

CsPbBr₃ Perovskite Quantum Dots/Ultrathin C₃N₄ Nanosheet 0D/2D Composite: Enhanced Stability and Photocatalytic Activity

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Abstract: Metal-halide perovskite quantum dots (QDs) have emerged as a potential photocatalyst owing to their remarkable optoelectronic properties. However, the poor stability and insufficient charge transportation efficiency of this type of materials hindered their applications in the photocatalysis field. Herein, we decorated CsPbBr₃ QDs on two-dimensional (2D) ultrathin g-C₃N₄ (UCN) nanosheets to develop a 0D/2D CsPbBr₃/UCN composite photocatalyst. The introduction of UCN can not only improve the stability of CsPbBr₃ QDs by passivating the surface ligands of CsPbBr₃ QDs, but also facilitate the charge transfer due to the suited band gap alignment. Consequently, the obtained CsPbBr₃/UCN heterostructure exhibited superior photocatalytic performance to both pristine CsPbBr₃ QDs and UCN. This work has provided an efficient strategy for the design of CsPbX₃-based heterostructure with high stability and photocatalytic activity.

Key words: perovskite quantum dots; 2D ultrathin nanosheets; photocatalysis; CsPbBr₃; g-C₃N₄

In the past few years, metal-halide perovskite quantum dots (QDs) have attracted enormous attention for its remarkable optoelectronic properties, such as excellent absorption ability, high-quantum-yield photoluminescence, tunable band gap, long carrier lifetime and so on^[1-4]. The outstanding advantages of these materials have triggered great interest for optoelectronic and photovoltaic applications, such as light-emitting diode devices, photodetectors, displays and solar cells^[5-9]. More recently, the metal-halide perovskite QDs (CsPbBr₃) was found to be a promising photocatalyst owing to its outstanding optical features with the combined advantages of wide spectral absorption scope and suitable bandgap^[10-11]. Despite of all these advantages, the inherent poor stability of metal-halide perovskite QDs has always been the obstacle to restricting these materials for photocatalytic applications, especially in aqueous solution. If the instability issues of these materials can be addressed, metal-halide perovskite QDs are expected to be strong candidates for photocatalytic applications on considering their remarkable optical properties.

Recently, two-dimensional (2D) materials have aroused extensive attention from researchers due to their exceptional electronic and optical properties compared

with their bulk counterparts^[12-14]. According to the previous studies, metal-halide perovskite QDs can be passivated by anchoring them on some two dimensional materials (*e.g.*, Graphitic carbon nitride (g-C₃N₄) and graphene oxide)^[10,15], to prevent the crystal structure of the perovskite QDs from decomposition. Especially, 2D g-C₃N₄ nanosheets have gained special attractions owing to its suitable bandgap, high chemical stability, abundance and low cost, which makes it a potential candidate for solar energy conversion, environment purification, and bioimaging applications^[16-21]. In view of the above advantages, g-C₃N₄ can be served as an ideal material to passivate perovskite QDs. Besides stability enhancement, the combination of CsPbBr₃ and g-C₃N₄ can bring about another benefit: the energy band structure between CsPbBr₃ and g-C₃N₄ is a type II band alignment, which can facilitate the charge carrier transfer between the two components^[22]. Zhao *et al.*^[22] have coupled CsPbBr₃ QDs with bulk g-C₃N₄ and demonstrated its enhanced photocatalytic degradation activity for penicillins 6-APA. You *et al.*^[23] have also combined CsPbBr₃ QDs with bulk g-C₃N₄ to fabricate a CsPbBr₃@g-C₃N₄ composite, which showed enhanced photocatalytic activity in CO₂ reduction. The above research results suggested that the

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construction of CsPbBr₃/g-C₃N₄ heterostructure can be an efficient strategy to develop an ideal photocatalyst with desirable stability and photocatalytic activity.

