Superior adsorption and photoinduced carries transfer behaviors of dandelion-shaped Bi$_2$S$_3$@MoS$_2$: experiments and theory

Mengjiao Li, Junyong Wang, Peng Zhang, Qinglin Deng, Jinzhong Zhang, Kai Jiang, Zhigao Hu & Junhao Chu

The enhanced light-harvesting capacity and effective separation of photogenerated carriers in fantastic hierarchical heterostructures enjoy striking attention for potential applications in the field of solar cells and photocatalysis. A three-dimensional (3D) dandelion-shaped hierarchical Bi$_2$S$_3$ microsphere compactly decorated with wing-shaped few layered MoS$_2$ lamella (D-BM) was fabricated via a facile hydrothermal self-assembly process. Importantly, the as-prepared D-BM microsphere presents pH-dependent superior adsorption behavior and remarkable visible light photocatalytic activity for degradation of organic dyestuffs (Rhodamine B/RhB and Methylene blue/MB), far exceeding those for the pure Bi$_2$S$_3$ and MoS$_2$. It is understandable that D-BM with high surface area possesses more active sites and promotes light utilization due to the unique porous structure with outspread wings. Besides, based on the experiments and theoretical calculations, the staggered type II band alignment of D-BM permits the charge injection from Bi$_2$S$_3$ to MoS$_2$, subsequently accelerates the separation and restrains the recombination of carriers, leading to excellent photocatalytic activity, as well as the photoconductance and photoresponse performance (with $I_{\text{light}}/I_{\text{dark}}$ ratio 567).

The intense demand for photocatalysis applying to the pollutants degradation and the effective solar energy conversion keeps moving due to the worsening environment and energy crisis. It is believed that the desired photocatalysis should have high light-harvesting capability and retardative recombination of photoexcited carriers. A promising approach to enhance the photoactivity is to increase the light absorption range, the surface area and active site of the catalysts. Numerous studies have shed light on the importance of the semiconductor-based composites with certain modification in improving the performance, such as photovoltaic conversion, catalytic, and electrochemical properties. Thus, studying the hierarchical semiconductor nanocomposite with controllable morphologies becomes the frontier strategy. Among these semiconductors, mater sulfides (ZnS, CdS) have been extensively surveyed for the generation of new optoelectronic performance with effective electron-hole separation and transport.

Typically, as a eco-friendly lamellar-structured semiconductor, Bi$_2$S$_3$, with a typical band gap (1.3–1.7 eV) for solar photovoltaic, has attracted lots of research interests. In recent years, reported Bi$_2$S$_3$ nanocrystal with various morphologies have promising applications in solar cells, photodetectors, gas sensors, electrochemical hydrogen storage and X-ray computed tomography imaging due to the suitable band gap. Besides, it also has been used as a stability sensitizer and photocatalyst derived from the broad absorption of visible light up to 800 nm. However, the photocatalytic performance of Bi$_2$S$_3$ has been restricted because of the toilless recombination of photogenerated carriers and therewith the low quantum yield. Hence, as a feasible method so far to prolong the lifespan of electron-hole pairs, establishing composite structures with metal oxides, metal chalcogenides...
or 2-dimensional (2D) hexagonal graphene, for instance Bi\textsubscript{2}S\textsubscript{3}/Bi\textsubscript{2}WO\textsubscript{6}, Bi\textsubscript{2}S\textsubscript{3}/TiO\textsubscript{2} and Bi\textsubscript{2}S\textsubscript{3}/Pd\textsubscript{3}S, has been paid significant attention\textsuperscript{12,26–29}. In particular, the 3-dimensional (3D) porous architecture with Bi\textsubscript{2}S\textsubscript{3} skeleton, keeping superiority in large active contact area, is considered to have potential in synergistically enhancing the photocatalytic features.

The wide researches and successful applications of graphene recently have triggered great attention on 2D-layered materials. The 2D transition metal dichalcogenides (TMD) exhibit ultrathin physical characteristic, excellent optical, electronic, mechanical properties and potential applications in field-effect transitions (FET) and sensing devices\textsuperscript{30–34}. As a representative 2D TMD, consisted of the weakly coupled S-Mo-S atoms sandwich layers, Mo\textsubscript{S\textsubscript{2}} nanoarchitectures have been synthesized with plentiful morphologies of nanosheet, nanoribbon and nanosphere\textsuperscript{35–38}. Different from graphene, the controlled band gap (1.2–1.9 eV) and thermal stability, make Mo\textsubscript{S\textsubscript{2}} be widely applied to biosensors, memory, capacitors, logic circuit devices, and lithium batteries\textsuperscript{39–41}. Importantly, 2D-layered Mo\textsubscript{S\textsubscript{2}} possesses a large surface area and massive active sites, which can provide sufficient contact and effective reactions\textsuperscript{42}. Hence, forming hierarchical composites with Mo\textsubscript{S\textsubscript{2}} has been proven to be promising and it also opens opportunities for optoelectronic applications. Zhou et al. have successfully fabricated Mo\textsubscript{S\textsubscript{2}} nanosheet-coated TiO\textsubscript{2} nanobelt heterostructures, which showed a high photocatalytic hydrogen production and strong photocatalytic degradation of the dye molecules\textsuperscript{43}. It is believed that the formation of this Mo\textsubscript{S\textsubscript{2}}-TiO\textsubscript{2} nanocomposite forcefully retard the photogenerated electron-hole recombination. Moreover, Chen et al. have put forward a bottom-up strategy of solvothermal method for 2D Mo\textsubscript{S\textsubscript{2}} nanosheets composites, which exhibited preeminent properties in biomedicine and realized considerable applications in photothermal regression of tumor\textsuperscript{44}.

