Size-controlled Synthesis of Highly Luminescent Organometal Halide Perovskite Quantum Dots

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ABSTRACT: Size-tunable organometal halide perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ quantum dots (QDs) were successfully synthesized by a simple surfactant-assisted reprecipitation technique, in which the size-tunability was realized by varying the molar ratios of methylammonium bromide ($\text{CH}_3\text{NH}_3\text{Br}$) to PbBr_2 while the total amount of octylamine (OTAm) and $\text{CH}_3\text{NH}_3\text{Br}$ remained unchanged. The diameters of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs could be effectively tuned from 1.6 to 3.9 nm, and these QDs exhibited an obviously size-dependent optical properties, whose photoluminescence (PL) covered the spectral region from 440 to 530 nm and the emission width was 20-32 nm. The maximum absolute PL quantum yield (PLQY) was measured to be as high as approximately 80% at room temperature. A plausible formation mechanism was proposed and the quantum confinement effect was discussed based on effective mass approximation. Moreover, this synthetic approach could also be extended to prepare different halide perovskite QDs including $\text{CH}_3\text{NH}_3\text{PbCl}_x\text{Br}_{3-x}$ and $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{I}_x$ ($x=1\sim3$), which realized the color-tunability over the entire visible spectral region of 390-750 nm. The size- and compositional-tunable emission colors of organometal perovskite QDs endows them wide potential applications in next-generation optoelectronic devices.

Keywords: Organometal halide perovskite; Quantum dots; Photoluminescence; Quantum confinement effects

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1. Introduction

In the past few decades, colloidal semiconductor QDs were extensively studied due to their size- and surface-dependent optical properties as well as their wide potential applications in optoelectronics and biological labels.[1-6] However, the complicated synthetic technique and high-cost raw materials limited their further commercialization. Very recently, organometal halide perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X}=\text{Cl}$, Br and I) have drawn extensive attention due to their breakthrough in solar energy conversion, and nearly 20% power conversion efficiency has already been reported.[7-14] Moreover, the inherent superiorities including band-gap tunability, low solution-processing temperature and narrow band emission make halide perovskites alternative candidates for application in low-cost and large-area light-emitting diodes and photodetectors.[15-20]

It is well known that the unique feature of the colloidal semiconductor QDs endows them with imponderable optical advantages compared to their bulk counterparts due to the quantum-confinement effects, which play an important role in the interfacial charge transfer, photo-physics and carrier multiplications of the semiconductor QDs [21-24]. As a newly emerging candidate of QDs family, what can the optical and electrical properties of the perovskites become if their size is reduced to be comparable or smaller than the exciton Bohr diameter? Therefore, it is interesting and necessary to study the optical properties of perovskite QDs. To date, some work has been reported on the quantum-confinement effects of organic-inorganic $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}$, Br and I) and all inorganic perovskite cesium lead halides (CsPbX_3 , $\text{X}=\text{Cl}$, Br and I) QDs.[25-30] For example, Kovalenko and co-workers reported the synthesis of all inorganic CsPbX_3 ($\text{X}=\text{Cl}$, Br and I) QDs with composition- and size-dependent emission color, which exhibited obvious quantum-size effects.[25] Very recently, Alivisatos' group[26] and Prato's group[27] realized the quantum confinement effects of CsPbBr_3 by controlling the self-assembly of CsPbBr_3 nanoplates and tuning the amount of HBr in the reaction, respectively. Moreover, the synthesis of organic-inorganic $\text{CH}_3\text{NH}_3\text{PbX}_3$ QDs was also reported

recently. Zhong and co-workers developed a ligand-assisted reprecipitation strategy to prepare highly luminescent colloidal $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}$, Br and I), and all of these perovskite exhibit slight quantum confinement effect.[15] Rogach's group prepared highly luminescent $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs by changing the reprecipitation temperature, but the controlling mechanism is not clear.[28] More recently, Urban's group[29] and Ma's group[30] both studied the quantum size effects in colloidal organometal halide perovskite nanoplatelets with different thickness, but the highest PLQY in their study is not over 50% due to the quantum confinement just in one dimension. Therefore, it remains challengeable to prepare highly luminescent and color-tunable organometal $\text{CH}_3\text{NH}_3\text{PbX}_3$ QDs and to study both their quantum confinement effects and formation mechanism, which is conducive to specifically engineer $\text{CH}_3\text{NH}_3\text{PbX}_3$ QDs with desired optical properties.