In this contribution, ultrathin g-C₃N₄ (UCN) nanosheets were employed to combine with CsPbBr₃ QDs, with the aim of coupling 2D ultrathin g-C₃N₄ nanosheets with 0D CsPbBr₃ QDs to obtain a 0D/2D composite photocatalyst with high performance. The photocatalytic performance of the obtained 0D/2D CsPbBr₃/UCN composite was evaluated by the degradation of a typical pollutant in water, Rhodamine B (RhB). Benefitting from the suitable energy band structure, such a 0D/2D heterostructure exhibited enhanced photocatalytic activity than both pristine CsPbBr₃ QDs and UCN. Furthermore, due to the strong interaction between CsPbBr₃ QDs and UCN, the stability of CsPbBr₃ QDs was greatly enhanced.

1 Experimental

1.1 Material preparation

1.1.1 Preparation of ultrathin g-C₃N₄ nanosheets

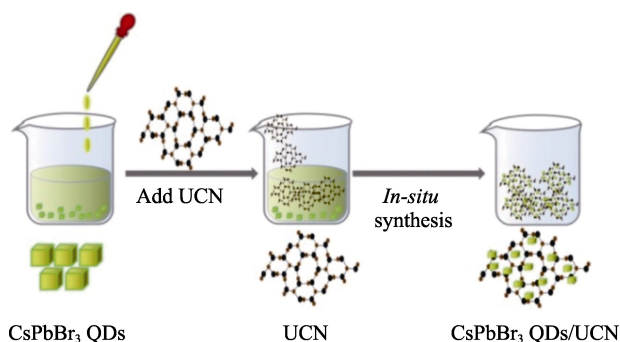
Bulk g-C₃N₄ was first prepared by pyrolysis of melamine at 550 °C for 4 h with a ramp rate of 2.5 °C/min, which was donated as BCN. Ultrathin g-C₃N₄ nanosheets were synthesized by exfoliating BCN as follows: 320 mg of BCN was mixed with 6 mol/L HCl solution (80 mL), which was then transferred into a 100 mL Teflonlined autoclave and heated at 110 °C for 5 h. Upon cooling, the precipitate was filtered, washed and dried at 80 °C under vacuum for 12 h. The obtained ultrathin g-C₃N₄ nanosheets was donated as UCN.

1.1.2 Preparation of CsPbBr₃ QDs

CsPbBr₃ QDs was synthesized using a typical hot-injection method published by Protesescu *et al.*^[24]. Firstly, the Cs-oleate solution was prepared by adding 0.817 g Cs₂CO₃, 3 mL oleic acid, and 30 mL octadecene into a three-neck flask under Ar atmosphere, which was heated to 130 °C until all Cs₂CO₃ was dissolved. Then 0.132 g PbBr₂, 10 mL octadecene, 1 mL oleic acid, and 1 mL oleylamine were loaded into another three-neck flask, which was dried at 130 °C under Ar atmosphere. After the complete dissolution of PbBr₂, the temperature was increased to 160 °C, and 1 mL Cs-oleate precursor was quickly injected. 5 s later, the reaction was terminated by ice water. The final product was obtained by centrifugation, washing and drying at 60 °C under vacuum for 12 h.

1.1.3 Preparation of CsPbBr₃/UCN composite

The preparation process of the CsPbBr₃/UCN composite was illustrated in Scheme 1: 10 mg of the obtained CsPbBr₃ QDs was dispersed in 10 mL toluene, then 90 mg of the as-prepared UCN was added into the CsPbBr₃ QDs



Scheme 1 Illustration of the preparation process of CsPbBr₃/UCN composite.

ink solution. After stirring for several hours, the color of ink solution turned from yellow to colorless, indicating that CsPbBr₃ QDs have anchored on UCN. The precipitate was centrifuged to obtain the CsPbBr₃/UCN composite.

1.2 Characterization

The phase identification of the as-prepared products were characterized by X-ray diffraction (XRD, D/max 2200PC) using Cu K α radiation. The morphologies of the products were observed by transmission electron microscope (TEM, FEI tecnaIG2F30) operated at 200 kV. The optical absorption spectra of the products were obtained from a PE Lambda 900 UV-visible spectrophotometer. The carrier separation ability of the samples were characterized by Photoluminescence (PL) spectra on a fluorescence spectrometer (FluoroMax-4) and photo-electrochemical experiments on an electrochemical system (CHI-650E) with three-electrode system.

