Study on MA(Pb, Cu)Br₃ Perovskite Nanocrystal with Both Controlled Color Emission and Improved Stability

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Abstract

Organic-inorganic hybrid perovskite quantum dots have always been the focus of research in recent years. However, the toxic Pb²⁺ in MAPbBr₃ (MA = CH₃NH₃⁺) quantum dots and low stability restrict the application in the field of lighting display. In order to solve this problem, the MA(Pb,Cu)Br₃ perovskite quantum dots with Pb²⁺ replaced by non-toxic Cu²⁺ were synthesized via the auxiliary ligand precipitation. The phase evolution, controlled-color and fluorescent properties were systematically studied. The photoluminescence (PL) spectra monitored at the wavelength of 400 nm showed that the fluorescence emission intensity of quantum dots gradually decreased with the increase of the concentration of Cu²⁺, and the phenomenon of blue shift appeared. Moreover, the decay lifetime decreased when the dopant concentration of Cu²⁺ gradually increased. The influence mechanism was discussed in details. In order to improve the stability, the MA(Pb, Cu)Br₃@SiO₂ quantum dots were prepared by the hydrolysis of tetramethyl orthosilicate (TMOS). Meanwhile, the effect of temperature on the fluorescence properties of quantum dots was investigated in detail. The high stability and low toxicity of the MA(Pb, Cu)Br₃@SiO₂ quantum dots are expected to be used in the fields of lighting display and solar cells.

Keywords: Organic-inorganic hybrid perovskite quantum dots; Low toxic; Water-stability; Luminescent property.

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1. Introduction

Organic-inorganic hybrid perovskite shows the great potential in luminescence by altering the formation of constituent ions and mixtures to fine-tune the properties of materials.^[1-3] Due to its excellent optoelectronic properties, such as narrow half peak width,^[4] high photoluminescence quantum yield,^[5] high carrier mobility and band tenability,^[6,7] etc., the organic-inorganic hybrid perovskite quantum dots have been widely studied in the field of solar cell, display and laser.^[8-10] As the main ingredient in perovskite quantum dots, the toxicity of Pb²⁺ seriously limits the practical application of perovskite in the field of optoelectronics.^[11-13] Therefore, replacing Pb²⁺ with non-toxic metal ions is an important measure to reduce the toxicity of perovskite quantum dots, and the Cu²⁺ is selected as alternative metal cations to develop a new luminescent

material in this paper.^[14,15]

With the doping concentration of Cu²⁺ increases significantly, the tolerance factor value increases in the octahedral structure of quantum dots, indicating that this organic-inorganic hybrid perovskite possesses stabilized internal structures. Furthermore, the radiation recombination of electrons in the conduction band and the holes have overlapped with T₂ level of Cu²⁺,^[16,17] and thus the color of Cu²⁺ doped quantum dots can be controlled with changing the proportion of Cu²⁺ and Pb²⁺. However, it is difficult for the divalent transition metal cation to be doped in the perovskite quantum dots. The luminous intensity is sharply reduced due to the lattice distortion of [PbX₆]⁴⁻ octahedral with increasing the doping concentration of metal ions.^[18,19] Therefore, it is particularly important to study the synthesis process of MA(Pb,Cu)Br₃ quantum dots.

To address the above mentioned challenges, the MA(Pb,Cu)Br₃ quantum dots have been synthesized via the auxiliary ligand precipitation in this paper. In order to improve the stability and water solubility of quantum dots, the SiO₂ coating method was adopted to change the poor water solubility of MA(Pb,Cu)Br₃.^[20,21] Finally, the phase

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evolution, controlled-color and fluorescent properties of $\text{MA}(\text{Pb,Cu})\text{Br}_3$ and $\text{MA}(\text{Pb,Cu})\text{Br}_3/\text{SiO}_2$ quantum dots were systematically studied by various instruments including X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence (PL), UV-vis and fluorescence decay analysis.

2. Experiment procedure

2.1 Materials

In a study, hydrobromic acid (HBr, 40%, McLean), methylammonium solution (CH_3NH_2 , 99.7%, traditional Pharmaceutical Group Chemical Reagent Co., Ltd.), anhydrous methanol (CH_3OH , 99.7%, McLean), lead bromide (PbBr_2 , 99.999%, McLean), copper bromide (CuBr_2 , 99.9%, McLean), N, N-dimethyl formamide (DMF, 99%, Tianjin Fuyu Fine Chemical Co., Ltd.), oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$, 90%, McLean), octylamine ($\text{C}_8\text{H}_{19}\text{N}$, 99%, McLean), tetramethoxysilane ($\text{C}_4\text{H}_{12}\text{O}_4\text{Si}$, 95%, McLean), toluene (C_7H_8 , 99.5%, Yantai Far East Fine Chemical Co., Ltd.), and acetone (CH_3COCH_3 , AR, McLean), etc were used without any further purification.