In this work, we propose a novel heterostructure of 3D-dandelion Bi\textsubscript{2}S\textsubscript{3}@Mo\textsubscript{S\textsubscript{2}} microsphere using a facile hydrothermal method for the first time. Intriguingly, the layers of Mo\textsubscript{S\textsubscript{2}} coating likes the wring of the dandelion. This unique architecture offered a high light utilization as a result of large surface area and massive active sites for reactions. Moreover, the formation of the staggered type II band alignment in D-BM made a prolonged lifespan of electron-hole pairs, based on calculated energy band positions and the corresponding electronic structures. Obviously, evaluated by the degradation of Rhodamine B (RhB) and Methylene blue (MB) under visible light, the as synthesized heterostructure exhibits more remarkable adsorption and visible light photocatalytic properties than the pristine Bi\textsubscript{2}S\textsubscript{3} and Mo\textsubscript{S\textsubscript{2}}. Also, it presents improved photoresponse property with a high $I_{\text{light}}/I_{\text{dark}}$ ratio of 567.

**Results and Discussion**

**Phase structure and Raman studies.** As shown in Fig. 1a, the phase information and purity of D-Bi\textsubscript{2}S\textsubscript{3}, Mo\textsubscript{S\textsubscript{2}} nanoflowers and their composites were characterized by XRD analysis. Pattern I corresponded well to the lattice planes of orthorhombic Bi\textsubscript{2}S\textsubscript{3} (JCPDS#65-2431 $a = 11.290\, \text{Å}$, $b = 3.978\, \text{Å}$, and $c = 11.150\, \text{Å}$) without some impurity as Bi\textsubscript{2}O\textsubscript{3}. And pattern II can be indexed to the standard peaks of hexagonal Mo\textsubscript{S\textsubscript{2}} (JCPDS#37-1492; $a = 3.16\, \text{Å}$, $b = 3.16\, \text{Å}$, and $c = 12.30\, \text{Å}$). As for hierarchical D-BM structure (5 MBS, pattern III), the weak diffraction peak at $2\theta = 14.2^\circ$, corresponding to the Mo\textsubscript{S\textsubscript{2}} lattice plane of (002), can be inferred that the few-layered Mo\textsubscript{S\textsubscript{2}} petals have been broken by D-Bi\textsubscript{2}S\textsubscript{3}. Raman spectroscopy was further utilized to identify the hybrid production. In Fig. 1b, two characteristic peaks of Mo\textsubscript{S\textsubscript{2}} can be observed at 375 and 402 cm\textsuperscript{-1} from the local amplification, which correspond to the E\textsubscript{2g} and A\textsubscript{1g} vibration modes, respectively\textsuperscript{41}. The vibrational modes of pure Bi\textsubscript{2}S\textsubscript{3} microspheres are located at 107 cm\textsuperscript{-1} and 260 cm\textsuperscript{-1}, which can be assigned as the A\textsubscript{1g} and E\textsubscript{2g} modes\textsuperscript{1}. Obviously, all the characteristic Raman spectral signatures of Bi\textsubscript{2}S\textsubscript{3} and Mo\textsubscript{S\textsubscript{2}} both are presented in the result of their hybrids, demonstrating the successful incorporation of D-BM structures. Note that there is a blue shift of the B\textsubscript{1g} mode compared to the pure Bi\textsubscript{2}S\textsubscript{3}. It probably suggests the surface strain is due to the novel coated Mo\textsubscript{S\textsubscript{2}} on each Bi\textsubscript{2}S\textsubscript{3} nanorod.

**Morphology analysis.** The morphology and micro-structure of all the samples have been investigated by SEM images. Figure 2a,b display the pure D-Bi\textsubscript{2}S\textsubscript{3} microspheres in different magnifications. It can be seen that the Bi\textsubscript{2}S\textsubscript{3} structures are distributed in the shape of irregular microspheres with the average diameter of 5 μm. Apparently (inset of Fig. 2b), these D-Bi\textsubscript{2}S\textsubscript{3} microspheres were composed of a large number of acicular crystalline nanorods with uniform diameters of about 80 nm. Moreover, the broken D-Bi\textsubscript{2}S\textsubscript{3} microsphere shown in Fig. 2c indicates that the acicular Bi\textsubscript{2}S\textsubscript{3} nanorods radiate from the center and stack uniformly. It is extremely vital that the interstices between Bi\textsubscript{2}S\textsubscript{3} nanorods can provide particular framework for the embedded of layered Mo\textsubscript{S\textsubscript{2}} petals. As presented in Fig. 2d, the pure Mo\textsubscript{S\textsubscript{2}} flowers reveal the diameter of 4 μm, with number of thinnish petals aggregated closely. The inset of Fig. 2d provides a chapped Mo\textsubscript{S\textsubscript{2}} flowers, and it illustrates that these disordered petals grown from a common center to form the spherical structure. Figure 2e exhibits the morphology of the hydrothermal synthesized D-BM (5 MBS) hetero-microspheres. Detaiely, some other SEM information on Bi\textsubscript{2}S\textsubscript{3}, Mo\textsubscript{S\textsubscript{2}}, and hybrids are shown in Figs S1 and S2 (ESI). Generally, the whole D-Bi\textsubscript{2}S\textsubscript{3} microspheres are uniformly covered with 2D Mo\textsubscript{S\textsubscript{2}} nanosheets. A high magnification top view SEM image shown in the inset of Fig. 2e, the composites present apparent differences from the pristine D-Bi\textsubscript{2}S\textsubscript{3} or Mo\textsubscript{S\textsubscript{2}}. Interestingly, almost each Bi\textsubscript{2}S\textsubscript{3} nanorod is compactly decorated with a pair of expanding wings of Mo\textsubscript{S\textsubscript{2}} nanosheets, thus forming the Mo\textsubscript{S\textsubscript{2}} coated Bi\textsubscript{2}S\textsubscript{3} heterostructure. In the inset of Fig. 2f, a section of the broken composites elucidates that Mo\textsubscript{S\textsubscript{2}} nanosheets have grown along the Bi\textsubscript{2}S\textsubscript{3} nanorods and deeply rooted in the center of Bi\textsubscript{2}S\textsubscript{3} spheres, which expects that this unique hierarchical architecture can provide more effective activity sites and enhance the photoelectric properties.