In this paper, a simple surfactant-assisted reprecipitation technique was adopted to realize the size-tunability of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, in which the ratio of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 was varied while the amount of OTAm and $\text{CH}_3\text{NH}_3\text{Br}$ remained unchanged. The size of these $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs can be effectively tailored from 1.6 to 3.9 nm, and the PL emission is size-dependent and covers the spectral region of 440-530 nm. The experimental data could fit well to the calculation results based on the effective mass approximations. The excellent optical properties including narrow emission linewidth of 20-32 nm and high absolute PLQY (*ca.*80%) made $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs comparable with the classical semiconductor QDs such as CdSe and CdTe QDs. Besides, through compositional modulations by different halogen elements in the perovskite QDs the PL emission spectra could be readily regulated over the entire visible spectral region of 390-750 nm. The size- and composition-tunable optical properties make halide perovskite QDs become a contender in the next-generation optoelectronic applications.

2. Experiment Section

2.1 Materials

Lead(II) chloride (PbCl_2 , 99%), lead(II) bromide (PbBr_2 , 98%), lead(II) iodide (PbI_2 , 98.5%), methylamine (CH_3NH_2 , 40wt% in methanol) and hydriodic acid (HI , 57wt% in water) are purchased from Alfa Aesar. 1-octylamine (OTAm, 99%) is purchased from Acros Organic. Oleic acid (OA, 90%) is purchased from Aladdin Reagent Company. Other reagents and solvents including hydrochloric acid (HCl , 37%), hydrobromic acid (HBr , 47%) and common ethanol, toluene, diethyl ether and N,N-dimethylformamide (DMF) are commercially available analytical-grade products and purchased from Beijing Chemical Reagent Company. All chemicals were used in our experiments as received without any further purification.

2.2 Synthesis of methylammonium halid ($\text{CH}_3\text{NH}_3\text{X}$, $\text{X}=\text{Cl}$, Br , I)

The $\text{CH}_3\text{NH}_3\text{X}$ ($\text{X}=\text{Cl}$, Br , I) was synthesized through the reaction of CH_3NH_2 with the corresponding acid based on previous work.[31] A typical synthesis of $\text{CH}_3\text{NH}_3\text{Br}$ is listed as follows: 45 mL of CH_3NH_2 and 20 mL of HBr were added into 100 mL of round-bottom flask, and then the reaction was stirred for 2 h at 0 °C. Afterwards, the precipitates were obtained by rotary evaporation at 50 °C for 1 h. The precipitates were washed three times by diethyl ether, and then dried in vacuum at 75°C overnight. Similarly, the synthesis of $\text{CH}_3\text{NH}_3\text{Cl}$ and $\text{CH}_3\text{NH}_3\text{I}$ was performed according to the above procedures except different amounts of HCl and HI was used to replace HBr .

2.3 Synthesis of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}$, Br , I) QDs

For a typical synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, 0.19 mmol of $\text{CH}_3\text{NH}_3\text{Br}$, 0.2 mmol of PbBr_2 , 0.01 mmol of OTAm and 0.5 mL of OA were dissolved in 5 mL of DMF under magnetic stirring at room temperature to form a precursor solution. Then 0.5 mL of the precursor solution was injected into 10 mL of toluene under vigorous magnetic stirring. Once the precursor solution was mixed with the toluene, the color of the mixture became green immediately. Afterwards, the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs were obtained by centrifugation at 13000 rpm for 20 min. To obtain different-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, some control experiments were performed based on the above procedure except the variation of the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 while the

total amount of $\text{CH}_3\text{NH}_3\text{Br}$ and OTAm was kept at 0.2 mmol.