2.2 Preparation procedure

2.2.1 Synthesis of MABr precursor

Methylamine alcohol solution (17.4 mL) was added to methanol (30 mL) for dilution in 100 mL three-mouthed flask. The mixture was cooled to 0–5 °C while the hydrobromic acid (13.6 mL) was mixed at the rate of 0.5 mL/min. The mixture solution continually reacted for 2 h in the same environment. After the reaction was over, the target products were removed from the mixture solutions by rotary evaporation. Lastly, the depositions were washed repeatedly three times using methanol and acetone, and dried at 80 °C for 24 h to obtain white products.

2.2.2 Synthesis of $\text{MA}(\text{Pb,Cu})\text{Br}_3$ quantum dots

The methylamine salt, PbBr_2 and CuBr_2 were mixed as the mother salt according to the chemical formula of $\text{MA}(\text{Pb}_{1-x}\text{Cu}_x)\text{Br}_3$, and dissolved in DMF with a total volume of 5 mL. Then, 20 μL octylamine and 0.5 mL oleic acid were added and stirred fully to form the precursor solution. After that, 1 mL of the precursor solution was rapidly injected into 10 mL of toluene solution and vigorously stirred to obtain quantum dots solution. Finally, the colloidal solution was centrifuged at the speed of 8000 rpm/s for 5 min, and washed repeatedly with toluene to remove the by-products, and finally the solution of $\text{MA}(\text{Pb,Cu})\text{Br}_3$ quantum dots was obtained.

2.2.3 Synthesis of $\text{MA}(\text{Pb,Cu})\text{Br}_3/\text{SiO}_2$ quantum dots

Tetramethyl orthosilicate (TMOS, 120 μL) was added into 25 mL bottle which contained 15 mL of the $\text{MA}(\text{Pb,Cu})\text{Br}_3$ perovskite quantum dots toluene solution. The mixture solution was stirred for 5 min at room temperature. After

that, the bottle was put on a light-shielded environment at room temperature, and stirred for 48 h. After the reaction was over, the target products were obtained from the mixture solutions by centrifugation. Lastly, the depositions were washed thrice with acetone, and dried at 80 °C for 24 h to obtain the yellow products.

2.3. Characterization

The phase composition analyses were performed by XRD. And the patterns were recorded at room temperature using nickel-filtered $\text{Cu K}\alpha$ radiation in the 2θ range 10–50° at a scanning speed of 4.0° $2\theta/\text{min}$ (Model D8 ADVANCE, BRUKER Co., Germany). The morphology of resultant products was collected via the HR-transmission electron microscope (HR-TEM, JEM-2100F, JEOL, Japan). The UV-vis absorption spectra were performed by UV-vis spectrophotometer (UV-3600, Shimadzu Corporation). The photoluminescence (PL) spectra were obtained using a Fluorescence Spectrophotometer (FP-6500, JASCO Co., Japan) at room temperature equipped with a $\Phi 60\text{-mm}$ integrating sphere (ISF-513, JASCO, Tokyo, Japan) and a picosecond laser/diode was used as the excitation source. The optical performances for all samples were conducted under identical conditions with the slit breadth of 5 nm. The sample was excited with a selected wavelength and the intensity of the intended emission was recorded as a function of elapsed time after the excitation light was automatically cut-off.

3. Results and discussion

Fig. 1(a–f) shows the TEM images of $\text{MA}(\text{Pb,Cu})\text{Br}_3$ perovskite quantum dots with different concentrations of Cu^{2+} . It can be seen that the $\text{MA}(\text{Pb,Cu})\text{Br}_3$ perovskite quantum dots possess nanosphere morphologies with a good dispersion compared with the MAPbBr_3 perovskite quantum dots from Fig. 1(g), and the average size is ~ 6 nm. As shown in the inset of Fig. 1(a), the HR-TEM micrograph of nanospheres $\text{MA}(\text{Pb,Cu})\text{Br}_3$ perovskite quantum dots indicates that the interplanar spacing of $\text{MA}(\text{Pb,Cu})\text{Br}_3$ perovskite quantum dots is ~ 0.253 nm, which corresponds to the (210) lattice plane.