In addition, a sequence of TEM and HRTEM images of D-BM nanocomposite have been employed to reveal more specific structural information. In Fig. 3a, homogeneous Mo\textsubscript{S\textsubscript{2}} sheets are detected at the edge of each Bi\textsubscript{2}S\textsubscript{3} nanorod from the low magnification TEM survey. Not only Fig. 3b,c clarify the intimate interfacial contact between Mo\textsubscript{S\textsubscript{2}} sheets and elongated Bi\textsubscript{2}S\textsubscript{3} rods, but also they indicate that the Mo\textsubscript{S\textsubscript{2}} sheets are ultrathin compared with the pure Mo\textsubscript{S\textsubscript{2}} flowers. In the HRTEM image (Fig. 3e), the lattice fringes of $d = 3.54\, \text{Å}$ and $d = 3.74\, \text{Å}$,
corresponding to the (130) and (101) planes of Bi₂S₃, respectively. The coated MoS₂ exhibits the lattice spacing of 6.19 Å, which matches well with the (002) planes of hexagonal MoS₂. Furthermore, the related cleaved crystal structure in theoretical section indicates the distance between adjacent Bi atoms on the (130) crystal surface of Bi₂S₃ (3.4148 nm), which is eleven intervals of the adjacent S atoms on the (001) crystal surface of MoS₂ (0.3169 nm × 11). It is believed that Bi₂S₃ nanorods might be available for the growth of the MoS₂ nanosheets to form the heterostructure between the mutual effect of S and Bi atoms. Thus, it can be inferred that the MoS₂ sheets, with about 5–8 layers, embellished at the surface of the Bi₂S₃ rods. Moreover, the selected area electron diffraction (SAED) pattern (inset of Fig. 3b) further proves the mixed-phase nature of single crystal Bi₂S₃ (bright diffraction spots) and layered superimposed MoS₂ sheets (diffraction rings). In order to accurately confirm the elemental composition and spatial distribution, energy dispersive X-ray spectrometry (EDS) analysis in Fig. 3e have been performed. The well-proportioned distributions of S, Bi, and Mo can be obtained from the mapping results. Besides, the EDS line scan (Fig. 3f) of the marked region sheds light on the unique hierarchical heterostructure, as well as in agreement with SEM and TEM observation.

**XPS analysis.** We also performed XPS analysis to elucidate the surface chemical composition and valence states of the pristine Bi₂S₃, MoS₂, and D-BM (5 MBS) heterostructures. The Fig. 4a shows the survey XPS spectra of Bi₂S₃ and MoS₂. After the second hydrothermal reaction, the overall XPS spectra in Fig. 4b indicates the main constituent of Bi, S, and Mo elements. Figure 4c,d display the spin-orbit components of Bi 4f (158.46/163.76 eV) and Mo 3d (228.84/231.99 eV) for pure Bi₂S₃ and MoS₂, respectively. In addition, the XPS spectrum of the hybrids in Fig. 4e can be well fitted into several dominate peaks with binding energies of 158.75 eV, 162.05 eV, 163.30 eV, and 164.05 eV, which are assigned to Bi 4fₓᵧ and Mo 3dₓᵧ, respectively. The high resolution Mo 3d (Fig. 4f) binding energies of the hybrids are located at around 229.23 eV and 232.38 eV, corresponding to Mo 3dₓᵧ and Mo 3dᵧₓ, respectively. Notably, the Bi 4f and Mo 3d peaks shift toward the high banding energy, with dotted lines mark. Hence, it could be deduced that chemical bonds of Bi–S–Mo formed probably, related to the electronic shielding effect. A weak peak at 226.31 eV has also been found, which is attributed to the S 2p.
Take the spin orbit separation into consideration, the phenomenon among Bi $4f$ (5.30 eV), S $2p$ (1.25 eV), and Mo $3d$ (3.15 eV) peaks disclose the existence of Bi$^{3+}$, S$^{2-}$, and Mo$^{4+}$, based on the reported results.

**Growth mechanism investigation.** The growth mechanism of the D-BM nanomaterials has been studied for potential applications and controllable synthesis of other novel structures. For D-Bi$_2$S$_3$, the formation process has been investigated by SEM at different reaction times, as shown in Fig. 5a–f. At the early reaction stage (1 h), the half-baked microspheres (diameter of 2 μm) have been formed and proven to be orthorhombic Bi$_2$S$_3$ by XRD analysis (Fig. S3), which indicate the fast nucleation of Bi$_2$S$_3$. As the reaction proceeded (3 h), some actinomorphic-shaped Bi$_2$S$_3$ (diameter of 5 μm) can be captured in Fig. 5b. From the close inspection (Fig. S4), however, the surface of the radial Bi$_2$S$_3$ nanorods are rough and inhomogenous, indicating a rapid growth of Bi$_2$S$_3$ microspheres. By prolonging the reaction time to 8 h, massive intact D-Bi$_2$S$_3$ microspheres have been successfully

**Figure 2.** (a,b) SEM images of the dandelion-shaped Bi$_2$S$_3$ microspheres under different magnifications. The inset shows the high magnification SEM image of vimeous Bi$_2$S$_3$ nanorods. (c) The broken Bi$_2$S$_3$ microspheres. (d) SEM image of MoS$_2$ nanoflower and the inset is the several chapped MoS$_2$ nanoflowers. (e,f) SEM image with different magnifications of the synthesized D-BM heterostructures. The insets are a local amplification from the side views and a broken section.

