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Two-dimensional black phosphorus-modified Cs₂AgBiBr₆ with efficient charge separation for enhanced visible-light photocatalytic H₂ evolution†

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Lead-free double halide perovskite (Cs₂AgBiBr₆) is considered to be a potential candidate material for photocatalytic hydrogen production due to its excellent visible light capture capability. However, the rate of the hydrogen evolution reaction (HER) taking into account these catalysts is still insufficient. In this study, two-dimensional black phosphorus (BP) anchored on Cs₂AgBiBr₆ (CABB) by electrostatic coupling was prepared. The resulting catalyst BP/CABB was quite stable in a HBr solution during the entire light reaction and reached a hydrogen production rate of 104.6 μmol h⁻¹ g⁻¹ under visible light, which was higher than that of CABB alone. Significantly enhanced HER activity was explored by optical/photochemical measurements, indicating that BP can be used as an electronic accelerator, transmitted by a Z-scheme heterojunction in the interface of the catalyst to transfer electrons, and further produce hydrogen. This has been instrumental in the high-efficiency photocatalyst by anchoring the nonmetallic active sites on CABB.

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1. Introduction

Energy and the environment are currently the two most important issues in society. With the development of technology and the varied demands of the world, the global energy crisis and various environmental issues have become increasingly severe.^{1–3} Photocatalytic hydrogenation technology involving various semiconductor materials has attracted extensive attention as a clean and sustainable solar–hydrogen energy conversion technology.^{4–6} Many efforts regarding photocatalytic hydrogen production technology are committed to utilizing low-cost and efficient photocatalysts. Although huge progress has been achieved, better candidates will always be sought. Among the various photocatalytic systems, the ideal photocatalyst should have a suitable optical bandgap and the ability to capture visible light and convert the absorbed solar energy into hydrogen energy.⁷

In recent years, due to their unique light absorption capacity and efficient charge separation properties, lead-based halide perovskites have become promising photocatalysts and have developed rapidly in the fields of H₂ evolution, pollutant degradation, organic reactions, and carbon dioxide reduction.^{8–10} However, the instability and ecological toxicity of lead-based

perovskites hinder their practical applications. In recent years, lead-free double perovskites have been studied gradually deepen, for example, Cs₃Bi₂X₉ (X = Cl, Br, I), (MA)₃Bi₂I₉, DMASnBr₃, and Cs₂AgBiBr₆ (CABB).^{11–13} Bi-based double perovskite CABB has shown potential in photocatalytic hydrogen production because of its good stability and suitable light absorption coefficient.^{14–16} In 2018, Kuang *et al.* prepared CABB nanocrystals *via* a simple heat injection method and used them for photocatalytic CO₂ reduction.¹⁷ Zhao *et al.* constructed a Cs₂AgBiBr₆/rGO photocatalyst for H₂ evolution by an *in situ* photoreduction method, reporting a photocatalytic system for the construction of a lead-free halide perovskite/semiconductor heterojunction.¹⁸ Most recently, N-C,¹⁹ Cu-RGO,²⁰ g-C₃N₄,²¹ MoS₂,²² and NiCoP²³ have been exploited as costructures, and the obtained composites showed an obvious enhancement of photocatalytic activity compared to pristine CABB.

Two-dimensional black phosphorus (2D BP) with a large surface area, abundant active sites and adjustable band gaps (0.3–2.0 eV) is widely studied as a photocatalytic semiconductor catalyst.^{24,25} In particular, BP exhibited excellent characteristics as a potential high-performance cocatalyst: (1) the large surface area has rich active sites, and the photocatalyst is structurally coupled electronically; (2) it has good carrier mobility; (3) the tunable bandgap provides a huge opportunity for a good structure. Shi's group²⁶ prepared black phosphorus quantum dot/CdS (BPQDS/CDS) composites with tight interfacial contact for efficient photocatalytic H₂ evolution, benefiting from the strong interfacial interaction between CdS and BPQDS for efficient charge separation. Zhu and colleagues²⁷ anchored

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inorganic perovskite (CsPbBr_3) on BP to obtain a new effective $\text{CsPbBr}_3/\text{BP}$ photocatalyst for CO_2 reduction. The introduction of BP gave more active sites to promote the activation of CO_2 reduction and capture excitation electrons of CsPbBr_3 with high charge separation efficiency. Therefore, the use of BP as a metal-free costructure for photocatalytic H_2 production is promising and challenging.

