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Constructing CsPbBr_xI_{3-x} nanocrystal/carbon nanotube composite with improved charge transfer and light harvesting for enhanced photoelectrochemical activity^{\dagger}

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The past few years have witnessed the impressive development of all-inorganic halide perovskite nanocrystals. In this report, a series of CsPbBr_xI_{3-x} nanocrystal/carbon nanotube (CsPbBr_xI_{3-x} NC/CNT, x=3, 2, 1.5, 1) hybrid photoelectrodes have been fabricated and further employed in photoelectrochemical cells. Benefiting from the high conductivity of CNTs, the hybrid samples showcase accelerated charge separation and transfer actions after photoexcitation. Moreover, increasing the I/Br ratio in CsPbBrxI_{3-x} nanocrystal accounts for a wider adsorption range but inferior phase stability, which calls for a delicate balance. As a result, a highest photocurrent density of $420 \ \mu A/cm^2$ is finally achieved by CsPbBr_{1.5}I_{1.5} NC/CNT (200), which corresponds a 7.7-fold improvement over the prototype CsPbBr₃. This report offers in-depth understandings on the charge transfer behavior along with photoelectrochemical performance of CsPbBrxI_{3-x} nanocrystal/CNT, which can surely stimulate metal halide perovskite nanocrystal-based hybrid materials for promising optoelectronic, photocatalysis and photoelectrochemical applications.

Introduction

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As an eye-catching research topic in the past few years, metal halide perovskites have been demonstrated with remarkable properties (e.g., high light extinction coefficient, tuneable band structure and facile charge transfer) and thus have been successfully applied into a vast of optoelectronic devices including solar cells, light-emitting diodes (LEDs). photodetectors, etc.¹⁻⁵ Notably, a record power conversion efficiency (PCE) of 23.7% has been delivered in the state-of-theart perovskite solar cell device,⁶ as well as an external quantum efficiency exceeding 20% in LEDs,^{7,8} which conceivably will be continuously updated.

Motivated by the impressive advances achieved in optoelectronic applications, very recently the employment of metal halide perovskites for photochemical applications has aroused intense attentions. For instance, our group has for the first time reported the photocatalytic CO₂ reduction by CsPbBr₃ nanocrystal in nonaqueous solutions,⁹ or in gaseous phase,¹⁰ which have inspired a wave of researches on photocatalytic CO₂ conversion¹¹⁻¹⁵ and other light-driven organic synthesis such as 3,4-ethylenedioxythiophene (EDOT) polymerization,¹⁶ selective oxidation of benzylic alcohols^{17,18} α -alkylation of aldehydes¹⁹ by metal halide perovskite materials. Besides, MAPbl₃ microcrystal powders have also reported to afford a photocatalytic HI



Other than the aforementioned particulate photocatalytic fabricating semiconductor materials into systems, photoelectrodes to perform the photoelectrocatalysis is known to exhibit numerous attractive advantages.²⁴⁻²⁷ For example, the applied external bias is beneficial for the photo-induced charge separation and transfer, thereby availing the charge collection efficiency.^{28,29} Moreover, the applied external bias also increases the redox potential of the electrons or holes, hence contributing their injection across the semiconductorliquid junction towards high-rate chemical reactions.^{30,31} Thus, recently researchers have encapsulated the solar cell devices into water-proof materials to conduct the water splitting under light illumination and external bias.³²⁻³⁵

In this work, the CsPbBr_xI_{3-x} NCs with superior stabilities have been selected architypes explore their as to photoelectrochemical applications. In addition, CsPbBr_xI_{3-x} NC/carbon nanotube hybrid electrodes have also been assembled. Electrochemical and transient spectroscopic methods have been resorted to investigate the effect of introducing CNT and I dopant on photoelectrochemical performance. The results revealed that the charge transfer and light absorption capability have been significantly enhanced by CNT incorporation and ion doping, respectively, and a multiple improved photocurrent density is achieved on an optimized CsPbBr_{1.5}I_{1.5} NC/CNT (200) based photoelectrode. This work provides a simple but effective method to shed light on the photoelectrochemical properties of metal halide perovskite materials, along with guiding significance on its potential

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application in the future. The main text of the article should appear here with headings as appropriate.