**Figure 3.** (a) TEM image of D-BM microstructures. (b) The surface of D-BM and the inset is the SAED pattern. (c,d) HRTEM images of D-BM. (e) SEM image of D-BM and the corresponding EDS mapping images of Bi, S, and Mo elements. (f) The corresponding EDS line scan along the pink line in (e).
synthesized. Then the products under hydrothermal condition have been collected at 5 h, 8 h, and 12 h. The SEM images in Fig. 5d–f manifest that the coated MoS₂ nanosheets become increasing and orderly along with the prolonged reaction process. It can also be verified through the related XRD survey (Fig. S4). At the beginning, the characteristic peak of MoS₂ at 2θ = 14.2° is indeed indetectable. With prolonging the reaction time, the emergence of MoS₂ (002) plane provides the convincible proof for the formation of the MoS₂ coated Bi₂S₃ nanocomposites. Based on the results of the time-dependent experiments and analysis, the probable morphology evolution process of the hetero-Bi₂S₃@MoS₂ structure is illustrated in Fig. 5g. In our experiments, thiourea was chosen to act as the sulfide source, for constituting the Bi₃⁺-thiourea complexes, initially. Under elevated temperature, these complexes decomposed, accompanied by shaping into needle-like nanospheres with nucleated Bi₂S₃. As time went on, Bi₂S₃ grew gradually to improve the rough surface, at the expense of Bi₂S₃ particles or rods. It can be attributed to the typical Ostwald ripening process, which could significantly reduce the total surface free energy. Besides, the solution of PEG is necessary to build a suitable viscous surroundings, which promotes the unique geometrical patterns. For comparison, the morphology and crystallinity of the product obtained without PEG

Figure 4. XPS spectra of as-synthesized products. (a,b) The overall spectra of Bi₂S₃, MoS₂, and 5 MBS, respectively. The Bi 4f and Mo 3d spectra for Bi₂S₃ (c), MoS₂ (d), and D-BM (e,f), respectively. Note that the scatter and solid lines indicate the experimental data and fitting results, respectively. The dotted lines mark the peak shifts of Bi 4f and Mo 3d.
also have been surveyed. As a result (Fig. S5), the regular Bi$_2$S$_3$ microspheres with short tomentum ascertain the role of PEG as the important template. Finally, the 3D D-Bi$_2$S$_3$ microspheres could provide available high active sites for the growth and insertion of MoS$_2$ nuclei, leading to the hierarchical and porous framework.

**BET surface areas and photocurrent response.** As shown in Fig. 6a, the nitrogen adsorption-desorption measurements have been performed to ascertain the surface area and the porous structure of the as-synthesized samples. According to the Brunauer-Deming-Deming-Teller (BDDT) classification, the isotherms of D-BM displays a typical hysteresis loops as type IV. The specific Brunauer-Emmett-Teller (BET) surface area have been
estimated to be about 19.48 m²/g for the hybrid. Obviously, the characteristics with enlarged surface area and porosity of the composite recognized the embedded structure of MoS₂ nanosheets into Bi₂S₃ microspheres. By the Barrett-Joyner-Halenda analysis, the pore-size distribution of Bi₂S₃@MoS₂ (inset of Fig. 6a) indicates the main mesopores with about 4.5 nm.

Before moving toward the photocatalytic study of the as-synthesized products, the separation of charge carriers, as a crucial factor, needs to be investigated indispensably. Hence, the photocurrent transient response measurements of pure Bi₂S₃, MoS₂, and their mesoporous composites have been carried out to verify the extended lifespan of the photogenerated charges. Under visible-light irradiation, Fig. 6b records the fast and consistent photocurrent responses over several on-off cycles, illustrating that all three samples are reproducible and stable. Apparently, pure Bi₂S₃ and MoS₂ both present low photocurrent densities, consisted with the low quantum efficiency. However, the photocurrent density of the D-BM electrode is enlarged about one order of magnitude higher than the pure Bi₂S₃ electrode. It can be interpreted that this novel heterostructure possess particular tunnel for transformation of photogenerated carries, subsequently retards the recombination and extends the lifetime of carries.