In this work, two-dimensional black phosphorus was first coupled with the CABB double perovskite applied for hydrobromic acid (HBr) splitting under visible light irradiation. Layered BP with good electron transfer properties and acid stability was introduced to further improve the H_2 evolution. The H_2 evolution rate of BP/CABB can reach $104.6 \mu\text{mol h}^{-1} \text{g}^{-1}$, which is 6 times higher than that of pristine CABB. Excitingly, the BP/CABB composites are quite stable in a saturated HBr solution, and their activity does not significantly decrease during the entire light reaction process. BP/CABB heterogeneous structures have good stability, providing new examples for the design and preparation of high-efficiency lead-free double perovskite catalysts.

2. Experiment

2.1 Photocatalyst synthesis

2.1.1 Preparation of CABB. CABB was synthesized from aqueous solution according to a previous report.¹⁴ A total of 1.0 mmol BiBr_3 , 1.0 mmol AgBr , and 2.0 mmol CsBr were dissolved in 10 mL of a 48% HBr solution, and then the mixture was heated to 110°C for 2 h under continuous magnetic stirring in an oil bath. After cooling to room temperature naturally, the precipitates were collected and dried in a vacuum oven at 60°C for 12 h, and the obtained orange sample was named CABB. As shown in Fig. 1, the saturated HBr solution (saturated with CABB power) for photocatalytic H_2 evolution was prepared by mixing HBr and H_3PO_2 at a volume ratio of 5 : 1.

2.1.2 Preparation of BP. BP was prepared with red phosphorus as the raw material and diethylenetriamine (DETA) as the solvent. In a typical synthesis process, red phosphorus (2.0 g, 0.06 mol) was added to an agate mortar and ground.

Then, the mixture with 40 mL deionized water (DI) was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 200°C for 12 h. After cooling to room temperature, the mixture was washed, centrifuged, and dried overnight at 60°C , and the sample was labeled RP. Next, the prepared RP (0.90 g) was added to 60 mL of a DETA solution and was stirred for 30 min; the mixture was then heated at 160°C in a 100 mL Teflon-lined stainless steel autoclave for 24 h. After cooling to room temperature, the mixture was washed and centrifuged, and the product was collected and named BP.

2.1.3 Preparation of BP/CABB composites. We adjusted the mass ratio of the samples to achieve the optimum photocatalytic activity. Therefore, we conducted a series of experiments measuring the hydrogen evolution of the BP/CABB composite materials. Specifically, the prepared 50 mg CABB was first added to a saturated HBr aqueous solution, and then different BP mass ratios were added to the above solution and ultrasonicated for 20 min. During the precipitated crystalline cycle, the BP/CABB photocatalysts were obtained directly for photocatalytic hydrogenation or rinsed and dried to carry out further characterization. Samples were labeled as $x\%$ BP/CABB ($x = 5, 10, 15, 20$), where x is the mass percentage of BP and CABB. And the actual content of the catalyst 10% BP/CABB was also quantified by EDX testing (Table S1 and Fig. S1, ESI[†]).

2.2 Characterization

Powder X-ray diffraction (XRD) analysis was performed on a PANalytical X'pertProAlpha-1 X-ray diffractometer with $\text{Cu K}\alpha$ radiation to explore the crystalline structure. The zeta potentials of the samples were measured on a Malvern zeta analyzer (Zetasizer Nano-S 90, Malvern Instrument, UK). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2100 F electron microscope operated at an accelerating voltage of 200 kV. The UV-vis diffuse reflectance absorption spectrum (DRS) was measured using an ultraviolet-visible spectrophotometer (UV-3600, Shimadzu) with BaSO_4 as a reference sample; X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB Xi +, the excitation



Fig. 1 Schematic diagram of the BP/CABB composite fabrication process.

source was monochromatic Al K α , and C 1s = 284.6 eV was used for reference calibration. Raman spectra were recorded on an Alpha 300 Access Raman microscope (Witec, Germany) with a 532 nm laser as an excitation source at room temperature.