Experimental

Chemicals and materials

Octadecene (ODE, 90%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was purchased from Alfa Aesar. Lead bromide (PbBr₂, 99.0%), lead iodide (PbI₂, 99.0%), caesium carbonate (Cs₂CO₃, 99.9%), oleylamine (OLA, 80-90%), carbon nanotube (CNT, multi-walled, >70%), Benzoquinone (99%) and ethyl acetate were purchased from Aladdin. Toluene, dichloromethane, acetone, ethanol and hydrochloric acid (HCl, 36%~38%) were purchased from Chemical Reagents Factory of Guangzhou. 4A molecular sieves were added in solvents to remove the remaining water before use.

Purification of CNT

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The commercial CNTs was purified via an acid treatment beforehand. In detail, the CNTs were dispersed into concentrated HCl, followed with an ultrasonic washing treatment for 8 h at room temperature. Afterwards, the CNTs were collected by centrifugation at 8000 rpm for 3 min, and further washed by the deionized water and ethanol for 3 times to remove the acid. Finally, the CNTs were re-dispersed into toluene to afford a uniform colloid solution (0.5 mg/mL).

Synthesis of the CsPbBr_xI_{3-x} NC

CsPbBr_xI_{3-x} (x=0, 1, 1.5, 2) NC was prepared by a hot-injection method according to the previous report.³⁶ Typically, an Csoleate precursor was prepared firstly by dissolving the Cs₂CO₃ (0.814 g) into ODE (40 mL) with OA (2.5 mL) at 120 °C under vacuum for 1 h, and at 150 °C in N₂ atmosphere until all the Cs₂CO₃ was completely dissolved. Particularly, the Cs-oleate precursor must be preheated to 150 °C before the subsequent hot injection synthesis procedure since it would precipitate at room temperature.

To synthesize the CsPbBr_xI_{3-x} nanocrystals, ODE (5 mL) and PbX₂ (0.188 mmol, X=I, Br or their mixture) were added into 25 mL 2-neck flask and dried at 120 °C under vacuum for 1 h with continuous stirring. OA (0.5 mL) and OAm (0.5 mL) were then injected and the whole system was refilled with N_2 and heated to 180°C. Subsequently Cs-oleate precursor solution (0.4 mL) was quickly injected into the 2-neck flask under N₂ flow and 5 s later the reaction was inhibited by a fast ice bath cooling process. The CsPbBr_xI_{3-x} nanocrystals products were collected by centrifugation at 8000 rpm for 10 min and then dispersed in dry toluene (5 mL). The dispersion was further centrifuged at 10000 rpm for 3 min, after which the precipitate was reserved for subsequent rinsing with ethyl acetate. Finally, the purified precipitate was collected and re-dispersed in anhydrous toluene (1000, 900, 800 and 600 $\mu L)$ to form CsPbBr_xI_3-x NC solution with different concentration.

 $\label{eq:reparation} Preparation of CsPbBr_{x}I_{3-x} \ NC/CNT \ Composite \ based \\ Photoelectrode$

Firstly, CsPbBrxI3-x NC colloidal solution was mixed with CNT dispersion solution. In order to optimize the article of the CNT, the concentration CsPbBr_xI_{3-x} NC was maintained identical by mixing NC colloidal solution with different amounts of CNT dispersion (0, 100, 200 and 400 µL) leading to a total volume as 1 mL, as presented in Table S1. A centrifugally-deposition method was utilized to deposit the CsPbBrxI3-x and CsPbBrxI3-x NC/CNT thin-film onto the FTO conducting glass substrate. The FTO glasses (1 cm x 2.5 cm) were thoroughly cleaned via sequential sonicating in deionized water, alcohol and acetone. Before centrifugation, the CsPbBr_xI_{3-x} NC or CsPbBr_xI_{3-x} NC/CNT toluene/ethyl acetate suspension (2mL) was added into a 10 mL centrifuge tube, and then an FTO glass was subsequently lay inside it with the conducting side facing down. The deposition process was conducted at 6000 rpm for 2 min, and the asfabricated films were dried at 70 °C for 30 min under vacuum to remove residual solvents.