Adsorption and photocatalytic properties. To demonstrate the photocatalytic ability of the D-BM heterostructures, photodegradation of RhB in aqueous solution has been investigated under visible-light irradiation. In Fig. 7a, at pH = 7, the corresponding decomposition rate of bare Bi₂S₃ (26%) and MoS₂ (50%) are indistinctive after 40 min. Whereas, when the MoS₂ was introduced to Bi₂S₃, the decomposition rate significantly increases to near 92%. The time-dependent absorption spectra of RhB solutions by D-BM and others were shown in Fig. 7e and Fig. S6. It could conclude that the hierarchical D-BM structure owns outstanding photocatalytic performance than two others. As it has been proposed by Daage, the “rim-edge” mode of MoS₂ have massive dege active sites, where strong interaction occurs with dye molecules. Also, these ultrathin and wrinkled surfaces of MoS₂ may lead to several internal intersections, which make it possible to bring much more effective area for absorption. Likewise, it is favoring to transfer excited carries between MoS₂ and Bi₂S₃ heterostructure, leading to reduce the recombination efficiency and prolong the lifetime of carries. In addition, the photocatalytic activity can also be related to the amount of the coated MoS₂ nanosheets, which highlights the optimization of 5 MBS. As for 2 MBS samples, fewer MoS₂ nanosheets cannot provide enough multiplex refraction for the incident path, as well as...
the more active site for the adsorption of reactant molecules. On the other hand, 8 MBS samples with superabundant MoS₂ nanosheets impeded the transformation of photogenerated carries in reverse, thus facilitating their recombination. To make a more specific comparison, the reaction kinetics of all catalysts have been linear fitted as \( \ln \left( \frac{C_0}{C} \right) = kt \) according to the Landau-Hinshelwood mechanism shown in Fig. 7b.\(^{54–58}\) Note that \( C \) and \( C_0 \) are the real-time concentrations and initial concentration of RhB. \( t \) and \( k \) denote the irradiation time and the overall photodegradation rate constant, respectively. The rate constant of pristine Bi₂S₃ and MoS₂ are 0.007 and 0.016 min\(^{-1}\). Nevertheless, a dramatic improvement (0.073 min\(^{-1}\)) of 5 MBS can be achieved. Specifically, the increased reaction rates were attributed to the unique porous structure, with faster mass transport and more accessible active sites, resulting in an increased reaction rate. The stability and reusability of the composites (sample 5 MBS at pH = 7) also have been evaluated under irradiation by collecting and reusing them over 3 cycles. As shown in Fig. 7f, the insignificant decline in photocatalytic activity after three runs (90%) confirms the stability of the catalysts, excepting the incomplete collection. The constancy can be recognized through the XRD result after photocatalytic tests (Fig. S7).

It is believed that the effective photocatalysis need handle both the mass transfer and the light transfer issues. The adsorption capacity of catalyst surface for dyes during illumination is a defining factor in photodegradation. In addition, the initial pH plays a dominant role to the adsorption process. Therefore, based on the above adsorption behavior of the D-BM product in dark and neutral surroundings, the pH-dependent adsorption (3.0–11.0) and photocatalysis survey have been conducted. Note that the initial pH of the RhB solution was adjusted by HCl and NaOH solution (1 M). The Fig. 7c reveals that the adsorption capacity of D-BM hybrids has been promoted under acidic conditions and pH ≤ 5 appears to the most beneficial. The adsorption efficiency reaches approximately 76% (Fig. S8) and photodegradation rate \( k = 0.157 \text{ min}^{-1} \) (Fig. 7d) at pH = 5. For verifying the adsorption behavior and photocatalytic activity of D-BM hybrid, the colors of the degraded MB solutions (Fig. S8) and photodegradation of MB solution under pH of 3, 5, 7, 9, and 11 have been obtained in Fig. 7g,h. Obviously, D-BM shows a superior adsorption and photodegradation properties compared with pure Bi₂S₃ and MoS₂, especially when pH < 7. Accordingly, although the initial pH affects the adsorption process of dyes onto the catalyst, the photodegradation process of D-BM remains resultful at a large range of pH values. It indicates that D-BM hybrid can serve as a high efficiency catalyst for wastewater treatment, which contained a mild acid commonly.

In order to further investigate the stability of the catalyst, the XRD and EDS mapping results after adsorption and photodegradation tests have been shown in Fig. 8a,b. Compared with the XRD results (Fig. 1a) and EDS mapping (Fig. 3e) before photocatalysis, there exist minor change among the elemental composition, spatial distribution, and the phase characterization results. Therefore, the composite has presented relative stability in view of its unique heterostructure and synergistic effect attributed to the intense interaction between Bi₂S₃ and MoS₂, which favors the separation of the photinduced carriers. However, a small percentage of the samples might have undergone hydrolysis which was unavoidable, taking the slight decrease through cycling experiments and photocorrosion into consideration.

### Relevant kinetics mechanism

In Fig. 7j,k, the related adsorption and photocatalysis kinetic mechanism of the D-BM heterostructure under visible light irradiation has been put forward. In mild acidic environment (pH < 7), the surfaces of the catalyst is exposed to acidic (positive) conditions and positively charged, as shown in Fig. 7. In addition, both the \( \pi \)-bond of RhB and MB can beneficially excite electrons with irradiation, as well as the existence of the functional groups (-COO⁻) as the shown molecular structure of RhB in Fig. 7. Thus, we can conclude that the dyes might be adsorbed by D-BM hybrid through complex relationship involving electrostatic attraction or hydrogen bonds. Subsequently, these adsorbed dyes on the surface of D-BM could be in situ degraded promptly (Fig. 7). The mass transfer and the chemical reaction process can be guaranteed by the opposite concentration difference and the visible light irradiation, which help to accomplish the degradation synergistically. In order to make it clear, the right part of the Fig. 7j illustrates the complete process simply, which contains both the adsorption and the photocatalysis behaviors of the D-BM hybrid.