2.3 Photocatalytic experiments

Photocatalytic H₂ production experiments were performed in an instrument equipped with a quartz vessel under the illumination of a 300 W Xe lamp ($\lambda \geq 420$ nm). The BP/CABB photocatalyst (0.05 g) was added to 10 mL of CABB-saturated HBr/H₃PO₂ solution, and the temperature of this mixture was maintained at 15 °C through a cooling water circulation system. The suspension extracted dissolved air before the reaction by a vacuum pump. After that, the reaction solution was irradiated to produce H₂ under continuous stirring. The amount of H₂ produced was automatically removed and analyzed at given time intervals with a CEL-SPH2N fully automatic online catalytic system (Beijing China Education Au-light Co., Ltd).

2.4 PEC measurements

The photocurrents and electrochemical impedance spectroscopy (EIS) profiles of the catalysts were evaluated using a standard three-electrode system (CHI760E), where a Pt electrode was used as the counter electrode, an Ag/AgCl electrode was used as the reference electrode, photocatalysts were coated on FTO (1 cm \times 1 cm) as the working electrode, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dichloromethane (CH₂Cl₂) was the electrolyte. The working electrode was prepared as follows: 10 mg samples were added to a mixture of 500 μ L absolute ethanol and 10 μ L Nafion and then sonicated for 60 min. Finally, a certain amount of the mixture was dripped onto FTO to prepare the working electrode.

3. Results and discussion

3.1 Structure, composition, and optical properties of the photocatalyst

To achieve large-scale and low-cost BP production, BP was prepared from bulk red phosphorus using a solvent thermal

reaction. After the solvent thermal reaction, the resulting solution was observed to become black, and a black product was obtained after washing. The X-ray diffraction pattern of the prepared BP powder sample showed the main features of orthogonal BP (PDF#76-1967); diffraction peaks located at 17.6°, 26.8°, 35.2°, and 57.2° correspond to the (020), (021), (040), and (151) crystalline planes, respectively (Fig. S2a, ESI†).²⁸ It is worth noting that the synthetic BP had an additional peak at 10.2° in the XRD pattern, which was due to a stacking breaking layer or periodic distortion in the *c*-axis direction.²⁹ Raman spectroscopy also confirmed the successful preparation of BP and composites. In Fig. S2b (ESI†), we recorded the Raman spectrum of BP and obtained three typical Raman peaks: A_g¹ (outdoor patterns), B_{2g} and A_g² (in-plane mode), and the wavenumbers were \sim 361, \sim 437, and \sim 460 cm⁻¹, respectively.³⁰ These results suggest that this bottom-up solvothermal method is a reliable method for preparing large-scale and low-cost BP.

To verify the structural stability of the BP, we tested the XRD of the prepared BP after 12 h of stirring in a HBr solution. As shown in Fig. S3a (ESI†), the structure of BP did not change significantly after HBr treatment, but the intensity of the diffraction peak was reduced, which is possibly due to BP oxidation by the environment. As seen in Fig. S3b (ESI†), CABB and BP had zeta potentials of -16.4 mV and 8.98 mV, respectively. The opposite potentials generate strong electrostatic attraction between CABB and BP, which increases interfacial contacts. We used the ultrasonic electrostatic self-assembly method to prepare a series of *x*% BP/CABB composites. As seen in Fig. 2a, the XRD of the BP/CABB composites showed all the characteristic peaks of CABB with a good cubic structure. The characteristic diffraction peaks were located at 13°, 15.9°, 22.3°, 26.1°, 27.4°, 31.8°, 35.7°, 39.2° and 45.5° belonging to the (111), (002), (022), (113), (222), (004), (024), (224) and (440) planes, respectively (JCPDS # 01-084-8699).²⁰ No additional diffraction peaks attributed to BP were observed even at higher addition amounts, probably due to the high dispersion of BP and the high crystallinity of CABB.^{31–33} The presence of BP in the composites was also confirmed by comparing the UV-visible diffuse spectra (DRS) of the original BP, CABB and BP/CABB composites. As shown in Fig. 2b, the light absorption of the BP/