Characterizations

Powder XRD patterns were obtained on a Riguku MiniFlex X-ray diffractometer. The morphology and nanostructure were recorded by FE-SEM (SU8010) and TEM (Tecnai G2 F30). The UV-vis absorption spectra were acquired on UV-Vis spectrometer (Shimadzu UV-3600). The photoluminescence (PL) spectra and the time-resolved photoluminescence (TRPL) decay spectra were characterized on a photoluminescence spectrometer (FLS980, Edinburgh Instruments Ltd.) with a laser excitation of 369.6 nm. A triexponential decay kinetic was used to fit the data of the TRPL decay curves, and the formula of the average PL life times ($\tau_{average}$) was listed below:

$$A(t) = A_1 e^{\left(-\frac{t}{\tau_1}\right)} + A_2 e^{\left(-\frac{t}{\tau_2}\right)} + A_3 e^{\left(-\frac{t}{\tau_3}\right)}$$

$$\tau_{average} = (A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2) / (A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3)$$

Transient absorption spectroscopy (TAS)

A regeneratively amplified Ti:sapphire laser source (Coherent Legend, 800 nm, 150 fs, 5 mJ/pulse, and 1 kHz repetition rate) and Helios (Ultrafast Systems LLC) spectrometers were equipped for transient absorption tests. The pump light was generated by frequency-doubling the 75% of 800 nm output in a BaB_2O_4 (BBO) crystal and was focused at the sample with a beam waist of about ~360 µm. Meanwhile the white light continuum (420 nm-780 nm) probe light was produced by concentrating the remaining 800 nm output into a sapphire window. The pump repetition frequency was synchronized to 500 Hz by a mechanical chopper, while the probe and reference beams which were split from the white light continuum would be sent into a fibre optics-coupled multichannel spectrometer by complementary metal-oxide-semiconductor sensors with a frequency of 1 kHz.

Photoelectrochemical (PEC) characterizations

The photoelectrochemical tests were measured on a Zennium electrochemical workstation (Zahner) under a 3-electrode configuration in which a Pt mesh served as counter electrode, Ag/AgCl (3 M KCl) as the reference electrode and the prepared CsPbBr_{xl3-x} or CsPbBr_{xl3-x} NC/CNT film as working electrode.

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Fig. 1 (a) The photos of the as-prepared CsPbBr₃ NC/CNT dispersion (b) XRD patterns of the CsPbBr₃ NC and CsPbBr₃ NC/CNT. (c) TEM image of CsPbBr₃ NC/CNT (200). (d) the as-fabricated films under ultraviolet radiation (365nm). (e-h) The cross-sectional SEM images of the CsPbBr₃ NC and CsPbBr₃ NC/CNT (100, 200 and 400).

The electrolyte was prepared by dissolving TBAPF₆ (0.1 M) and benzoquinone (4 mM) into dry dichloromethane. An Xe lamp (LSXS-150, ZOLIX Instruments, 150 W) with an AM 1.5G filter was equipped to offer the simulated solar illumination, and the light intensity was calibrated to 150 mW cm⁻² with an NREL- Si solar cell.