1.3 Photocatalytic experiments

Photocatalytic experiments were carried out under a 500 W Xe lamp with 420 nm UV filter. In a typical procedure, 50 mg of as-prepared photocatalyst and 50 mL of RhB solution (10⁻⁵ mol/L) were mixed in a beaker. After being stirred in the dark for 60 min, the mixture was illuminated under visible light and 3 mL of the suspension was withdrawn at given intervals. After the photocatalyst particles being removed by centrifugation, the absorption spectral change of the supernatant was measured with a PE Lambda 900 UV-Vis spectrophotometer. The concentration change of RhB was obtained by monitoring the absorption band maximum at 552 nm.

2 Results and discussion

2.1 Crystal structure

The crystal structures of CsPbBr₃ QDs, UCN and CsPbBr₃/UCN composite were characterized by XRD patterns. As exhibited in Fig. 1, the peaks of the as-prepared CsPbBr₃ QDs matched well with the orthorhombic CsPbBr₃ (JCPDS 18-0364). For the UCN sample, two diffraction

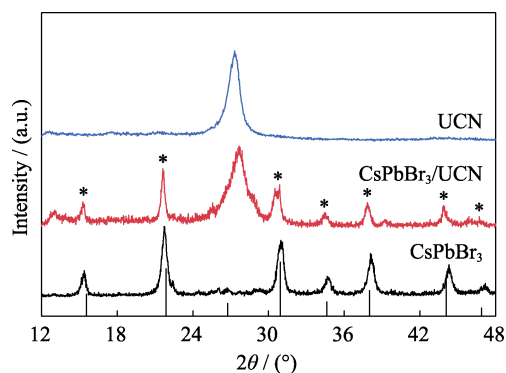


Fig. 1 XRD patterns of CsPbBr₃, UCN and CsPbBr₃/UCN composite

peaks at $2\theta=13.2^\circ$ and 27.7° can be observed, corresponding to the (100) and (002) diffraction planes of g-C₃N₄, respectively^[25]. The characteristic diffraction peaks of both CsPbBr₃ QDs and g-C₃N₄ could be observed in the XRD pattern of the CsPbBr₃/UCN composite, suggesting the successful loading of CsPbBr₃ QDs on UCN.

2.2 Morphology analysis

TEM was employed to investigate the morphology of the as-fabricated CsPbBr₃ QDs, UCN and CsPbBr₃/UCN composite. Fig. 2(A) shows the TEM image of CsPbBr₃ QDs, demonstrating a cubic-shaped morphology with fairly uniform size of around 10 nm. As shown in Fig. 2(B), the UCN sample is composed of thin nanosheets, indicating the successful exfoliation of bulk g-C₃N₄. In the TEM image of CsPbBr₃/UCN composite (Fig. 2(C)), it can be seen that CsPbBr₃ QDs are dispersed on UCN

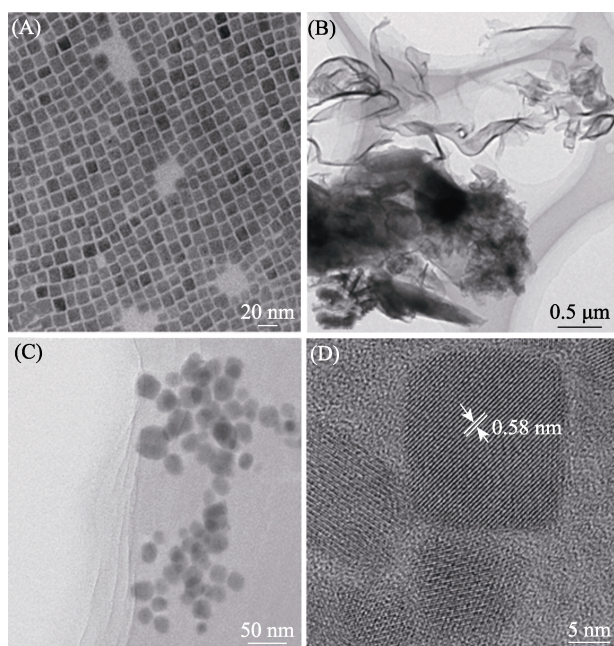


Fig. 2 TEM image of (A) CsPbBr₃ QDs, (B) UCN and (C) CsPbBr₃/UCN composite; (D) HRTEM image of CsPbBr₃/UCN composite

nanosheets. Moreover, a clear lattice spacing of 0.58 nm is observed from the HRTEM image of the CsPbBr₃ QDs on UCN (Fig. 2(D)), which is attributed to the (100) plane of orthorhombic CsPbBr₃^[26].