On the other hand, since the band-edge potential levels play a crucial role in determining the migration directions of the photoexcited carriers in a heterojunction, the relative band positions of the two semiconductors have been investigated to approach the mechanism of the enhanced photocatalytic activity of their composites. Significantly, a staggered type-II configuration formed at the interface of D-BM structures by the calculated band edge positions, according to the empirical formula:

\[
E_{\text{VB}} = X - E_g + 0.5E_f \tag{12}
\]

where \( E_{\text{VB}} \) is the valence band (VB) edge potential and \( E_g \) refers to the free electrons energy based on the hydrogen scale (4.5 eV). Based on previous studies, \( X \) is the electronegativity of the corresponding semiconductor (5.28 eV for Bi₂S₃ and 5.32 eV for MoS₂), expressed as the geometric mean of the electronegativity for the component atoms, and the band gap energy \( E_g \) of Bi₂S₃ and MoS₂ are 1.33 eV and 1.3 eV, respectively.\(^{12,19}\) Correspondingly, the \( E_{\text{CB}} \) and \( E_{\text{CB}} \) (CB, the conduct band) of Bi₂S₃ are estimated to be 0.12 eV and 1.45 eV, both higher than those of MoS₂, with \( \Delta E_{\text{VB}} = 0.02 \text{ eV} \) and \( \Delta E_{\text{CB}} = 0.05 \text{ eV} \), respectively. Compared with the pure samples, the heterostructure of D-BM presents an obvious enhanced absorption (Fig. 7i), both in range and intensity. As illustrated in Fig. 7k, under visible-light irradiation, excited electrons-holes are generated facilely in both Bi₂S₃ and MoS₂. With the suitable type II band alignment, the transfer of carriers are also performed from the CB of Bi₂S₃ to MoS₂, as well as the reflux of holes mainly from the VB of MoS₂ to Bi₂S₃. Therefore, more vacancies have been left at the bottom of CB and top of VB for Bi₂S₃/ MoS₂, resulting in pruning the lifetime of carriers and boosting more available separation. After the photoexcited carries fleetly flow to the CB of MoS₂, the reaction of \( \text{O}_2^{-}\rightarrow \text{O}_2\cdot\cdot \) has been further promoted through one-electron reducing. Then hydroxyl radicals \( \text{OH}^{-}\) may be the dominating active species of RhB photodegradation, since it can be generated by the reaction between water and the unstable superoxide radical anion \( \text{O}_2^{-}\cdot\cdot \) \(^{57}\). Meanwhile, the remaining holes in the valence band of Bi₂S₃ also participate in the degradation of RhB as the trapped active species.
Photoconductance and photoresponse performances. Besides photocatalysis, the as-synthesized D-BM hybrid is expected to have improved photoconductance and photoresponse properties compared with the pure Bi$_2$S$_3$ structure. In order to spin coating, the photodetector devices (Fig. 9a) were fabricated by these disrupt NR-BM and Bi$_2$S$_3$ nanorods (NR-Bi$_2$S$_3$). Figure 9b plots the typical current-voltage (I–V) curves of NR-BM based nano-photodetector exposed to 650 nm illumination (1.0 mW cm$^{-2}$) and in dark, respectively. It is obvious that the quasilinearity of the I–V curves indicates the formation of an good Ohmic contact between Au electrode and NR-BM interface. With illumination, the NR-BM shows a remarkable photocurrent reaches about 0.703 $\mu$A under $-1.5$ V bias voltage, resulting a higher $I_{\text{light}}/I_{\text{dark}}$ ratio to about 567, which compared to the NR-Bi$_2$S$_3$ of 126 with the shortened lifetime of the electron-hole pairs (Inset of Fig. 9b). The electrical characteristics of the NR-BM based device have been investigated in dark and at increasing illumination intensities from 0.25 mW cm$^{-2}$ to 5 mW cm$^{-2}$ (Fig. 9c). Clearly, the photocurrent increases with the enlarged light intensity and exhibits a high dependence on it, and their relationship can be described by a simple power law as $I = AP_0^{0.58}$. Where $A$ and $\theta$ represent a constant for a certain wavelength and the response of photocurrent to light intensity, respectively. The fitting curve leads to $\theta = 0.89$, which suggests that there exists little trap states (Inset of Fig. 9c) in the NR-BM photodetector. In addition, Fig. 9d provides the time dependent photoresponse of the D-BM device at a bias voltage of 1 V, which sheds light on a readily switch between high- and low-conduction states by illumination on/off. It is known that the responsivity ($R$) serves as a critical metric to the photodetector sensitivity, which is defined as $R(\text{AW}^{-1}) = I_p/P_{\text{opt}}$. Where $I_p$ and $P_{\text{opt}}$ are the photocurrent and incident light power, respectively. Based on the results, the $R$ of the D-BM device is estimated to be 13.3 AW$^{-1}$. Consequently, the improvement of
photoconductivity and photoresponse performance supports the efficient carries separation resulting from the heterostructures of dandelion-shaped Bi$_2$S$_3$@MoS$_2$.

**Theoretical investigation.** The obtained band structures and the density of states (DOS) of Bi$_2$S$_3$ and MoS$_2$ have been shown in Fig. 10a–f, respectively. As we can see, the top of VB contains S 3\textit{p} and few contributions of Bi 6\textit{s}, while the bottom of CB are mostly Bi 6\textit{p} and S 3\textit{p} for Bi$_2$S$_3$, with calculated $E_g = 1.44$ eV. As for MoS$_2$ (with calculated $E_g = 1.29$ eV), the top of VB originates from Mo 4\textit{d}, and the bottom of CB are Mo 4\textit{d} and some hybridization with S 3\textit{p}. Note that Fig. 10f shows the crystal surface matching of MoS$_2$ (top) and Bi$_2$S$_3$ (down). By aligning the Fermi level relative to the vacuum energy level, the obtained work functions for Bi$_2$S$_3$ and MoS$_2$ are 4.88 and 5.00 eV, respectively. Due to the differential work functions, a built-in electric field from Bi$_2$S$_3$ to MoS$_2$ can be established near the interface. Thus the built-in electric field of the composites is expected to facilitate the separation of photo-generated carriers. It can be concluded that the theoretical calculations of the band energy positions (Fig. 10e) keep highly unanimous with the experimental results. In consequence, the MoS$_2$ nanosheets uniformly layer-coated the Bi$_2$S$_3$ microspheres sufficiently absorb visible-light and retard the electron-hole recombination, eventually leading to improvement of the photocatalytic and optoelectronic properties. Moreover, the unique novel architecture can provide valuable references to take advantage of solar energy in the future.