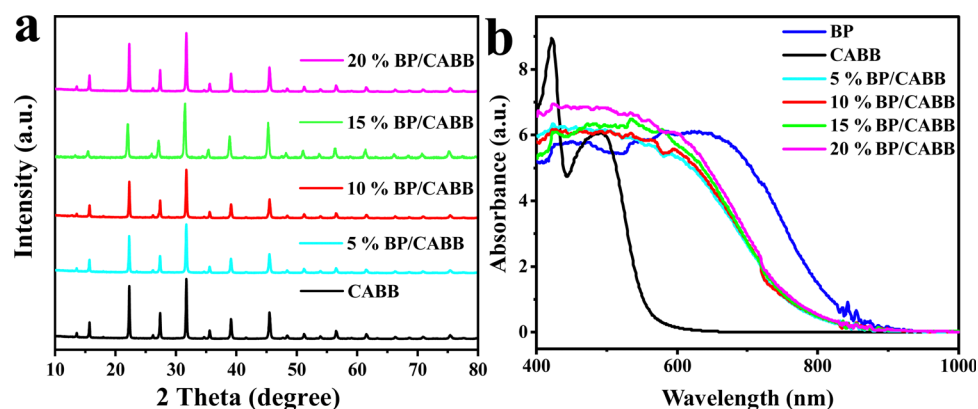


Fig. 2 (a) XRD and (b) DRS patterns of the obtained CABB, BP and BP/CABB.

CABB composite was enhanced between 600 and 750 nm relative to the original CABB due to the black effect of the BP. With the increase of black phosphine loading, the optical absorption intensity of the composite material also increased, but the increase amount changed little.

To clarify the interface interactions in BP/CABB, TEM and SEM images were obtained, and the corresponding elemental mapping analysis was performed. The original CABB particles had a relatively smooth and large bulk, and BP showed a laminate stacked structure (Fig. S43a and b, ESI[†]). The surface of the BP/CABB composite becomes rougher due to the coupling of layered BP (Fig. 3a). Thus, more contact sites in the reaction are provided. The TEM image of composite BP/CABB showed small, layered BP in close contact with large CABB particles (Fig. 3b), and the size of the BP was approximately 500 nm. The EDS mappings (Fig. 3c) of composite BP/CABB confirmed the uniform distribution of Cs, Ag, Bi, Br, and P elements on the catalyst surface. In the high-resolution TEM image (Fig. 3d), two different lattice fringes of 0.33 nm and 0.23 nm were present, corresponding to the (021) plane of BP and the (004) plane of CABB, respectively. The TEM images show that the composites are tightly bound together; in particular, the high-resolution TEM images (Fig. S4c and d, ESI[†]) show that BP and CABB are embedded together rather than physically adsorbed. These results revealed the successful coupling of CABB with BP.

X-Ray photoelectron spectroscopy (XPS) was further used to explore the chemical state of the resulting BP, CABB and CABB/CABB composites. The XPS survey spectra (Fig. 4a) confirmed the presence of BP in the BP/CABB composites. As shown in Fig. 4b, Cs 3d can be divided into two peaks at 723.9 eV and 739.9 eV, corresponding to Cs 3d_{5/2} and Cs 3d_{3/2}, respectively. Ag 3d can be divided into peaks located at 367.5 eV and 373.6 eV,