2.3 Optical properties

The optical properties of CsPbBr₃ QDs, UCN and CsPbBr₃/UCN composite were investigated by UV-Vis diffused absorption spectra, which were exhibited in Fig. 3. UCN displayed a visible absorption edge at 473 nm, which corresponded to a bandgap energy of 2.62 eV. CsPbBr₃ QDs showed the absorption edge at around 550 nm, illustration of a bandgap energy of 2.25 eV. Compared to the pure CsPbBr₃ QDs and pure UCN, a notable red-shift of the absorbance and enhanced light-harvesting of the CsPbBr₃/UCN composite is observed, which can be ascribed to the synergistic effect of CsPbBr₃ QDs and UCN, implying a more efficient utilization of visible light during the photocatalytic reaction.

2.4 Evaluation of photocatalytic activity

In order to assess the practicability of the CsPbBr₃/UCN composite in the photocatalytic applications, the degradation of RhB was performed. As shown in Fig. 4(A), the CsPbBr₃/UCN composite exhibited noticeably improved photocatalytic activity than pure CsPbBr₃ QDs and pure UCN, which can almost completely degrade RhB after 15 min visible light irradiation, accompanied with a total organic carbon (TOC) removal efficiency of 82.6%. The high degree of mineralization of organic species confirms that RhB has been photocatalytically decomposed. Moreover, to assess the superiority of UCN, the photocatalytic activity of bulk g-C₃N₄ (BCN) was also evaluated, which was much lower than that of UCN and CsPbBr₃/UCN composite. In addition, the stability of the photocatalyst is an important factor limiting its practical application. As is known, CsPbBr₃ QDs have poor water stability, since they are subjected to structural decomposition in aqueous phase^[27]. To assess the stability of the photocatalyst, the powders are recovered after the photocatalytic experiments and characterized by XRD.

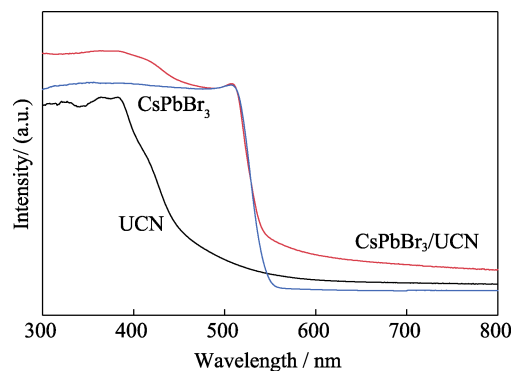


Fig. 3 UV-Vis diffuse reflectance spectra of CsPbBr₃, UCN and CsPbBr₃/UCN composite