The XRD patterns of $\text{MA}(\text{Pb,Cu})\text{Br}_3$ quantum dots with different doping concentrations of Cu^{2+} are shown in Fig. 1(h). The results show the similar diffraction peaks of (100), (110), (200), (210) and (300) to the XRD diffraction behavior of MAPbBr_3 quantum dots in published reports^[22–24] indicated that the doping of Cu^{2+} has no effect on the crystal phase structure of the quantum dots. Furthermore, the strong diffraction peaks of (100) and (200) drift towards high angles with gradually increasing the doping concentrations of Cu^{2+} . The lattice shrinkage of quantum dots increases with increasing the concentrations of Cu^{2+} , owing to the smaller radius of Cu^{2+} (0.073 Å) than that of Pb^{2+} (0.119 Å).

The PL spectra and UV-vis spectra of $\text{MA}(\text{Pb,Cu})\text{Br}_3$

quantum dots with different concentrations of Cu^{2+} are depicted in Fig. 2(a) and 2(b), respectively. As marked in the figure, the $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ perovskite quantum dots exhibit green emission (~ 525 nm) monitoring at 400 nm excitation. The fluorescence intensity decreases with changing the doping concentration of Cu^{2+} from 0.1 to 0.6. Moreover, the luminescence peak exhibited a slight blue shift from 528 to 515 nm with increasing the concentration of Cu^{2+} . The lattice shrinkage of $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ perovskite quantum dots can be ascribed to the smaller radius of Cu^{2+} than that of Pb^{2+} . Furthermore, the lattice shrinkage of $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ perovskite quantum dots is attributed to the shortened Pb-halide bond and a stronger ligand field within the $[\text{PbX}_6]^{4-}$ octahedral. Meanwhile, this phenomenon of blue shift can also be seen in Fig. 2(b), and is similar to the result of PL spectra. In addition, the wide absorption peaks at 650–800 nm are vest in the absorption of Cu^{2+} ions, which may be from the Cu^{2+} ions in a quantum dot solution that is not completely purified. [25]

In order to further study its fluorescence properties, the Commission International de L'Eclairage (CIE) chromaticity coordinates for the emission of the $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ perovskite quantum dots under 400 nm excitation are shown

in Fig. 3(a). The $\text{MA}(\text{Pb}_{1-x}\text{Cu}_x)\text{Br}_3$ perovskite quantum dots are analyzed to have color coordinates (x, y) of (~ 0.15 , ~ 0.75), (~ 0.15 , ~ 0.74), (~ 0.13 , ~ 0.73), (~ 0.14 , ~ 0.69), (~ 0.16 , ~ 0.65), and (~ 0.14 , ~ 0.61) with the temperature of ~ 8117 K, ~ 8171 K, ~ 8579 K, ~ 8673 K, ~ 8573 K and ~ 9397 K for $x=0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6 , respectively, which prove the results of emission peaks in Fig. 3(a). Fig. 3(b) shows the fluorescence decay curve of $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ perovskite quantum dots. It was found that the decay data can be well fitted with the following double exponential equation in each case:

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + B \quad (1)$$

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

where I is the luminescence intensity at a certain moment, t is the time, A_1 , A_2 and B are constant, τ_1 and τ_2 show the time with the luminescence intensity rapidly and slowly weaken, respectively. Among them, the A_1 , A_2 , B , τ_1 and τ_2 are obtained from the double exponential fitting curve, and the effective decay time (τ) is calculated by

Fig. 1 (a-f) the TEM morphologies of $\text{MAPbBr}_3: x\text{Cu}^{2+}$ ($x=0.1-0.6$) quantum dots, and **Fig. 1(g)** TEM morphologies of MAPbBr_3 quantum dots. The inset of **Fig. 1(a)** shows the HR-TEM micrograph of $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ perovskite quantum dots; and **Fig. 1(h)** the XRD patterns of $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ perovskite quantum dots with different concentrations of Cu^{2+} ($x=0-0.6$).

Fig. 2. (a) The PL spectra of $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ quantum dots with different concentrations of Cu^{2+} monitoring at 400 nm, and (b) the UV-vis spectra of $\text{MA}(\text{Pb}, \text{Cu})\text{Br}_3$ quantum dots with different concentrations of Cu^{2+} ($x=0.1-0.6$).