corresponding to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively (Fig. 4c). As shown in Fig. 4d, Bi 4f can be divided into two peaks located at 158.7 eV and 164.1 eV, corresponding to Bi 4f_{7/2} and Bi 4f_{5/2}, respectively. Br 3d can be divided into two peaks located at 67.2 eV and 68.3 eV, corresponding to Br 3d_{5/2} and Br 3d_{3/2}, respectively (Fig. 4e). Interestingly, Bi 4f is shifted to a lower binding energy (0.3 eV) (Fig. 4d), while the P 2p peaks migrate to a higher binding energy (0.5 eV) (Fig. 4f). The study shows that the binding energy migration is closely related to the electron density outside the nucleus. When the binding energy is shifted to a high field, the electron density decreases.³⁴ This is consistent with the results reported in the literature.^{21,35,36} The binding energy migration of P and Bi greatly confirms the strong electronic coupling between BP and CABB, which is in accordance with the Raman spectroscopy results. It is worth noting that a small P oxide species is apparent at 134 eV due to the inevitable local oxidation during the preparation process. All the results show that the prepared BP/CABB composite has a strong interfacial electron coupling rather than simple physical mixing, which is very beneficial to the efficient migration of interfacial carriers.

3.2 Photocatalytic hydrogenation activity

The photocatalyst was evolved in a saturated HBr/H₃PO₂ mixed solution (v/v = 5:1) under visible light irradiation, and the photocatalytic H₂ evolution activity of the different catalysts is shown in Fig. 5a. Bare BP (50 mg) showed little H₂ evolution activity, while CABB (50 mg) showed an H₂ evolution rate of 17.7 μmol g⁻¹ h⁻¹, which was extremely low due to the rapid recombination of photogenerated electron-hole pairs. As the amount of BP added to the BP/CABB increased, the hydrogen production rate was further improved, and the catalyst 10% BP/CABB composite gave the best rate of 104.6 μmol h⁻¹ g⁻¹, which was 6 times higher than that of pristine CABB. When the



Fig. 3 (a) SEM image, (b) TEM image, (c) elemental mapping of Cs, Ag, Bi, Br and P and (d) HRTEM images of the 10% BP/CABB composite.



Fig. 4 (a) Survey XPS spectra of CABB, BP and the 10% BP/CABB composite; high-resolution XPS spectrum of (b) Cs 3d, (c) Ag 3d, (d) Br 3d, (e) Bi 4f and (f) P 2p.



Fig. 5 (a) Yield of H₂ reduction by CABB, BP and the 10% BP/CABB composite after 3 h of photochemical reaction, error bar: ± 0.03 ; and (b) recycling test of the 10% BP/CABB composite.



Fig. 6 Schematic illustration of the H_2 evolution of the BP/CABB composites.

BP addition further increased to 15%, the incident light was blocked by excess BP, resulting in a decrease in photocatalytic activity. The results showed that BP can show photocatalytic H_2 evolution under visible light as a highly active cocatalyst of CABB.

Cyclic performance is an important index for evaluating heterogeneous catalysts. In this catalytic system, no significant decline in H_2 evolution was observed after 7 cycles of 3 h of continuous photoreaction (Fig. 5b). After being reused, the catalyst showed no crystallographic phase change in the XRD pattern (Fig. S5, ESI[†]). The good structural stability of BP/CABB composites can be rationalized, and CABB surfaces can constantly resume sustained oxidation of Br^- – Br_3^- due to the perfect dynamic equilibrium of the CABB crystal in a saturated aqueous solution. Therefore, both CABB and BP in the composite material were highly stable due to the strong interaction. BP, as a photosensitizer and H_2 evolution cocatalyst, also enhanced the efficient and sustainable photocatalytic H_2 evolution.

3.3 Activation mechanism

We studied the photocatalytic mechanism of the BP/CABB system by optical absorption and valence band (VB) XPS. According to the Tauc plot method, $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where the direct bandgap semiconductor is $n = 1/2$ and the indirect bandgap semiconductor is $n = 2$. BP is a direct band gap semiconductor, CABB is an indirect bandgap semiconductor, and the E_g values of BP and CABB were