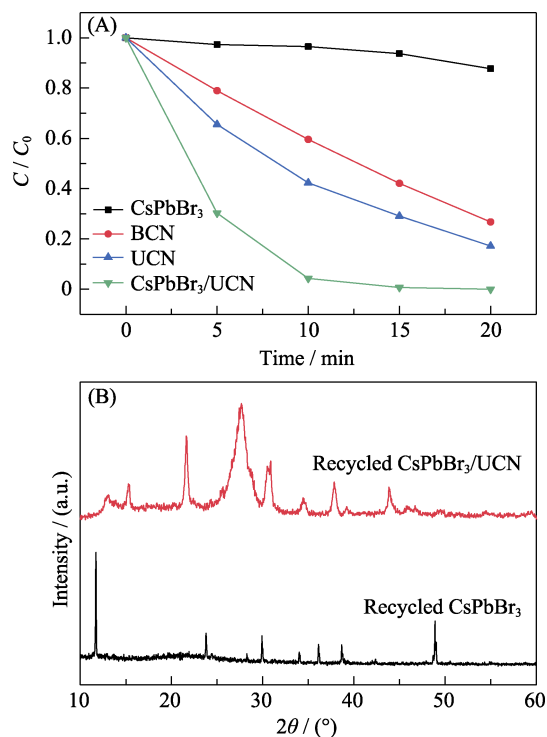


Fig. 4 (A) Photocatalytic degradation of RhB over CsPbBr₃, BCN, UCN and CsPbBr₃/UCN composite; (B) XRD patterns of recycled CsPbBr₃ and CsPbBr₃/UCN composite

As shown in Fig. 4(B), severe structure degradation is observed for the CsPbBr₃ QDs after water immersion, while the crystal structure of the CsPbBr₃/UCN composite is well preserved, demonstrating the good water stability of the CsPbBr₃/UCN composite. The stability enhancement could be ascribed to the formation of N–Br bonding between CsPbBr₃ QDs and UCN. Since amino group can interact strongly with CsPbBr₃ QDs through the surface bromide, the resultant CsPbBr₃/UCN composite is more stable than organic ligands passivation.

2.5 Photocatalytic mechanism

For an ideal photocatalyst, the expanded spectral response scope, and the effective charge separation and transportation ability are desired. As shown in Fig. 3, the spectral response scope of the CsPbBr₃/UCN composite were obviously extended compared with pure CsPbBr₃ and UCN, indicating more light-harvesting of the CsPbBr₃/UCN composite. In order to investigate the photon-generated charge separation and migration abilities of the as-prepared products, PL spectra and transient photocurrent response experiments were performed. As shown in Fig. 5(A), CsPbBr₃ QDs exhibited a strong emission peak at 520 nm, while anchoring CsPbBr₃ on the UCN drastically reduced the PL intensity. Besides, the emission intensity originated from UCN also decreased slightly, implying the occurrence of photo-generated carrier transfer between CsPbBr₃ and UCN. Moreover, the transient photocurrent response spectra (Fig. 5(B))

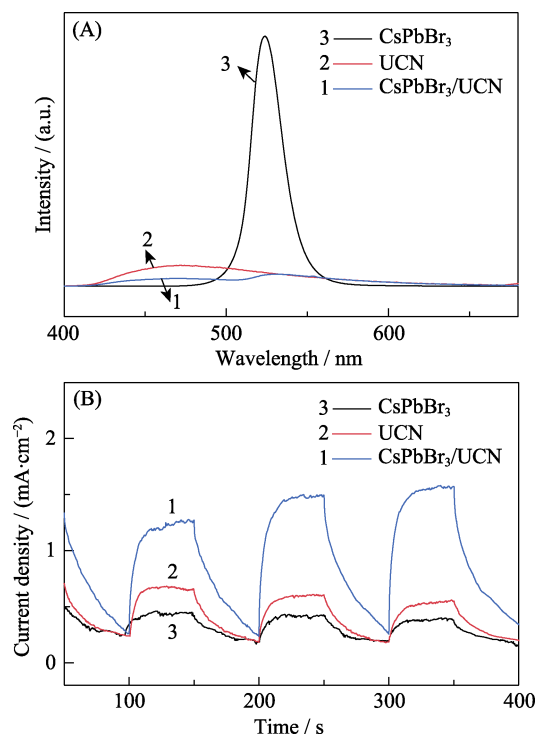


Fig. 5 (A) PL spectra and (B) transient photocurrent responses of CsPbBr₃, UCN and CsPbBr₃/UCN composite

showed that the CsPbBr₃/UCN composite exhibited significantly higher photocurrent response intensities than both CsPbBr₃ QDs and UCN, which indicated more efficient charge transfer of the CsPbBr₃/UCN composite.