**Conclusion**

In summary, a green strategy based on the hydrothermal method has been developed for the fabrication of hierarchical 3D dandelion-shaped Bi$_2$S$_3$ microspheres coated with layered MoS$_2$ nanosheets. The novel heterostructure with unique porosity and intimate interfacial contact can provided efficient visible-light utilization and penetrable paths for reactant molecules to reach the inner structure. Compared with the pristine Bi$_2$S$_3$ or MoS$_2$, the as-synthesized D-Bi$_2$S$_3$@MoS$_2$ composite has exhibited much higher adsorption behavior and photocatalytic activity under visible-light irradiation. The formed staggered type II band alignment of Bi$_2$S$_3$@MoS$_2$ has expected to promote the separation of carries, accelerate the transportation and prolong lifespan of electron-hole pairs, which can be verified by the excellent photoconductance and photoresponse properties. Correspondingly, the Bi$_2$S$_3$@MoS$_2$-0.5 mol (5 MBS) has been proven to achieve an optimal photocatalysis performance, highlighting the importance of novel core/shell heterostructures for environmental remediation and solar energy harvesting applications in the future.
Methods

Synthesis. Generally, the D-BM heterostructure were synthesized by a two-step hydrothermal method. Firstly, the dandelion-shaped Bi$_2$S$_3$ microspheres were prepared at 180 °C\textsuperscript{19}. Then, for forming the hybrids, another hydrothermal process was employed to embed MoS$_2$ nanosheets onto Bi$_2$S$_3$ microspheres (molar ratios of Mo$^{4+}$ to Bi$^{3+}$ were 20%, 50%, and 80%, with the labels of 2 MBS, 5 MBS, and 8 MBS, respectively). Further information about the experimental details are available in the ESI.

Characterization. The crystallinity and purity of the resulting products were assessed by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) equipped with Cu Kα radiation ($\lambda = 1.5418$ Å). Field emission scanning electron microscopy (FESEM, JEOL-JSM-6700F) was employed to investigate the morphologies of the synthesized samples, equipped with an energy dispersive X-ray spectroscopy (EDS). For detailed insight into the 2D-layered MoS$_2$ coated Bi$_2$S$_3$, Transmission Electron Microscope (TEM) and high resolution transmission

Figure 10. Calculated band structures (a,b), the density of states (c–e), and the crystal surface matching between the (130) and (001) crystal surfaces (f) of Bi$_2$S$_3$ and MoS$_2$, respectively.
electron microscopy (HRTEM) studies were analyzed at the accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS, RBD upgraded PHI-5000C ESCA system, Perkin-Elmer) measurements were carried out with Mg-Kα radiation (hv = 1253.6 eV). Raman spectroscopy experiments were implemented by Jobin-Yvon LabRAM HR 800 micro-Raman spectrometer using a 532 nm line from a He-Cd laser. The absorption spectra have been obtained using the PerkinElmer Lambda 950 spectrophotometer in dilute solution. The specific surface area were calculated by the Brunauer-Emmett-Teller (BET) method (TriStar II 3020, America).

**Photocatalytic test.** The photocatalytic performance of the as-synthesized D-BM composites were evaluated by degrading RhB and MB (organic pollutant of dye wastewater) under visible light irradiation. More details about the photocatalytic tests have been provided in ESI. In addition, transient photocurrent responses for the as-prepared catalysts were performed over an electrochemical analyzer (CHI660D Instruments, China) in a standard three electrode system. Under the irradiation of simulated sunlight (500 W Xe lamp with a cutoff filter), the prepared samples acted as working electrode (ITO as supporter). A Pt wire worked as counter electrode, and Ag/AgCl (saturated KCl) as reference.

**Measurement of photoconductance.** The photoconductance and photoresponse behavior of the D-BM was studied based on the nano-photodetectors. Typically, the disrupt Bi2S3@MoS2 nanorods (NR-BM) from D-BM microspheres by oscillating (Sonics VCHX800, America) were drop-deposited on the SiO2 (300 nm)/Si substrate. Then the Au electrodes (100 μm × 150 μm) were defined on the NR-BM film by photolithography and high-vacuum electron beam (EB) vaporation process. The optoelectronic properties of the fabricated device were measured by a semiconductor parameter analyzer system (Keithley 4200-SCS) with the illumination laser of 650 nm.

**Theoretical calculation.** In the present work, the first-principles calculations of the heterogeneous structure have been performed to provide the theoretical basis of the promoted photocatalytic activity. In details, the plane-wave pseudopotential calculation with the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) have been carried out using the Materials Studio 7.0 Package61–63. The cutoff kinetic-energy (Bi2S3 and MoS2) are 600 eV/450 eV and the 3/5 μ of 650 nm.

**References**

1. Zou, Z. G., Ye, J. H., Sayama, K. & Arakawa, H. Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature* **21**, 625–627 (2001).

2. Bian, T. et al. Spontaneous Organization of Inorganic Nanoparticles into Nanovesicles Triggered by UV Light. *Adv. Mater.* **26**, 5613–5618 (2014).

3. Feng, X. L. et al. Hollow Mesoporous Alumíniosilica Spheres with Perpendicular Pore Channels as Catalytic Nanoreactors. *ACS Nano* **6**, 4434–4444 (2012).

4. Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. & Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* **6**, 269–271 (2001).

5. Qin, N. et al. One-Dimensional CdS/TiO2 Nanofiber Composites as Efficient Visible-Light-Driven Photocatalysts for Selective Organic Transformation: Synthetic Characterization, and Performance. *Langmuir* **6**, 1203–1209 (2000).

6. Pu, Y. C. et al. Au Nanostructure-Decorated TiO2 Nanowires Exhibiting Photoactivity Across Entire UV-visible Region for Photoelectrochemical Water Splitting. *Nano Lett.* **6**, 3817–3823 (2013).

7. Li, W. et al. Hydrothermal Etching Assisted Crystalization: A Facile Route to Functional Yolk-Shell Titatane Microspheres with Ultrathin Nanosheets-Assembled Double Shells. *J. Am. Chem. Soc.* **31**, 593–597 (2011).

8. Zhu, C. B. et al. A General Strategy to Fabricate Carbon-Coated 3D Porous Interconnected Metal Sulfides: Case Study of SnS/C Nanocomposite for High-Performance Lithium and Sodium Ion Batteries. *Adv. Sci.* **2**, 1500200 (2015).

9. Li, L., Li, P. F., Lu, N., Dai, J. & Zeng, X. C. Simulation Evidence of Hexagonal-to-Tetragonal ZnSe Structure Transition: A Monolayer Material with a Wide-Range Tunable Direct Bandgap. *Adv. Sci.* **2**, 1502990 (2015).

10. Wang, M. G., Han, J., Xiong, H. X. & Guo, R. Yolk@Shell Nanoarchitecture of Au@r-GO/TiO2 Hybrids as Powerful Visible Light Photocatalysts. *Langmuir* **31**, 6220–6228 (2015).

11. Alessandro, L. T. et al. Assembly, Growth, and Catalytic Activity of Gold Nanoparticles in Hollow Carbon Nanofibers. *ACS Nano* **6**, 2000–2007 (2012).

12. Zhang, Z., Wang, W. Z., Wang, L. & Sun, S. M. Enhancement of Visible-Light Photocatalysis by Coupling with Narrow-Band-Gap Semiconductor: A Case Study on Bi2S3/β-WO3. *ACS Appl. Mater. Interfaces* **4**, 593–597 (2012).

13. Guo, S. Q. et al. Mesoporous Bi2S3 nanorods with graphene-assistance as low-cost counter-electrode materials in dye-sensitized solar cells. *Nanoscale* **6**, 14433 (2015).

14. Elena, K. et al. Suppression of the Plasmon Resonance in Au/CdS Colloidal Nanocomposites. *Nano Lett.* **11**, 1792–1799 (2011).

15. Hong, T. et al. Anisotropic photocurrent response at black phosphorus-MoS2 p-n heterojunctions. *Nanoscale* **7**, 18537 (2015).

16. Zhang, J., Liu, S. W., Yu, J. G. & Iarovicic, M. A simple cation exchange approach to Bi-doped ZnS hollow spheres with enhanced UV and visible-light photocatalytic H2-production activity. *J. Mater. Chem. B* **2**, 14655 (2015).

17. Malakooti, R. et al. Shape-Controlled Bi2S3 Nanocrystals and Their Plasma Polymerization into Flexible Films. *Adv. Mater.* **18**, 2189–2194 (2006).

18. Cademartiri, L. et al. Cross-Linking Bi2S3 Ultrathin Nanowires: A Platform for Nanostructure Formation and Biomolecule Detection. *Nano Lett.* **9**, 1482–1486 (2009).

19. Nambiar, S., Osei, E. K. & Yeow, J. T. W. Bismuth Sulfide Nanoflowers for Detection of X-rays in the Mammographic Energy Range. *Sci. Rep.* **5**, 9440 (2015).

20. Rath, A. K., Bernechea, M., Martinez, L. & Konstantatos, G. Solution-Processed Heterojunction Solar Cells Based on p-type PbS Quantum Dots and n-type Bi2S3 Nanocrystals. *Adv. Mater.* **23**, 3712–3717 (2011).

21. Tahir, A. A. et al. Photoelectrochemical and Photoresponsive Properties of Bi2S3 Nanotube and Nanoparticle Thin Films. *Chem. Mater.* **22**, 5084–5092 (2010).

22. Chen, G. H. et al. Fabrication of Ultrathin Bi2S3 Nanosheets for High-Performance, Flexible, Visible-NIR Photodetectors. *Small* **11**, 2848–2855 (2015).
Acknowledgements

One of the authors (M. J. Li) would like to thanks Prof. L. B. Luo, Y. Q. Yu, Dr. C. Li and H. L. Li for constructive discussions. This work was financially supported by Major State Basic Research Development Program of China (Grant No. 2013CB922300), the Natural Science Foundation of China (Grant Nos 11374097, 61376129, and...
Projects of Science and Technology Commission of Shanghai Municipality (Grant Nos 15JC1401600, 14XD1401500, 13JC1402100, and 13JC1404200), and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

Author Contributions
M.L. and Q.D. analysed data and prepared the manuscript and figures. M.L., P.Z., J.Z., and K.J. prepared the samples and performed experiments. M.L. and J.W. performed the first-principles calculations. The project was initiated and conceptualized by Z.H. and J.C. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Li, M. et al. Superior adsorption and photoinduced carries transfer behaviors of dandelion-shaped Bi₂S₃@MoS₂: experiments and theory. Sci. Rep. 7, 42484; doi: 10.1038/srep42484 (2017).

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2017