Electronic Supporting Information (ESI)

Lead-Free Silver-Antimony Halide Double Perovskite Quantum Dots With Superior Blue Photoluminescence

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Chemicals.

All reagents were used without further purification: CsCl (99.99%, Aladdin), AgCl (99.5%, Macklin), $SbCl_3$ (99.99%, Aladdin), CsBr (99.9%, Meryer), AgBr (99.5%, Alfa Aesar), $SbBr_3$ (99.99%, Aladdin), CsI(99.999%, Aladdin), AgI (99%, Aladdin), SbI_3 (99.999%, J&K Chemical), oleic acid (OA, 90%, SigmaAldrich), ethyl acetate (99.7%, Macklin), dimethylsulfoxide (DMSO,>99.8%, Aladdin), n-octane (96%, Macklin), acetone (AR, Shanghai Lingfeng)

Synthesis of Cs_2AgSbX_6 (X=Cl, Br, I) perovskite QDs.

Colloidal Cs_2AgSbX_6 perovskite QDs were fabricated following the ligand-assisted reprecipitation (LARP) technique, which could be briefly described as following. In a typical synthesis of $Cs_2AgSbCl_6$ perovskite QDs, 0.2 mmol of CsCl, 0.1 mmol of AgCl and 0.1 mmol of $SbCl_3$ were completely dissolved in 5 mL DMSO forming the transparent precursor solution. For the ligand-free $Cs_2AgSbCl_6$ perovskite QDs, 500 μL precursors was injected to the 10 ml ethyl acetate under vigorous stirring at room temperature. To synthesize oleic acid (OA) capped QDs, varying amounts of OA were added to the anti-solvent. For example, the preparation of 1% OA sample was in a mixed solution consist of 100 μL OA and 10 mL ethyl acetate, where 500 μL of the precursors were then added into it with vigorous stirring. In just a few minutes, followed by centrifugation at 5000 rpm for 3-5 minutes to discard the precipitate containing large particles, a pale yellow and white colloidal solution can be obtained. We have also tried some other common surfactants such as octylamine, oleylamine and tri-n-octylphosphine, which unfortunately failed to improve PL. Particularly, after the addition of the amine, the precursor turned to white and cloudy, and the actual composition of the final product also changed (as shown in Fig. S1). For the synthesis of $Cs_2AgSb(Cl_{0.5}Br_{0.5})_6$, $Cs_2AgSbBr_6$, $Cs_2AgSb(Br_{0.5}I_{0.5})_6$ and Cs_2AgSbI_6 QDs, the method is similar to the above synthesis procedure of $Cs_2AgSbCl_6$ QDs. The reactant source of metal halide salts (CsX, AgX and SbX_3) in different proportions formed a corresponding precursor solution for injection. Similarly, after the rapid recrystallization process, the crude solution was centrifuged to discard large crystals.The powder of Cs_2AgSbX_6 perovskites used for further structural characterization can be obtained by centrifugation at 8000 rpm for 5 minutes washing with a mixture of n-octane and acetone, and dried overnight in a vacuum oven at 60℃.

During the synthesis process, moderate solvent with low polarity were able to avoid suppressing degradation of ionic nanocrystals.[1] Although a series of common organic solvents for the perovskite nanomaterials in LARP method reported before were tried, it has been found that only using toluene and ethyl acetate can successfully acquire Cs_2AgSbX_6 QDs. Apparently, the latter was better for safe and green. Besides, the effect of reaction time on the fluorescence is negligible due to rapid nucleation and grain growth dynamic of intrinsic ionic properties, which is similar to the colloidal synthesis of Pb-based perovskites.

