sup>[57]</sup> Herein, the organic pollutant molecules could be efficiently 27 decomposed by the oxidation of  $\bullet O_2^-$ ,  $Br^0$  and  $h^+$  in the AAB-LMs-photocatalysis 28 29 system under visible-light irradiation.



Figure 13. Schematic representation of crystal structure, calculated band structures and density of states (DOS) of (a, b) Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> and (c, d) AgBr; Schematic diagram of the separation and transportation of photo-generated charges over the as-prepared AAB-LMs composites (e) the typical heterojunction and (f) the novel Z-scheme heterojunction combined with the proposed photocatalytic degradation mechanism under visible-light irradiation.

8

# 9 Conclusions

In summary, visible-light-driven plasmonic heterojunction photocatalysts
 Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs performed a significant potential for the catalytic degradation

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of refractory organic contaminants. After the decoration of Ag/AgBr, AAB-LMs 1 exhibited a remarkable improvement of photocatalytic efficiency than the pristine 2 Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs and Ag/AgBr for the degradation of AO7, PTBP and aniline under 3 visible-light. The boosted visible-light absorption and appreciable photocatalytic 4 performance of AAB-LMs were mainly ascribed to the surface plasmon resonance 5 6 effect of Ag nanoparticles and the synthetic interaction between Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, Ag and AgBr.  $\cdot O_2^-$  and h<sup>+</sup> were testified as the predominant radical species in this AAB-LMs-7 photocatalysis system. Moreover, the possible photodegradation routes of aniline in this 8 9 AAB-LMs-photocatalysis system were also proposed on the basis of theoretical analysis and GC-MS measurement. Since the active species Br<sup>0</sup> taking part in the 10 photocatalytic degradation process, the Z-scheme mechanism rather than the 11 12 conventional heterojunction mode of as-prepared AAB-LMs was more convincing to illustrate the elevated photocatalytic performance. Therefore, the in-situ deposition and 13 photoreduction strategy to construct the novel AAB-LMs may point out some new hints 14 on designing novel Z-scheme plasmonic heterojunction photocatalysts for wide 15 16 application in environmental remediation and solar-to-fuel conversion.

17

### **18** Experimental Section

## **19 Experimental Materials**

Ionic liquid 1-Octyl-3-methylimidazolium bromide ([Omim]Br, 99%) was obtained 20 from Shanghai Chengjie Chemical Co., Ltd. Triton X-100 (TX-100, p-Octyl 21 polyethylene glycol phenyl ether), silver nitrate (AgNO<sub>3</sub>), 22 ethanol and 23 sodium hydroxide (NaOH) were bought from Sinopharm Chemical Reagent Co., Ltd. Bismuth pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O) and nitric acid were obtained from Nanjing 24 Chemical Reagent Co., Ltd. Acid orange II (AO7), 4-tert-butylphenol (PTBP) and 25 aniline were purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd, Aladdin 26 Reagent Co. Ltd and Beijing Bellingway Technology Co., Ltd, respectively. Milli-Q 27 deionized water was used during this experiment. 28

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### **1** Preparation of Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs

Bi-rich bismuth oxybromide layered microspheres (Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs) were synthesized 2 3 via an ionic liquid-in-water (IL/W) microemulsion-mediated approach. First of all, in order to obtain the precursor, dissolving 0.56 g [Omim]Br and 0.2 g TX-100 into 25 mL 4 deionized water to get the solution A, while the solution B was prepared by dissolving 5 0.97 g of Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O into 5 mL of nitric acid (1M) to avoid hydrolyzation of Bi<sup>3+</sup> 6 ions. Afterwards, the yellow homogeneous solution could be clearly observed when 7 8 solution B was added drop by drop into the freshly ionic liquid microemulsion system 9 (solution A) with continuously energetic stirring at room temperature. And then, adjusting the pH of the mixed system with NaOH (2M) to 10.5, which should be 10 continuously stirred for another 1h later. Afterwards, the reaction liquid was transferred 11 into a 50 mL Teflon-lined autoclave and reacted at 160 °C for 12 h. Finally, the obtained 12 yellow precipitate needed to be washed three times each with deionized water and 13 ethanol and dried at 60 °C for 24 h. To compare the photocatalytic efficiency of the as-14 prepared materials, the same preparation method was used to synthesize BiOBr and 15 16 Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-plate. The former was prepared under the condition that the reaction system was at pH of 3, and the latter was synthesized in the absence of TX-100. 17

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### 19 Preparation of Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs

20 Silver/silver bromide supported Bi-rich bismuth oxybromide layered microspheres (Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs, AAB-LMs) were constructed via a facile in-21 situ deposition and visible-light photoreduction method. The details are as follows: 0.1g 22 of as-synthesized Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs was added into 48 mL deionized water, and then 23 24 dissolved 2 mL AgNO<sub>3</sub> (0.1M) with ultrasonicating for 5 min to obtain homogeneously dispersed solution. The photoreduction reaction was performed on a photochemical 25 reaction instrument (XPA-7, Nanjing, China). After stirring for 30 min under dark, the 26 suspension was irradiated by 500 W Xenon lamp with 400 nm cut-off filter for 10 min, 27 28 40 min, 90 min and 180 min, respectively. Subsequently, the obtained composites were 29 washed and dried at 60 °C for 24 h. The detailed preparation process of samples is

- 1 shown in Scheme 1. In addition, as the control group, Ag/AgBr was synthesized by the
- 2 same visible-light photoreduction method for 10 min, while AgBr was obtained through
- 3 precipitation of AgNO<sub>3</sub> and KBr at room temperature.