Results and discussion

A commonly used hot-injection method was adopted to synthesize the CsPbBr_xI_{3-x} NC. As shown in Fig. 1a, the archetype CsPbBr₃ NC prepared by hot injection method had a good dispersibility in the toluene solvent, and XRD patterns indicated that the as-prepared NC owned a cubic phase (Fig. 1b). Accordingly, a cubic morphology with an average size of 7.7 nm was observed in the TEM image (Fig. S1a), In addition, the corresponding high-resolution TEM image further confirmed its high crystallinity (Fig. S1b). To prepare the CsPbBr₃ NC/CNT composites, the CsPbBr₃ NC colloidal solution was well-mixed with the CNT dispersion solution by sonification. It is noteworthy that the commercial CNT was treated by an acidtreatment before use to remove the impurities (e.g., metal oxide). Obviously, a much smoother surface was displayed in the purified sample as well as a univocal XRD patterns which was indexed to individual CNT (as illustrated in Fig. S2 and Fig. S3). After incorporating CNTs, the colour of CsPbBr₃ NC solution turned from light green to dark olive and the resultant composite still possessed high dispersibility in toluene solvent. As demonstrated in Fig. 1c, the TEM measurements further claimed that the NCs were densely and closely stacked onto the surface of CNTs. Subsequently, depositing the CsPbBr₃ NC or CsPbBr₃ NC/CNT composite onto the FTO glass substrate was performed by centrifugal-cast method. The photoluminescence intensity of the pristine CsPbBr₃ NC thin film was gradually quenched under ultraviolet radiation (365 nm) as the CNT amount increased (Fig. 1d). The cross-sectional SEM images demonstrated that the CsPbBr₃ NCs had stacked onto the FTO electrode to form a thin-film with thickness of ~1.1 μ m (Fig. 1e). Interestingly, the film thicknesses were little changed when introducing the CNTs (Fig. 1f-h). Moreover, the CNTs obviously penetrated in the film, forming a 3D cross network. The absorption behaviour of the CsPbBr₃ NC and CsPbBr₃ NC/CNT (100, 200 and 400) thin films were further tested. As illustrated in Fig. 2, CsPbBr₃ NC was featured with a light absorption edge at ~518 nm, corresponding to a bandgap of 2.39 eV. It can be clearly found that the absorbance of the CsPbBr₃ NC/CNT composite film was significantly increased compared with the pristine CsPbBr₃ NC due to the interband absorption of CNT.³⁷

The photoelectrochemical (PEC) characterizations were subsequently conducted in a 3-electrode configuration under AM 1.5G illumination (150 mW cm⁻²). It is worth noting that the PEC method is a powerful tool to probe the physical and chemical properties of metal perovskite material. Routine PEC tests including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), spectroelectrochemistry have been successfully adopted to detect the band structures and the charge transfer behaviours of metal halide perovskites, providing significant guidance towards novel material design and device optimization.³⁸⁻⁴¹ In this work the electrolyte was



Fig. 2 UV-vis absorption spectra of CsPbBr₃ NC and CsPbBr₃ NC/CNT.

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Fig. 3 (a) Time course of photocurrent density curves and (b) EIS Nyquist plots for PEC cell with the working electrodes of CsPbBr₃ NC/CNT (100, 200, and 400), the reference electrode (Ag/AgCl in 3 M KCl) and the counter electrode (Pt mesh) at -0.4 V upon on/off illumination in 0.1 M TBAPF₆ and 4 mM Benzoquinone in dichloromethane. A 150 W Xe lamp with an AM 1.5G filter and 150 mW cm⁻² was used as a light source. (c) Steady-state PL spectra and (d) transient-state PL spectra with an excitation wavelength of 369.6 nm.