Characterization

Rigaku Smartlab (3) diffractometer was operated to collect X-Ray Diffraction (XRD) data at 40 kV and 40mAa, using a Cu Kα radiation source. X-ray Photoelectron Spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250XI machine (Thermo Fisher Scientific) with Al Kα as the X-ray source to analyze the chemical nature of $Cs2AgSbCl_6$ perovskite QDs. The results of Transmission Electron Microscopy (TEM) , High-Resolution Transmission Electron Microscopy (HRTEM) and Selected Area Electron Diffraction (SAED) were recorded using a JEM-2100 instrument. The steady-state absorption measurement of the as-synthesized QDs were performed on a Varian Cary 5000 UV−Vis near infrared (NIR) spectrophotometer. PL measurements were carried out using a Fluoromax-4 photoluminescence system. The samples were prepared as the homogeneous dispersed solutions in ethyl acetate by centrifugation to discard the large crystals. Time-resolved photoluminescence decays were performed with a FluoroLog-3 TCSPC (Horiba Jobin Yvon Inc) spectrofluorometer.

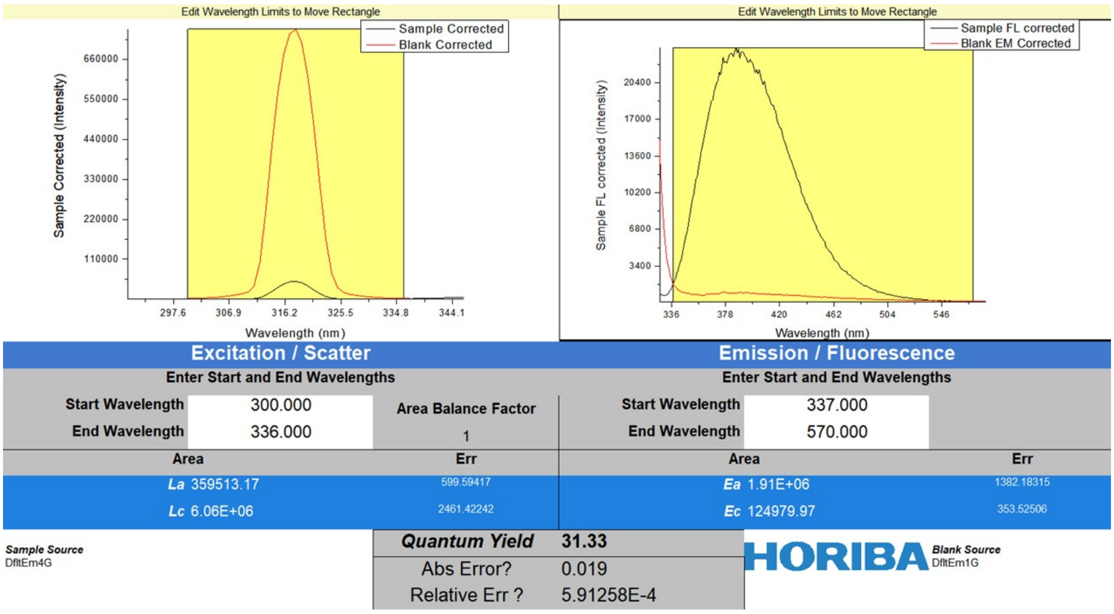
If B_1, B_2 are normalized coefficients and τ_1, τ_2 are the corresponding lifetime constants, the PL decay can be fitted with bi-exponentials:

$$\mathrm{decay}\,(t) = B_1 e^{t/\tau_1} + B_2 e^{t/\tau_2} \tag{1}$$

$$\mathrm{t}_{\mathrm{average}} = \frac{B_1\tau_1^2 + B_2\tau_2^2}{B_1\tau_1 + B_2\tau_2} \tag{2}$$

Photoluminescence Quantum Yield (PLQY) measurements

The absolute PLQY of $Cs_2AgSbCl_6$ QDs solutions were measured using FluoroLog-3 TCSPC (Horiba Jobin Yvon Inc) spectrofluorometer equipped with the integrating sphere. The samples for PLQY measurements were diluted in ethyl acetate in quartz cuvettes capped with white PTFE stoppers to protect from air before the measurements. A cuvette of the consistent volume of ethyl acetate was used as a reference blank. The results are shown in the figure below:



Excitation / Scatter

Enter Start and End Wavelengths

Start Wavelength 300.000

End Wavelength 336.000

Area Balance Factor 1

Area	Err
La 359513.17	599.59417
Lc 6.06E+06	2461.42242

Emission / Fluorescence

Enter Start and End Wavelengths

Start Wavelength 337.000

End Wavelength 570.000

Area	Err
Ea 1.91E+06	1382.18315
Ec 124979.97	353.52506

Sample Source DfltEm4G

Quantum Yield **31.33**

Abs Error? 0.019

Relative Err ? 5.91258E-4

Blank Source DfltEm1G

Fig. S1 PLQY measurements result of 4% OA-capped $Cs_2AgSbCl_6$ QDs colloidal solution.

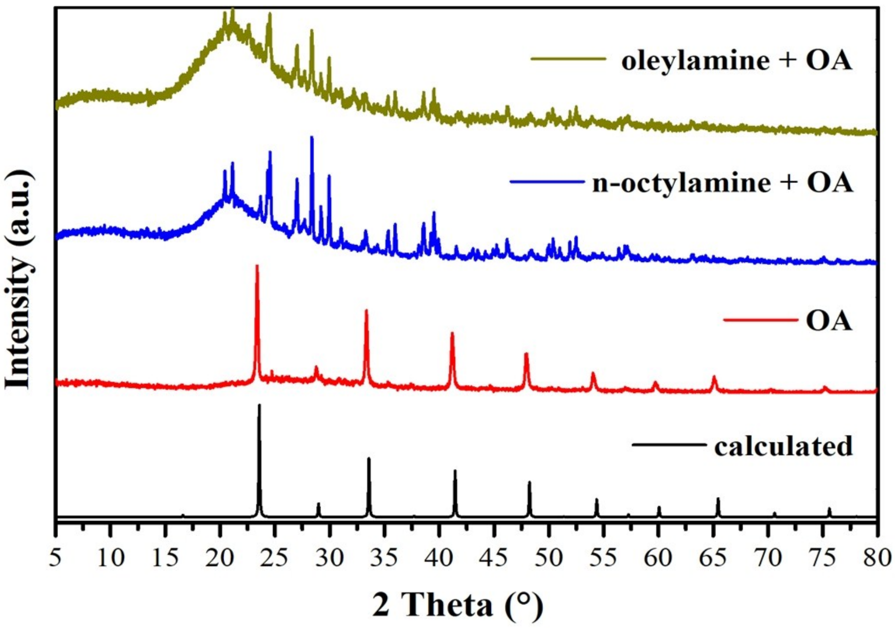


Fig. S2 XRD pattern of OA-capped $Cs_2AgSbCl_6$ obtained from precursor solution containing oleylamine, n-octylamine, and no-amine.