The synthesis of $\text{CH}_3\text{NH}_3\text{PbCl}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ QDs was carried out by using the similar synthetic procedure of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs except the precursors were changed to PbCl_2 , PbI_2 as well as $\text{CH}_3\text{NH}_3\text{Cl}$ and $\text{CH}_3\text{NH}_3\text{I}$. Moreover, $\text{CH}_3\text{NH}_3\text{PbCl}_{3-x}\text{Br}_x$ and $\text{CH}_3\text{NH}_3\text{PbBr}_x\text{I}_{3-x}$ QDs ($x=0\sim3$) were synthesized by varying the types and amount of PbX_2 and $\text{CH}_3\text{NH}_3\text{X}$ ($\text{X}=\text{Cl}$, Br and I) based on the above synthetic procedure.

2.4 Characterization

Transmission electron microscopy (TEM) images of the samples were recorded on a JEM-1400 transmission electron microscope operating at an accelerating voltage of 100 kV. High-resolution TEM (HRTEM) images were recorded on a JEM-2010 at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns of all the samples were obtained by using a Bruker D8 Advance diffractometer using a $\text{Cu K}\alpha$ radiation source ($\lambda=1.54056 \text{ \AA}$). Energy dispersive X-ray (EDX) spectroscopy analyses were recorded on a Hitachi S-4800 field-emission scanning electron microscope equipped with an EMAX-350 Horiba system, working at 15 kV. The UV-Vis absorption spectra were recorded on a Shimadzu-UV 3101 spectrophotometer. The PL spectra were taken by using a FLUORAT-02-PANORAMA spectrophotometer. The absolute PLQY of diluted solution of the perovskite QDs was determined by using an Orient KOJI QY-2000 Fluorescence Spectrometer equipped with an integrating sphere, which was excited with a blue LED light source. All of the measurements were performed at room temperature.

3. Results and discussion

3.1 Size-controlled synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite QDs

The organic/inorganic $\text{CH}_3\text{NH}_3\text{PbBr}_3$ consists of $[\text{PbBr}_6]^{4-}$ octahedron unit cell, and CH_3NH_3^+ cations filled the large 12-fold coordinated holes among the octahedrons through the binding to the Br^- anion of $[\text{PbBr}_6]^{4-}$ unit cell.[32-34] Bulk $\text{CH}_3\text{NH}_3\text{PbBr}_3$ was often synthesized by mixing $\text{CH}_3\text{NH}_3\text{Br}$ and PbBr_2 with

equivalent amount according to the stoichiometry. Considering that the number of surface atoms increases with a decrease of particle size[35, 36], In general, Br atoms are often exposed on the surface of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ in a ideal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ structure as mentioned above, the decrease of the size of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ means that the number of the Br atoms on the surface would increase, thus excess PbBr_2 compared with $\text{CH}_3\text{NH}_3\text{Br}$ was often used in the synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs. [15] Herein, inspired by the above analysis, a series of synthetic methods were designed to prepare different-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs by varying the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 . Moreover, the surfactants including alkyl amines and alkyl acid with a long chain were also used in the synthesis, in which the uncoordinated Br atoms on the surface could bind to the alkyl amines through the hydrogen bonding interactions to reduce the surface energy. To ensure that the uncoordinated Br atoms could bind with enough surfactants, the total amount of OTAm and $\text{CH}_3\text{NH}_3\text{Br}$ was unchanged. The presence of alkyl acid could suppress the QDs aggregation. As a consequence, the surfactants play an important role in suppressing further growth and aggregation of colloidal QDs.