prepared by dissolving 0.1 M TBAPF₆, 4 mM benzoquinone into anhydrous dichloromethane, where TBAPF₆ served as the supporting electrolyte for enhancing the conductivity while benzoguinone acted as redox couple to capture the photoelectrons of CsPbBr3. As shown in Fig. 3a, the amperometric I-t curves plotted at -0.4 V Ag/AgCl demonstrated the photocurrent responses were highly reproducible upon several light on/off cycles. Importantly, compared with the individual CsPbBr₃ NC photoelectrode, CsPbBr₃ NC/CNTs hybrid ones efficiently boosted the photocurrent densities (both transient and steady values, as shown in Table S2), and particularly a highest 2.6-fold enhancement was observed in the optimized CsPbBr₃ NC/CNT (200) sample (206 µA cm⁻²). Furthermore, the electrochemical impedance spectroscopy (EIS) was resorted to detect the charge transfer process. Similarly, a large arc in the testing frequency range was observed in all samples, and it was fitted by a simple RC circuit subsequently (Fig. 3b). As a result, the charge transfer resistances were calculated as 18271 Ω for CsPbBr3 NC, and 13943 $\Omega,$ 9153 $\Omega,$ 5138 Ω for CsPbBr3 NC/CNT (100, 200 and 400), respectively. Evidently, the transfer resistance was dramatically reduced after cooperating with CNT,⁴² implying a more facilitated charge separation and transfer process which can be ascribed to superior conductivity of CNT. To confirm this deduction, photoluminescence (PL) spectra were measured with an excitation wavelength of 369.6 nm. As shown in Fig. 3c, all the samples exhibited a coincident PL emission peak at 513 nm originating from CsPbBr3 NC. However, the PL emission intensity was quenched by comparing pristine CsPbBr₃ NC with

CsPbBr₃ NC/CNT composites, which was continuously declined when gradually increasing the CNT amounts. Especially, the decrement of PL intensity was measured to be as high as 88% for CsPbBr₃ NC/CNT (400) sample. Besides, the time-resolved photoluminescence (TRPL) tests further indicated that the PL decay kinetics were obviously accelerated in the CsPbBr₃/CNT hybrids (Fig. 3d). Accordingly, the decay curves were fitted with a tri-exponential decay kinetic and the resultant average PL lifetime ($\tau_{average}$) were listed in Table 1. The $\tau_{average}$ drop from 43.33 ns to 32.00 ns as the CNT amount increased from 0 to 400 μL. Based on the PL and TRPL tests, it can be concluded that CNTs can accelerate the separation of the photo-generated electron-hole pair in CsPbBr₃ NC and thereby suppress the potential charge carrier recombination, which further contribute to a higher photocurrent response. However, it is noteworthy that the optimal photocurrent density was featured in CsPbBr₃ NC/200 uL sample not the CsPbBr₃ NC/400 uL with the most facile charge transport. This phenomenon can be explained as excessive black CNT would shield the light absorption of CsPbBr₃ NC (Fig. 2), thus resulting in prejudicing to stimulation of CsPbBr₃ NC.

able 1 Summary of the average PL lifetimes for the CsPbBr $_3$ NC/CNT					
	Samples	$\tau_{average}/ns$	Х		
	CsPbBr ₃ NC	43.33	1.390		

CsPbBr₃ NC	43.33	1.390
CsPbBr ₃ NC/CNT (100)	34.84	1.149
CsPbBr ₃ NC/CNT (200)	32.84	1.125
CsPbBr₃ NC/CNT (400)	32.00	1.189

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Fig. 4 (a) Transient absorption spectra of $CsPbBr_3 NC$ with 400 nm pump pulse. (b) The decay kinetics curves probed at 510 nm.

To elucidate the impact of the CNT on the ultrafast carrier dynamic of CsPbBr₃ NC such as charge separation, the transient absorption spectroscopy (TAS) measurement was further carried out. As shown in Fig. 4a, a main peak emerged at around 510 nm, which can be attribute to the recovery of ground-state bleaching (GSB). Furthermore, the corresponding decay kinetics were fitted, and the parameters were listed in Table S3. Compared with the CsPbBr₃ NC, both the fast and slow time components process of CsPbBr₃ NC/CNT (100, 200 and 400) were accelerated simultaneously, which can be interpreted as an efficient charge carrier extraction from excited-state state of CsPbBr₃ NC to the CNT.⁴³⁻⁴⁴ Therefore, electrochemical and optical characterizations conjointly verified that CNT was beneficial to the fast charge transfer process, while the optimum CNT amount is 200 µL.