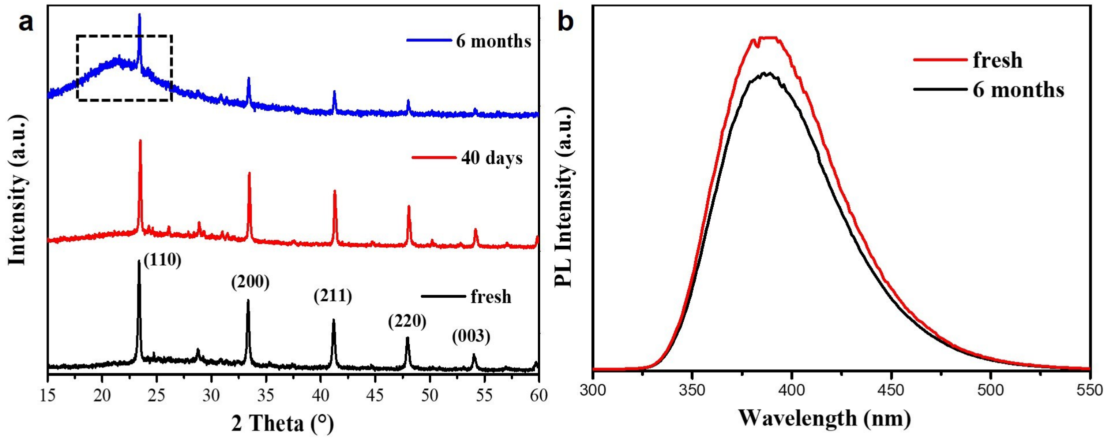


Fig. S3 (a) Air stability of washed $Cs_2AgSbCl_6$ powder stored in 55% humidity at 25 °C in the dark for 40 days and 6 months; (b) PL spectra of $Cs_2AgSbCl_6$ perovskites powder at different times re-dissolved in ethyl acetate.

The 6 months air stability of $Cs_2AgSbCl_6$ perovskites powder was obtained from the comparison XRD data at different period. Due to the loss of powder during the preservation, the bulge pattern in ~22° of the 6 months sample framed by the dotted line was attached to the glass substrate (silica) and the minute amount of $Cs_2AgSbCl_6$ perovskites powder. Besides the bulge part, the excellent air stability can be confirmed by the strong diffraction peaks and no obvious formation of impurity peaks of the 6-months XRD pattern.

We also compared the PL of two kind of perovskites powder at different times re-dissolved in ethyl acetate. One was the as-synthesized fresh $Cs_2AgSbCl_6$ Perovskites powder, and the other was the one exposed to the dark air for 6 months. We used the same method ensuring the same concentration, which 2 mg perovskite powder was dissolved in 5 ml ethyl acetate by sonication to make it evenly dispersed. The results showed that the fluorescence intensity of the solution with re-dissolved 6-months powder was only about 10% lower than the initial fresh one, which confirmed the stability of the $Cs_2AgSbCl_6$ perovskite convincingly.

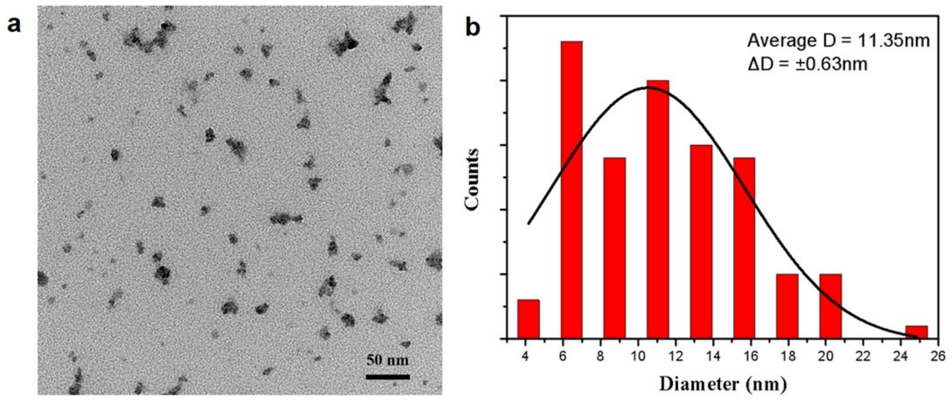


Fig. S4 TEM images of $Cs_2AgSbCl_6$ perovskite QDs without OA-capped.