In this synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, free-standing layered precursors were formed firstly by mixing $\text{CH}_3\text{NH}_3\text{Br}$, PbBr_2 , OTAm and OA in the solvent DMF (Fig.1A). After quick injecting the precursor solution into toluene under vigorous magnetic stirring, the solution color changed to bright green, then the perovskite QDs were obtained by centrifugation at a high speed. In this process, the dropping of precursors into toluene changed the solubility of the precursors in solution, and the layered free-standing constituents would gather and self-assemble into perovskite QDs through sharing the corners of $[\text{PbBr}_6]^{4-}$. [37] The structure of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs is depicted in Fig.1B, and the alkyl chain of OTAm is surrounded the periphery of the octahedral set with their alkyl chains dangling outside the QDs.[38]

TEM technique was employed to study the size and morphology evolution of the perovskite QDs synthesized by using different molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 while the molar ratio of total amount of OTAm and $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 was kept at 1:1, and the corresponding TEM images are depicted in Fig.2 (A-F). The perovskite

QDs exhibit a spherical shape with a narrow size distribution. The mean diameter in the range of 1.6-3.9 nm is obtained by measuring 100 particles and the corresponding size statistical histograms of different-sized perovskite QDs are given in Fig.S1 (Supporting Information). A typical HRTEM image of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs with a mean diameter of 3.3 nm exhibits clear lattice fringes throughout a single particle, which suggests the nature of high crystallinity. Fig.2G depicts the relationship between the mean diameter and the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 , which reveals an obvious increase of the diameter with an increase of the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 . Thus the size-tunability of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite QDs can be realized just by varying the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 . As mentioned above that the excess Br atoms play an important role in the size control of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, and the superfluous uncoordinated Br atoms interact with OTAm via the hydrogen bonding. When the amount of PbBr_2 in the synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs is unchanged, the decrease of the molar ratio of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 would lead to more Br ions exposed on the surface of QDs, thus higher specific surface area may be needed to make excess Br ions exist on the surface.[15] Therefore, the diameter is decreased with an increase of the redundant PbBr_2 , and the size of perovskite QDs can be controlled easily via varying the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 .

According to the aforementioned results, the amount of PbBr_2 is higher than that of $\text{CH}_3\text{NH}_3\text{Br}$ in the synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, thus the perovskite QDs should be non-stoichiometric due to the anion-rich surface, which has been discussed in the case of CdSe QDs.[39] EDX analysis was utilized to determine the elemental composition of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs. A typical example of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs with a mean size of 3.3 nm is given in Fig.3A, revealing the presence of both Pb and Br in the products, and the atomic ratio of Br/Pb is 3.3, which implies the presence of a Br-rich surface, and this result is in good agreement with the aforementioned design ideas. XRD patterns were employed to study the crystal structure of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite QDs, Fig.3B presents the XRD patterns of the QDs with a mean size of 3.3 nm. To further confirm the crystal structure, the XRD of the solid bulk $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is also given in Fig.3B, which was synthesized by drying the

precipitation from a direct reprecipitation process in absence of surfactants. The sharper diffraction peaks at the bottom of Fig.3B indicate the formation of bulk perovskite particles with a larger size. In contrast, two obvious diffraction peaks located at $2\theta=14.9^\circ$ and 30.2° together with a weak and broad peak between the two peaks are observed in the XRD patterns of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite QDs, and broadening of the characteristic peaks is in consistent with the nature of nanocrystals based on Debye-Scherrer equation.[28]

3.2 Size-dependent optical properties of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite QDs

Fig.4A shows the digital photos of different-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs dispersed in toluene under the illumination of 365 nm at room temperature, which indicates that the optical color of the colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs can be tuned from blue to green by varying their diameter. The corresponding optical absorption and PL spectra of the colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs are presented in Fig.4B and C, respectively. As shown in Fig.4B, an obvious red-shift of absorption band is observed with an increase of the mean diameter. It should be noted that the absorption peak changes gradually from distinct sharp to less distinct with an increase of the mean size, which is similar to that observed in other colloidal QDs systems including CdSe and CdTe QDs.[1] In addition, the PL peak shifts from 440 nm to 530 nm with the diameter increasing from 1.6 to 3.9 nm (Fig.4C), which exhibits an obvious blue-shift as compared to that of bulk $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (about 570 nm), implying an obvious quantum confinement effect.[40] As a matter of fact, the diameter of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs is comparable or smaller than the exciton Bohr diameter of bulk $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (~ 4 nm), thus the as-obtained QDs clearly exhibit the effect of quantum confinement.[41] Additionally, the PL spectra of different-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs also show narrow emission linewidth of 20-32 nm, which may arise from the narrow size distribution.