photoelectrochemical order to further promote In performances, we also alloy CsPbBr₃ NC with iodide composition to prepare mixed-halide CsPbBr_xI_{3-x} NC with a wider absorption range. The TEM and HRTEM images showcased that the domain size of the $CsPbBr_xI_{3-x}$ NCs were similar to that of CsPbBr₃ NC. (Figure S4) The XRD patterns revealed that CsPbBr_xI_{3-x} (x=2, 1.5, 1, 0) NC samples were indexed to pure cubic phase (Fig. S5), which can be wellpreserved after cooperation with CNTs. Similar to CsPbBr₃ NC/CNT nanostructure, CsPbBr_xI_{3-x} NC were closely packaged onto the surface of CNT as verified by the corresponding TEM images (Fig. S6). Forward spectroscopic analysis revealed that enlarging I/Br ratio in CsPbBr_xI_{3-x} NC advantageously broadened UV-vis absorption range, which can be further corroborated by



Fig. 5 Amperometric I-t curves of (a) the CsPbBr_xI_{3-x} NC and (b) the CsPbBr_xI_{3-x} NC/CNT (200) at -0.4 V. Testing conditions of PEC cell and illumination were the same with condition mentioned above.

a significant red-shift of the PL peak. Moreover, in the cases of the CsPbBr_xI_{3-x} NC/CNT hybrids, the PL decayed faster than those without CNTs as expected. (Fig. S7, Table S5) Subsequently, we assembled all the samples into thin-films to perform the photoelectrochemical tests (Fig. S8a). It is noteworthy that during the photoelectrode preparation process, the phase transition was occurred to CsPbBrl₂ NC sample as can be seen from its pristine colour change from dark red to yellow when exposed to the ambient environment (Fig. S8b-d). Such poor stability was further confirmed in the XRD tests. Therefore, much care should be taken during the photoelectrochemical tests. In addition, CsPbl₃ NC possessed an even poorer phase stability, which made it challenging to endure the photoelectrochemical tests, therefore it was absent in the following tests. To make a fair comparison, the thickness of the thin-films was adjusted to about 1.1 µm (Fig. S9). As shown in Fig. 5a and Table S4, the photocurrent density increased from 88.7 µA cm⁻² to 118 µA cm⁻ when varying the Br/l ratio from 2 to 1, benefiting from the expanded light absorption range. However, further decreasing the Br/I ratio to 0.5 was detrimental to the performance, due to the aforementioned phase transition. The photocurrent responses were further enhanced after mixing the CsPbBr_xI_{3-x} NC with the CNTs, and the champion photocurrent density of 417 µA cm⁻² was achieved by the CsPbBr_{1.5}I_{1.5} NC /CNT sample (Fig. 5b). In accord with CsPbBr₃/CNT hybrid, such photocurrent increments were also ascribed to the ameliorative charge transfer, as confirmed by the TRPL and EIS measurements (Fig. S10, Table S6).

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Conclusions

In summary, our work successfully implements the CsPbBr₃ NC into a prototypical photoelectrochemical reduction of benzoguinone. Moreover, the introduction of conductive CNT would facilitate the photo-generated electron-hole pairs separation, which significantly improves the photocurrent density. Particularly, it is found that the loading amount should be carefully optimized since excessive CNT will compete with perovskite NC in light absorption. In addition, alloying iodide to prepare CsPbBr_{xl3-x} NC could broaden the visible-lightabsorption range and further boost the PEC performance. As a result, a highest photocurrent density of 417 μA cm $^{\text{-}2}$ is attained on the CsPbBr_{1.5}I_{1.5} NC/CNT (200) sample, corresponding to a 2.6-fold increment than its individual CsPbBr_{1.5}I_{1.5} NC, or 7.7fold increment than the starting CsPbBr₃ NC. This work offers an efficient and facile way for material screening toward the fabrications of high-performance metal halide perovskite thinfilms, and their further applications in photoelectrochemical synthetic cells for solar-fuel production or light-driven organic synthesis.

Conflicts of interest

There are no conflicts to declare.

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CsPbBr₃I_{3-x}/CNT hybrid thin-film photoelectrodes are fabricated and showcase great potential in photoelectrochemical applications