Scheme 1. Schematic illustration of the synthetic process for AAB-LMs composites (A
and B refer to the solution A and solution B respectively).

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## 8 Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 9 10 Advance (Bruker AXS, Germany) X-ray powder diffractometer with Cu Kα radiation at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) spectra were 11 12 obtained by using a PHI5000 Versa Probe electron spectrometer (ULVAC-PHI, Japan) with the adventitious carbon (C 1s = 284.6 eV) as a reference. The scanning electron 13 microscopy (SEM), the elemental analysis and mapping images were conducted on a 14 QUANTA FEG 250 (Hitachi, Japan) equipped with an energy-disperse X-ray 15 spectroscope (EDS). JEM-200CX (JEOL, Japan) with the acceleration voltage of 200 16 kV was operated to measure the transmission electron microscopy (TEM) images. The 17

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surface area and the pore-size distribution of the as-synthesized materials were 1 measured on Brunauer-Emmett-Teller analysis (BET, ASAP 2020, Micromeritics, USA) 2 3 with nitrogen adsorption-desorption isotherm at 77 K. UV-vis. diffuse reflectance spectra (UV-Vis/DRS) was recorded on UV-3600 (Shimadzu, Japan) spectrophotometer. 4 Photoelectrochemical measurements were performed on a CHI-760E electrochemical 5 6 system (Shanghai Chenhua Apparatus Corporation, China) equipped with a standard three-electrode system. The Pt wire served as the counter electrode and the saturated 7 Ag/AgCl was used as the reference electrode, while the working electrode was prepared 8 9 by as-synthesized sample which was spread onto ITO glass to form film.  $Na_2SO_4(0.2M)$ and 500 W Xenon lamp were used as the electrolyte and the light source, respectively. 10 Electron paramagnetic resonance (EPR) analysis was conducted on an EMX-10/12 11 12 (Bruker, Germany) using 5,5-dimeyhyl-1-pyrroline-N-oxide (DMPO) as the spin-trap 13 reagent.

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### **Photocatalytic Activity Measurement** 15

16 The photocatalytic activities of the samples were systematically investigated by the degradation of acid orange II (AO7), 4-tert-butylphenol (PTBP) and aniline under 17 simulated visible-light irradiation. The whole process was performed on a 18 photochemical reaction instrument (XPA-7, Nanjing, China) with 1000 W Xenon lamp 19 20 and 400 nm cut-off filter. Briefly, 10 mg, 50 mg and 50 mg of the catalyst were suspended into 50 mL of AO7 (10 mg/L), PTBP (10 mg/L) and aniline (16 mg/L), 21 22 respectively. Before getting the light, the suspension needed to keep steady stirring for 1h in the dark to achieve the adsorption-desorption equilibrium. During the 23 24 photocatalytic degradation process, 4 mL of the suspension was pipetted out at regular time intervals and filtered with a 0.22 µm Millipore filter. Afterwards, the resultant 25 solution was examined by UV-vis. spectrophotometer (UV-1800, Shimadzu, Japan), 26 27 where the AO7, PTBP and aniline were measured at 484 nm, 274 nm and 280 nm, 28 respectively.

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The recyclability of the as-prepared photocatalyst was studied by cycling run tests,

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or hole (h<sup>+</sup>), etc.) of the AAB-LMs-photocatalytic system, photocatalytic degradation reactions of aniline (16 mg/L) with adding different scavengers were carried out. Acknowledgements This work was financially supported by National Natural Science Foundation of China (No. 51578279 and 21777067) and the Major Science and Technology Program for Water Pollution Control and Treatment of China (No. 2015ZX07204-007). Z-scheme photocatalytic mechanism

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### **Conflicts of Interest** 13

The authors declare no competing financial interest. 14

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Keywords: Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>-LMs · aniline · plasmonic · visible-light photocatalysis · 16

which was performed in the same visible-light photocatalytic degradation reaction

system. The used photocatalyst was collected, washed and dried after the reaction to

regenerate and prepare for the next photocatalytic degradation period. Moreover, to

investigate the main active species (hydroxyl radical ( $\bullet$ OH), superoxide radical ( $\bullet$ O<sub>2</sub><sup>-</sup>)

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### **Appendix A. Supplementary data** 19

Supplementary material associated with this article can be found in the online version. 20

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# **FULL PAPERS**

The novel plasmonic heterojunction photocatalysts of Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> layered microspheres (AAB-LMS) were successfully synthesized by the in-situ deposition and visible-light photoreduction approach. They performed elevated photocatalytic activities towards the degradation of acid orange II and aniline under visible-light irradiation than Bi-O-Br and Ag/AgBr, which was mainly credited to the surface plasmon resonance (SPR) effect of Ag nanoparticles and the synthetic interaction among Ag, AgBr and Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>.



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### Page:

 Title: Synthesis of Ag/AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>

 Plasmonic
 Heterojunction

 Photocatalysts: Elevated Visible-light

 Photocatalytic Performance and Z-scheme Mechanism