For the semiconductor QDs such as CdSe and CdTe, the shift of PL maximum is often explained by the quantum confinement effect, and the band gap of spherical QDs with the radius R can be estimated from the following equation based on effective mass approximation: [42]

$$E_g = E_{g,bulk} + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\epsilon R}$$

where E_g is the band gap of the QDs, $E_{g,bulk}$ is the band gap of bulk materials, $\hbar$ is the reduced Planck constant, m_e and m_h are the reduced mass of electron and hole of QDs, ϵ represents the effective dielectric constant. For $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, $m_e = 0.25m_0$ and $m_h = 0.12m_0$ (where m_0 is the mass of a free electron), respectively.[43] Based on the above equation, we try to fit the optical band gap of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs as a function of the diameter of the QDs, and the comparison between the experimental and fitting results is given in Fig.5A. The experimental data is in good agreement with the theoretically fitting results for the QDs with relatively large diameter ($d > 2.5$ nm), but the experimental values diverge from the fitting results for the QDs with the mean size less than 2.5 nm, which is similar to that observed in other quantum system such as CdSe QDs reported previously. [1] The deviation of small-sized QDs may result from the nonparabolicity of the optical bands at higher energy and the finite potential barrier at the particle surface.

The Stokes shift between the absorption and emission maximum is very small for CdSe and CdTe QDs due to the combination of relaxation into shallow trap states.[44] For $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs in our work, the Stokes shift of 10-20 nm is observed in the PL and absorption maximum as a function of the QDs diameter shown in Fig.S2 (Supporting Information). Such a small Stokes shift reveals the emission of the perovskite QDs is a direct exciton recombination process with comparably less energy loss, which has been confirmed by the time-resolved PL decay spectra reported previously.[15, 28] In addition, PLQYs is an important parameter to evaluate the optical intensity of the semiconductor QDs, herein, the absolute PLQYs of the different-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs were measured by a fluorescence spectrometer equipped with an integrating sphere at room temperature. The absolute PLQYs of the different-sized QDs (shown in Fig.5B) were measured from 10.4% (1.6 nm-sized QDs) to 78.8% (3.3 nm-sized QDs), which is comparable to the value reported previously.[45] Generally, the PLQYs of perovskite QDs are in close associated with the synergistic effects of the large exciton binding energy and the chemical

passivations of Br-rich surface when the size is comparable with or less than the exciton Bohr diameter.[15] As compared to the PLQYs of 3.9 nm-sized QDs, the PLQYs of 3.3 nm-sized QDs are enhanced, which may arise from an increase of the exciton binding energy, resulting in the formation of more stable exciton in QDs at room temperature and the radiative recombination of excitons increasing [35, 36]. However, with the size is further decreased to 1.6 nm, the PLQYs of QDs are reduced greatly. As is known to all, most of nanomaterials contain under-coordinated ions on their surface and also at the grain boundaries between individual crystals, and the density of the defects would increase with a decrease of the size, leading to the decrease of PLQYs of semiconductor QDs [36]. Therefore, we propose that a similar effect takes place upon reducing the size of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs. Herein, the number of under-coordinated Br ions may be increased when the size of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs is reduced for the perovskite QDs with Br-rich surface. Consequently, these under-coordinated Br ions on the surface of the QDs would act as trap states in the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, leading to an increase of nonradiative recombination rates, thus the PLQYs of QDs would be decreased with the reducing size [46,47]

3.3 Stability of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite QDs

The stability of the perovskite QDs is one of the most concerned aspects, which has become one of the research spots for exploring the applications of perovskites in optoelectronic devices. To study the stability of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, the as-obtained QDs were dispersed in toluene and stored in a quartz cell, which was placed under the dark at room temperature, and the PL spectra of the QDs were measured when they were exposed in air for different days. Herein, we take $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs with a mean diameter of 3.3 nm as an example, and the PL intensity variation as a function of exposure time in air is given in Fig.6A, and the inset shows the evolution of the PL spectra after exposure in air for different days. After 10 days, only less than 10% decrease of PL intensity is detected, and the PL peak position and the emission linewidths are almost unchanged. However, the PL