Mott-Schottky measurements were performed to determine the band potentials of UCN and CsPbBr₃. As shown in Fig. 6(A), both UCN and CsPbBr₃ feature a typical n-type semiconductor, with the flat band potential values of -1.01 and -0.91 eV *versus* the saturated calomel electrode (SCE), respectively. Correspondingly, the valance band positions for UCN and CsPbBr₃ are 1.61 and 1.14 eV (*vs.* NHE) based on the calculated bandgap, respectively. Hence, the band alignments of both samples are illustrated in Fig. 6(B). It is clear that the conduction band minimum (CBM) of UCN is lower than that of CsPbBr₃, and the valance band maximum (VBM) of UCN is lower than that of CsPbBr₃. Therefore, the conduction band electrons of CsPbBr₃ can transfer to that of UCN, while the valance band holes of UCN can migrate to that of CsPbBr₃. As such, effective charge separation and inhibition of charge recombination in the composite photocatalyst is realized, which led to the improved photocatalytic activity.

3 Conclusions

In summary, we have successfully fabricated a CsPbBr₃/UCN composite *via* a facile process, which can be used as an efficient and stable photocatalyst in water

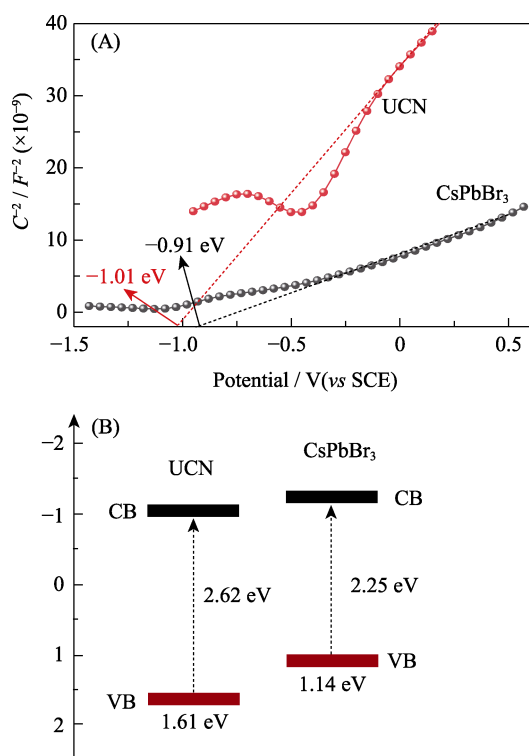


Fig. 6 (A) Electrochemical Mott-Schottky plots and (B) band alignments of CsPbBr₃ and UCN

medium. Microstructure characterization showed that the CsPbBr₃ QDs were anchored on the surface of UCN to form a 0D/2D heterostructure. The formation of the CsPbBr₃/UCN heterostructure can greatly facilitate photo-generated charge separation and transportation, as disclosed by the PL spectra and the photoelectrochemical measurements. The expanded light-harvesting scope, as well as the enhanced charge separation efficiency are responsible for the improved photocatalytic activity of the CsPbBr₃/UCN composite. This work may provide a useful guide towards the utilization of metal halide perovskite for photocatalytic applications.

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CsPbBr₃ 钙钛矿量子点/C₃N₄ 超薄纳米片 0D/2D 复合材料: 增强的稳定性和光催化活性

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摘要: 金属卤化物钙钛矿量子点(QDs)具有良好的光电性质, 是一种潜在的光催化剂材料。但是, 它的稳定性较差, 并且电荷传输效率不足, 阻碍了其在光催化领域的应用。本工作将 CsPbBr₃ 量子点装饰在二维超薄 g-C₃N₄ 纳米片(UCN)上, 制备了 0D/2D CsPbBr₃/UCN 复合光催化剂。引入 UCN 不仅可以通过钝化 CsPbBr₃ 量子点的表面配体来提高 CsPbBr₃ 量子点的稳定性, 而且两者的能带匹配还可以促进两种材料之间的电荷转移。因此, 所制备的 CsPbBr₃/UCN 异质结构比单纯的 CsPbBr₃ 量子点和 UCN 具有更优越的光催化性能, 这为设计具有高稳定性和光催化活性的基于 CsPbX₃ 的异质结构提供了有效的策略。

关键词: 钙钛矿量子点; 二维超薄纳米片; 光催化; CsPbBr₃; g-C₃N₄

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