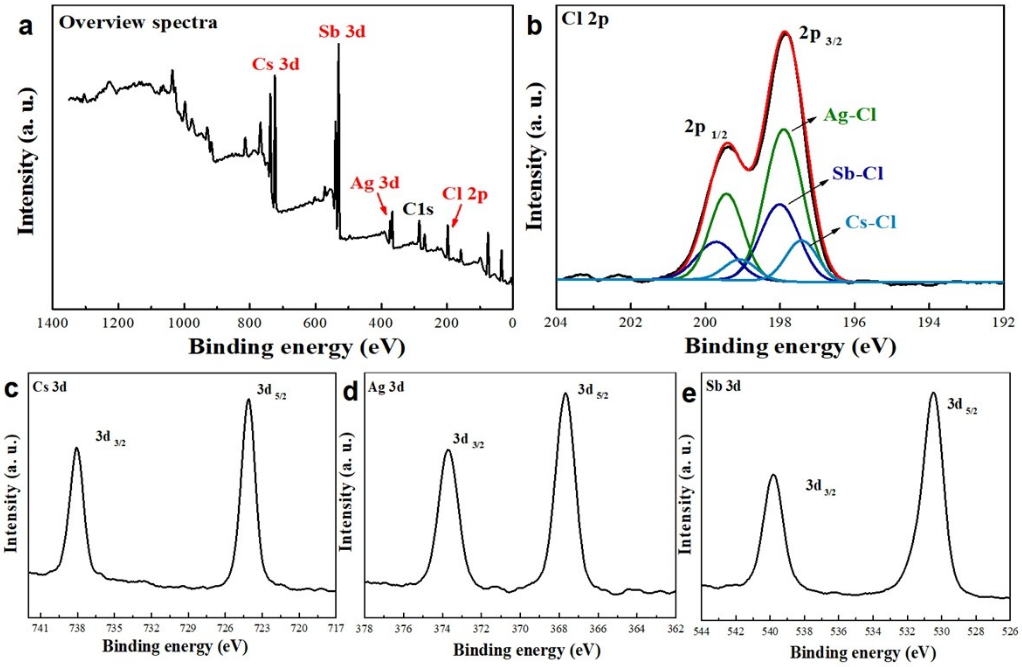


Fig. S5 X-ray photoelectron spectroscopy (XPS) patterns of $Cs_2AgSbCl_6$ QDs corresponding to (a) overview spectroscopy, (b) Cl 2p, (c) Cs 3d, (d) Ag 3d and (e)Sb 3d spectra.

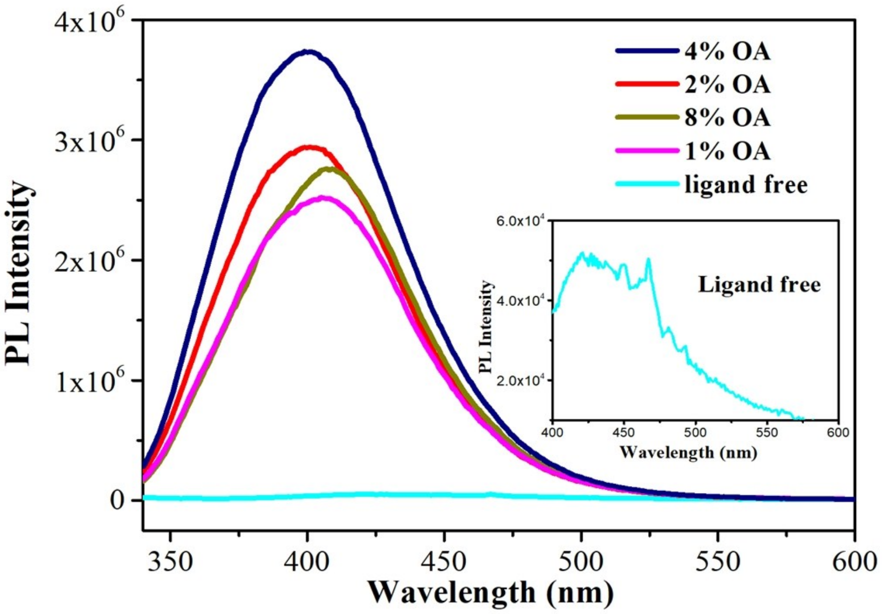


Fig. S6 PL spectra of ligand free and OA capped Cs2AgSbCl6 QDs. The optimum OA content is 4%, and the PL intensity can be increased by around 100 times compared to the ligand free QDs (Insert).