intensity is decreased to 67% of the original intensity after exposure in air for 30 days. Moreover, in accompany with the decrease of the PL intensity, a slight red-shift of the PL maximum and the broadening of the PL band width is also observed, which may arise from the size variation. To further confirm this deduction, TEM images of the QDs after exposure in air for 1 day and 30 days are depicted in Fig. 6B and C, respectively. Based on the statistical results of 100 particles, the average diameter of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs is increased from 3.3 to 3.7 nm, and the size deviation is increased from 12% to 30% (Fig.S3 of Supporting Information), which is responsible for the broadening of the emission linewidths and red-shift of the PL maximum.

3.4 Compositional-tunable optical properties of perovskite QDs

To date, some reports have demonstrated that the optical properties of inorganic or organometal halide perovskite QDs can also be tuned by varying the types of halogen in the perovskite QDs through the anion exchange reactions or replacement of PbX_2 and $\text{CH}_3\text{NH}_3\text{X}$. [25,48] In our work, $\text{CH}_3\text{NH}_3\text{PbCl}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ QDs were obtained by using PbCl_2 , $\text{CH}_3\text{NH}_3\text{Cl}$ and PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$ to replace PbBr_2 , $\text{CH}_3\text{NH}_3\text{Br}$ while the molar ratio of $\text{CH}_3\text{NH}_3\text{X}$ to PbX_2 was ($\text{X}=\text{Cl}$ or I) kept 9.5:10. The absorption and PL spectra as well as the corresponding TEM images are presented in Fig.7. As shown in Fig.7A, the all Cl-substituted perovskite QDs display a sharp PL peak at 393 nm with a narrow FWHM of only 15 nm, and the absorption peak is located at 374 nm (3.3 eV), which is blue-shifted as compared to that of bulk $\text{CH}_3\text{NH}_3\text{PbCl}_3$ ($E_g=3.1$ eV), implying a quantum confinement effect.[49] The TEM image of $\text{CH}_3\text{NH}_3\text{PbCl}_3$ QDs shown in Fig.7C exhibits a very small spherical shape with a mean diameter of 1.9 ± 0.3 nm (Fig.S4A of Supporting Information). As to $\text{CH}_3\text{NH}_3\text{PbI}_3$ QDs, a sharp peak at 750 nm is observed and the FWHM value is up to 40 nm, and no distinct absorption peak is detected. The as-obtained products are spherical with a mean diameter of 2.8 ± 0.6 nm (Fig.S4B of Supporting Information). It should be noted that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ QDs is very sensitive to air and the PL intensity is decreased quickly after exposure to air for several hours. Such a quick decrease of PL intensity has been also observed in the bulk $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, which is attributed

to the distorted crystal structure.[50]

Mixed-halide perovskite QDs including $\text{CH}_3\text{NH}_3\text{PbCl}_{3-x}\text{Br}_x$ and $\text{CH}_3\text{NH}_3\text{PbBr}_x\text{I}_{3-x}$ ($x=1\sim3$) can be easily synthesized by tuning the molar ratios of PbX_2 salts. Fig.8 depicts the absorption and PL spectra as well as the digital pictures of the $\text{CH}_3\text{NH}_3\text{PbCl}_{3-x}\text{Br}_x$ ($x=1.5, 1$) and $\text{CH}_3\text{NH}_3\text{PbBr}_x\text{I}_{3-x}$ ($x=3, 2, 1.5$ and 1) QDs dispersed in toluene before and after under 365 nm illumination. As shown in Fig.8A and B, the absorption peak shifts from 435 to 639 nm and the PL maximum shifts from 447 to 669 nm by adjusting the types of halogen from Cl to I, and the corresponding absorption peak becomes less distinct. The emission linewidths of the mixed perovskite QDs range from 30 nm to 50 nm, which are larger than that of $\text{CH}_3\text{NH}_3\text{PbX}_3$. The mixed perovskite QDs also have a spherical shape with a narrow size distribution (Fig.S5 of Supporting Information). The emission color can be tuned from ultraviolet blue to red by manipulating the ratios of halogen in the mixed QDs (Fig.8C).