Fig. 3. (a) the CIE coordinates of MA(Pb,Cu)Br₃ quantum dots with different concentrations ($x=0.1-0.6$); (b) the fluorescence decay curves of MA(Pb,Cu)Br₃ quantum dots monitored at emission wavelength of 400 nm with the concentrations of Cu²⁺ increase from 0.1 to 0.6, and the embedded curve shows the decay times curve changing of MA(Pb,Cu)Br₃ quantum dots.

formula (2).^[26-28] From Fig. 3(b), it can be seen that the fluorescence lifetime of MA(Pb, Cu)Br₃ quantum dots is 19.91-2.71 ns when the doping concentration of Cu²⁺ change from 10 to 60 at.%, which is similar to the published results.^[29,30] Fig. 3(b) shows the decay time curve changing of MA(Pb, Cu)Br₃ quantum dots. From which can be seen that the fluorescence lifetime gradually decreases with the increase of the doping concentration of Cu²⁺. The reason can be explained that the surface defects of MAPbBr₃ quantum dots increase with gradually increasing the doping concentration of Cu²⁺. Moreover, the stability of the [PbX₆]⁴⁻ octahedral in MA(Pb, Cu)Br₃ perovskite quantum dots becomes worse when the Cu²⁺ gradually replaces Pb²⁺. The above two reasons lead to the decrease of quantum dot lifetime.

The poor stability of perovskite quantum dots seriously limits the application as luminescent materials, when they are dispersed into strong polar solvent (such as water and alcoholic solution).^[31-34] SiO₂ is a more important shell structure in the coating material at present. The material is coated by the principle of hydrolysis of tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) with water to form SiO₂ shell. Based on this, the MA(Pb,Cu)Br₃@SiO₂ perovskite quantum dots were successfully obtained (depicted in the inset of Fig. 4a) via the slow hydrolysis of TMOS in toluene for 48 h and then dried in vacuum for 24 h. Fig. 4(a) shows the TEM morphologies of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ perovskite quantum dots phosphor exhibiting the spherical morphologies is ~200 nm, and larger than the size of MA(Pb,Cu)Br₃ quantum dots (~6 nm). To further analyze the coating of quantum dots, the HR-TEM morphology analysis of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ quantum dots with nanospheres is shown in Fig. 4(b), from which it can be seen that the interplanar spacing of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂

quantum dots is ~0.285 nm (the inset of Fig. 4b) corresponding to the (200) lattice plane, and the MA(Pb,Cu)Br₃ quantum dots are embedded in SiO₂ shell. Therefore, the quantum dots wrapped by SiO₂ shell will improve water-stability.

Fig. 4. (a) TEM images of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ perovskite quantum dots, and the inset of Fig. 4(a) is the digital image of the MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ perovskite quantum dots phosphor under 365 nm UV excitation from a hand-held UV lamp; the HR-TEM micrograph of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ perovskite quantum dots is shown in Fig. 4(b), and the inset of Fig. 4(b) is the partial enlarged drawing of Fig. 4(b).

In order to further investigate the fluorescence attenuation behavior of the quantum dots in the mixed solution of toluene and water (4:1), the PL behaviors of the MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ and MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots are shown in Fig. 5(a) and 5(b), respectively. It can be seen that the green emissions of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ and MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots are depicted in PL spectra with the emission bands located at ~525 and ~523 nm, respectively, and the PL intensity decreases over the exposure period. However, the phenomenon has been discovered that the quenching rate of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ quantum dots is slower than that of the MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots by contrasting MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ and MA(Pb_{0.8}Cu_{0.2})Br₃ quantum

dots. From Fig. 5(c), the fluorescence quenching is observed in the MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots after 16 hours, while MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ quantum dots maintain 40% of the original fluorescence intensity after 36 hours. This is further proved that the SiO₂ shell coated on the surface of the MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dot can protect the quantum dots better, and then improves the water stability and water solubility of the quantum dots effectively. In addition, the full-width half-maximum of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ quantum dots (~28 nm) increases compared with that of MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots (~23 nm) from Fig. 2(a), which is mainly due to the aggregation of quantum dots as the coating proceeds. Fig. 5(d) shows the XRD contrast patterns of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ and MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots. From this, it can be seen that the crystal diffraction of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ quantum dots appears at (100), (110), (200), (210) and (300) comparing to MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots, which match the crystal phase of MAPbBr₃ quantum dots in Fig. 1(h).^[22-24] The wide peaks at range of 15°-35° are attributed to the unformed silica. Therefore, the result certifies the success of SiO₂ coating.