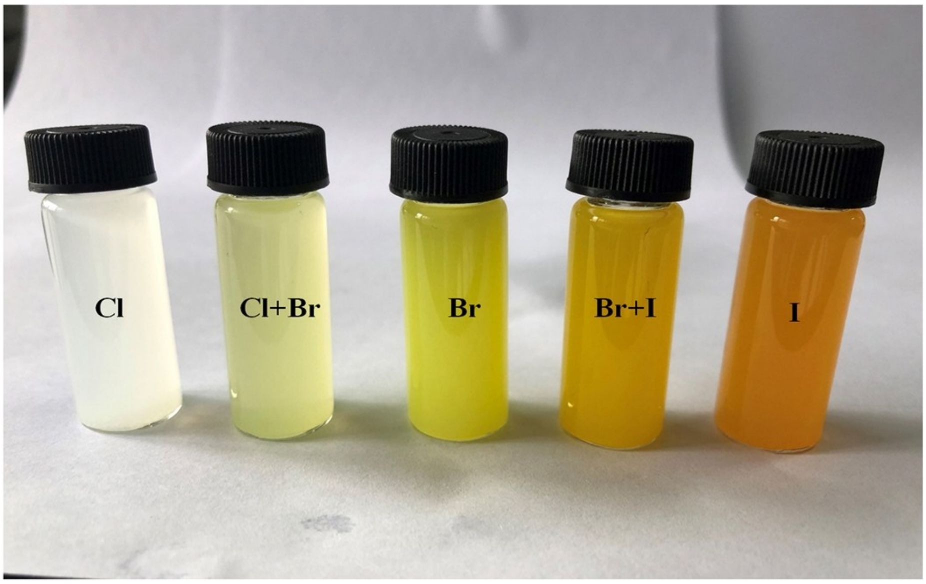


Fig. S7 Image of Cs_2AgSbX_6 QDs colloidal solution.

Table S1 quantitative analysis results of XPS.

Element	Peak BE/eV	FWHM/eV	Atomic/%
Cs 3d	724.12	1.35	20.67
Ag 3d	367.68	1.19	9.26
Sb 3d	530.49	1.43	27.16
Cl 2p	197.86	1.33	42.91

Table S2 Comparisons of all inorganic lead-free Perovskite nanomaterials.

Material	Synthetic Procedure	Emission Peak/nm	PLQY/%	Stability	Reference
$CsPb_XMn_{1-x}Cl_3$	hot injection,170 °C	579	54	3 months (ambient)	2
$CsSnBr_3$	hot injection,170 °C	660	0.14	5 months (ambient)	3
$Cs_3Bi_2Br_9$	LARP, 80 °C	410	19.4	78 hours, 80% (photo)	4
$Cs_3Sb_2Br_9$	LARP, RT	410	46	35 days,70% (air) 108 hours,50% (photo)	5
$CsPdBr_3$	LARP, RT	730	0.3	60 days (air) 45 days (photo)	6
$Cs_2AgBiCl_6$	LARP, RT hot injection, 200 °C	395	6.7	90 days (air), 500 hours (photo)	7, 8
$Cs_2AgInCl_6$	hot injection, 105 °C	395	1.6	2 days, 94% (air)	9
$Cs_2AgSbCl_6$	LARP, RT	409	31.33	6 months (ambient)	This work

Table S3 Optoelectronic properties comparisons of Bi-based and Sb-based perovskites.

Perovskites	Cs_2AgBiX_6			Cs_2AgSbX_6		
X sites	Cl	Br	I	Cl	Br	I
Phase Stability: Goldschmidt tolerance factor t ($0.75 < t < 1.0$)	√	√	√	√	√	√
Phase Stability: Octahedral factor c ($\mu > 0.41$)	√	√	×	√	√	√
Thermo-dynamic stability:						
Decomposition enthalphy ΔH (meV/atom)	121	69	11	95	83	17
Band gap E_g (eV)	2.77	2.03	1.32	2.02	1.67	0.95
Exciton binding energy ΔE_b (meV)	190	104	48	163	86	38

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