4. Conclusion

In summary, bright size-tunable $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs were synthesized through controlling the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}_3$ to PbBr_2 while the total amount of OTAm and $\text{CH}_3\text{NH}_3\text{Br}$ were kept unchanged. The size-tunability is in close association with the number of Br ions on the surface. Due to the quantum confinement effects, the emission color could be readily tunable from deep-blue to green and the emission spectra was tuned from 440 to 530 nm, and the PL spectra of Br-rich perovskite QDs were characterized by the narrow emission linewidths of 20-32 nm and the small Stokes shift. As for the PLQYs, the highest absolute PLQYs could reach up to nearly 80%, and the variation of the PLQYs with the tunable size was in close association with the Br-rich surface. Moreover, $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X=\text{Cl}, \text{I}$) and mixed perovskite QDs including Cl/Br and Br/I systems were synthesized via such a surfactant-assisted reprecipitation route, which exhibited a spherical shape with a narrow size distribution, and the emission spectra covered the entire visible spectral region from 390-750 nm. These optical characteristics of the organometal halide perovskite QDs are

comparable with the classical semiconductor QDs such as CdSe and CdTe, thus the perovskite QDs may be an alternative to CdSe or CdTe QDs. The excellent optical properties make organometal halide perovskite QDs have wide potential applications in optoelectronic devices.

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Figure captions

Fig. 1. Schematic illustration for the formation of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs: (A) Free-standing layered precursor solution; (B) Structure of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs.

Fig. 2. (A-F) TEM images of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs synthesized by using different molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 : (A)5:10, (B)6:10, (C)8:10, (D)9:10, (E)9.5:10 and (F)9.9:10; (G) The mean diameter versus the molar ratios of $\text{CH}_3\text{NH}_3\text{Br}/\text{PbBr}_2$. The scale bar in all the TEM images is 30 nm.

Fig. 3. (A) EDX spectrum and (B) XRD pattern of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs with a mean diameter of 3.3 ± 0.4 nm.

Fig. 4. (A) Digital photos of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs dispersed in toluene under illumination of 365 nm, and the corresponding (B) absorption and (C) PL spectra. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs were synthesized by using different molar ratios of $\text{CH}_3\text{NH}_3\text{Br}$ to PbBr_2 : (a) 5:10; (b) 6:10; (c) 7:10; (d) 8:10; (e) 9:10; (f) 9.3:10; (g) 9.5:10; (h) 9.7:10 and (i) 9.9:10.

Fig. 5. (A) Comparison between the experimental and theoretical fitting results of different-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs perovskite QDs in the diameter range of 1.6-3.9 nm; (B) Absolute PLQYs of different-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs.

Fig. 6. (A) PL intensity variation of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs versus the exposure time to air, and the inset shows the PL spectra of the QDs measured after exposure to air for different days; TEM images of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs measured after exposure in air for (B) 1 day and (C) 30 days.

Fig. 7. Absorption (open circle) and PL (closed circle) spectra as well as the TEM images of perovskite QDs: (A, C) $\text{CH}_3\text{NH}_3\text{PbCl}_3$; (B, D) $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Fig. 8. (A) Absorption and (B) PL spectra of composition-tunable $\text{CH}_3\text{NH}_3\text{PbX}_3$ QDs as well as (C) the digital pictures of the colloidal QDs dispersed in toluene before and after illumination under 365 nm light: (a) $\text{CH}_3\text{NH}_3\text{PbCl}_{1.5}\text{Br}_{1.5}$; (b) $\text{CH}_3\text{NH}_3\text{PbClBr}_2$; (c) $\text{CH}_3\text{NH}_3\text{PbBr}_3$; (d) $\text{CH}_3\text{NH}_3\text{PbBr}_2\text{I}$; (e) $\text{CH}_3\text{NH}_3\text{PbBr}_{1.5}\text{I}_{1.5}$; (f) $\text{CH}_3\text{NH}_3\text{PbBrI}_2$.

Figure.1

Figure.2

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