calculated to be 1.57 V and 2.15 V, respectively (Fig. S6a and b, ESI[†]). The calculated value of BP and CABB from the intercept between the tangent of the onset and the baseline of the spectra is 0.50 V and 1.69 V, respectively (Fig. S6c and d, ESI[†]). This is consistent with the reported valence band position (E_{VB}).^{21,37} Based on the relationships between E_{CB} and E_{VB} ($E_{\text{CB}} = E_{\text{VB}} - E_g$), the calculated conduction band positions (E_{CB}) for BP and CABB were -1.07 V and -0.46 V.²⁶ Based on the above results, a photocatalytic mechanism was proposed (Fig. 6). According to the H_2 evolution “band matching” theory, the E_{CB} of BP is more negative than CABB, and the E_{VB} of CABB is more positive than BP. When both BP and CABB were excited under visible light irradiation, the photogenerated electrons in the CB of CABB quickly combined with the photogenerated holes in the VB of BP and then combined with the photogenerated electrons of BP for the reduction reaction. The photogenerated holes in the VB of CABB are used for the oxidation reaction. These band structures suggest the possibility of constructing the Z-scheme photocatalysis feature to split HBr into H_2 and Br_3^- , where Br_3^- is then converted to Br^- by H_3PO_2 .

Photoelectric chemistry (PEC) analysis is widely used to provide effective evidence for the separation and metastasis of photogenerated electron–hole pairs. To explore the mechanism of BP effect on the photocatalytic activity on CABB, we performed a series of PEC measurements. BP/CABB exhibited a higher photocurrent response than bare CABB (Fig. 7a), and the photocurrent responses of the samples were highly repeatable upon on/off light cycling. This indicated the efficient separation of carriers in BP/CABB. Electrochemical impedance spectroscopy (EIS) measurements (Fig. 7b) indicated that BP/CABB had a smaller charge transfer resistor than the bare CABB, indicating that the coupled BP provides a rapid electron transfer pathway to improve charge separation efficiency. All the results demonstrated that coupling with BP can significantly increase the carrier separation efficiency of CABB, which greatly increases the photocatalytic efficiency of BP/CABB.

4. Conclusions

In summary, we successfully fabricated 2D BP/CABB composites with a high-quality interface *via* a facile electrostatic

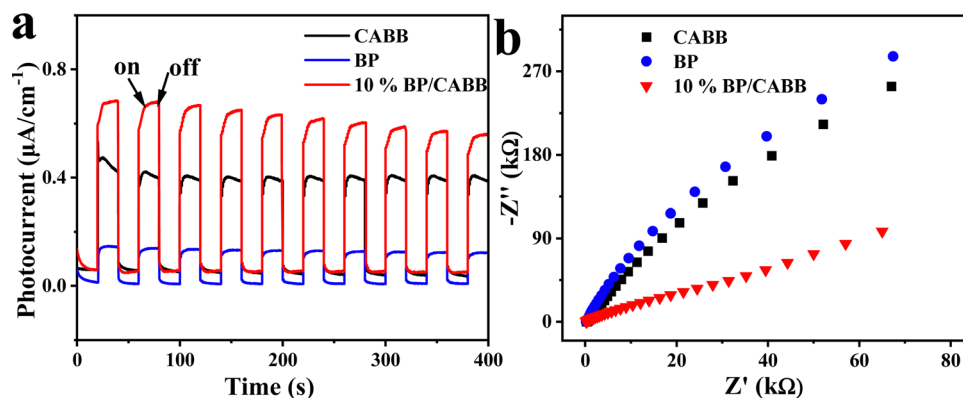


Fig. 7 (a) Chopped light amperometric I – t curves and (b) EIS Nyquist plots of CABB, BP and the 10% BP/CABB composite.

self-assembly method. The H₂ evolution rate of the most effective BP/CABB composite was 6 times higher than that of the original CABB and had excellent H₂ evolution stability. In the BP/CABB composites, the charge induction between BP and CABB made the interface interaction strong, which can realize efficient charge separation and improve the photocatalytic H₂ evolution activity. This work demonstrates a simple and effective strategy for the synthesis of BP/CABB composites with high-quality interactions. This study also provides new insight into the design of highly active photocatalysts based on lead-free double halides.

Author contributions

Kunpeng Song: guidance of experimental projects, revision and submission of papers; Jiaojiao Gou: experiment and the writing of the draft; Lin Wu: experiment; Chunmei Zeng: design of the experimental projects.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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