The temperature-dependent PL spectra for MA(Pb, Cu)Br₃ perovskite quantum dots are shown in Fig. 6(a). It can be seen that the emission intensity gradually decreases with the increase of temperature from 60 to 300 K, and the

half-maximum of the sample increases gradually. The lattice shrinkage of sample caused by thermal expansion is severe when the temperature is set to 60 K, and the lattices of sample expand with increasing the temperature which led to the increased half-maximum. Furthermore, as the temperature rises from 60 to 100 K, the reduction of the emission intensity is not obvious. As the temperature increases from 100 to 300 K, the fluorescence emission peaks of MA(Pb, Cu)Br₃ perovskite quantum dots show an obvious blue shift from about 560 to 540 nm which is due to the conversion from bound exciton to free exciton, and the emission of bound exciton was inhibited. Then, the blue shift of the emission peaks occurred. These phenomena are consistent with the temperature-dependent of CdSe and PbS quantum dots.^[35,36]

In order to further discuss the thermal quenching, the results can be explained by Arrhenius equation:^[37]

$$\ln\left(\frac{I_0}{I} - 1\right) = \ln A - \frac{E_a}{kT} \quad (3)$$

where E_a , T , A and k refer to activation energy, temperature (K), constant and Boltzmann constant, respectively. The I_0 and I represent the emission intensity at room temperature and operating temperature, respectively. The relationship between $\ln(I_0/I - 1)$ and $1/kT$ for the thermal quenching of MA(Pb, Cu)Br₃ perovskite quantum dots is

Fig. 5. the PL spectra of the MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ (a) and MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots (b) which are dispersed in the mixed solution of water and toluene, and the proportion of water and toluene is 1:4; (c) is the luminescence intensity comparison diagram of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ and MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots, and (d) is the XRD comparison diagram of MA(Pb_{0.8}Cu_{0.2})Br₃@SiO₂ and MA(Pb_{0.8}Cu_{0.2})Br₃ quantum dots.

Fig. 6. (a) the PL spectra of MA(Pb,Cu)Br₃ perovskite quantum dots as a function of temperature; (b) the relationship between $\ln(I_0/I-1)$ and $1/kT$ for the thermal quenching of MA(Pb,Cu)Br₃ perovskite quantum dots.

depicted in Fig. 6(b). It can be seen that the slope of fitting curve is -0.049, and thus the E_a can be calculated to be 0.049 eV via Equation (3). The good low temperature stability of MA(Pb, Cu) Br₃ perovskite quantum dots is expected to be widely used in the complex environment in the future.

4. Conclusions

In general, the hypotoxic MA(Pb, Cu)Br₃ perovskite quantum dots have been synthesized via the auxiliary ligand precipitation method. In order to improve the water stability of MA(Pb, Cu)Br₃ perovskite quantum dots, the MA(Pb, Cu)Br₃@SiO₂ quantum dots were obtained by the hydrolysis of TMOS. The conclusions can be summarized as follows:

(1) The color-controlled and hypotonic MA(Pb,Cu)Br₃ perovskite quantum dots were obtained with different concentrations of Cu²⁺. The blue shift of the PL emission peaks and ultraviolet absorption peaks occurred, and the lifetimes decreased gradually with changing the doping concentration of Cu²⁺ from 10 to 60 at.%. These phenomena were derived from the quantum size effect and surface effect.

(2) In order to further improve the quenching behavior of the MA(Pb, Cu)Br₃ perovskite quantum dots in the mixed solution of toluene and water (4:1), the MA(Pb, Cu)Br₃@SiO₂ quantum dots were obtained by the hydrolysis of TMOS. Compared to the MA(Pb, Cu)Br₃ quantum dots, the water-stability of MA(Pb, Cu)Br₃@SiO₂ was obviously improved. The improvements in the stability were attributed to the SiO₂ shell protecting to avoid contact between quantum dots and the environment.

(3) The fluorescence properties of the MA(Pb, Cu)Br₃ perovskite quantum dots manifested as stronger temperature dependence, which is expected to be widely used in the field of temperature sensors.^[38,39]

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Supporting information

Not applicable

Conflict of interest

There are no conflicts to declare.

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