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Supporting Information

Surface Engineering for Improved Stability of $CH_3NH_3PbBr_3$ Perovskite Nanocrystals

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EXPERIMENTAL SECTION

Materials

Lead (II) bromide ($PbBr_2$, 99 %), *n*-octylamine (≥ 99 %), triethylamine (≥ 99 %), stearylamine (≥ 99 %), and oleic acid (≥ 90 %) were obtained from Aldrich and used without any further purification. Methylamine water solution (CH_3NH_2, 33 %), hydrobromic acid (HBr, 48 %), toluene (99 %), and *N*,*N*-dimethylformamide (99.5 %) were received from Daechung Chemicals & Metals.

Preparation of methylammonium bromide (CH_3NH_3Br) solution

CH_3NH_3Br synthesis was carried out in an ice bath (0 °C, 2 h) to effectively remove the heat generated during the reaction and to prevent reagent evaporation. The water solvent was evaporated by a rotary evaporator at 40 ~ 45 °C. Finally, the obtained precipitate was washed with diethyl ether for three times and dried under vacuum (60 °C, 6 h) condition.

Synthesis of $CH_3NH_3PbBr_3$ nanocrystals

$CH_3NH_3PbBr_3$ nanocrystals were synthesized by the LARP method with a several modification. [Zhang F. at al. ACS NANO, 2015, 9, 4533] The typical synthesis procedure of $CH_3NH_3PbBr_3$ nanoparticles is as follows: first, we prepared a precursor solution that consists a mixture of 0.16 mmol CH_3NH_3Br and 0.2 mmol $PbBr_2$ dissolved in 5 mL of DMF. Additionally, 20 μL of *n*-octylamine and 0.5 mL of oleic acid were added into the precursor solution as a surfactant. Then, the precursor solution was added into a neat toluene while vigorously stirring. The perovskite nanoparticles were formed immediately and the successful formation of $CH_3NH_3PbBr_3$ nanocrystals was preliminary identified as colorless toluene becomes blueish-green. Additionally, the formation was confirmed by a bluish-green emission under UV illumination (365nm). We have prepared two type of samples:

A standard nanocrystal sample to demonstrate the stability issue and investigate particle transformation process. Here, we added 2 mL of precursor solution into 10 mL of toluene dropwise, stirred for 15 minutes followed by centrifugation. At first, we separated the microcrystals from nanocrystals at 8,000 rpm (15 min) to obtain nanocrystal solution for time-dependent stability examination. Second stage of centrifuging was performed at 12,000 for much longer time (30 min) to bring the nanocrystals down from the solution. Nanocrystals obtained at this stage were used to obtain X-ray diffraction pattern and scanning electron micrograph. The X-ray diffraction pattern confirming $MAPbBr_3$ crystal structure is presented in Figure S1. A reference bulk sample was prepared by the same method while excluding the *n*-octylamine and oleic acid from the precursor solution.

A modified nanocrystal sample to evaluate the effect of surface engineering by various type of surfactants. Here, the critical aspects of perovskite nanoparticles synthesis process are the amount of precursor solution being added and the pouring rate. The precursor solution was added dropwise with a fixed periodicity (~ 45 drops/min) by using Harvard Apparatus 11 Plus syringe pump and the amount was defined by counting the number of droplets. Each droplet weight 0.06 g. We prepared a sample that contend 5 drops of precursor solution corresponding to 0.35mg/ml perovskite NCs. The nanoparticle synthesis process was immediately followed by surface treatment process by adding predefined amount of surfactant dropwise. Here, the amount of surfactant solution was counted by droplets as well.

Preparation of surfactant solution

The surfactant solution was identical to the reactive solution without $PbBr_2$ and CH_3NH_3Br; 5mL of DMF contains 0.5 mL of oleic acid and 20 μL of *n*-octylamine. For the other alkyl-amine surfactant solutions, the *n*-octylamine was substituted by an equimolar mount of trimethylamine and stearylamine (17 μL and 31.3 mg), respectively.

Characterization

The phase formation is confirmed by X-ray diffraction method using a Bruker AXS D8 diffractometer with Cu-Kα radiation at $\lambda = 1.54$ Å. The scanning electron microscope (SEM) and the transmission electron microscope (TEM) was performed on a Hitachi S4800 and JEM 2100, respectively. Samples for XRD and SEM were prepared by drop-casting on a slide glass and Si wafer, respectively. TEM samples were prepared by drop-casting on carbon-coated Cu grid. The size distribution of nanoparticles was determined by measuring at least 100 nanoparticles from TEM images. UV–Vis absorbance were obtained using Shimadzu UV-2600 spectrophotometer. Photoluminescence (PL) spectra were recorded using Hitachi F-7000 fluorescence spectrometer at room temperature. The UV–Vis absorbance and photoluminescence spectra were obtained with as-prepared samples using a quarts cuvette with a 10 mm path length. Excitation wavelength of source light (λ_{Exc}) was fixed at 365 nm for photoluminescence and QY measurements. Photoluminescence quantum yield was measured based on a comparative method, and as a reference 9, 10-diphenylanthracene (DPA) was used. Tauc approximation of UV-Vis spectra is used to determine the $E_{b.g.}$ value based on the assumption that the scattering from the NCs is very low, and thus can be ignored. The absorbance is plotted as $(\alpha h\nu)^{1/n} = C(h\nu - E_g)$, where α is the absorption coefficient, h is Planck constant, ν is the frequency, E_g is the bandgap and C is a normalization constant. The absorption coefficient can be determined by $\alpha = 2.303 \times A/d$, where A and d is absorbance and thickness, respectively. $MAPbBr_3$ shows a direct electronic transition, thus n is 2, and the bandgap is calculated to be the intercept point on abscissa of a plot $(\alpha h\nu)^{1/2}$ vs $h\nu$.

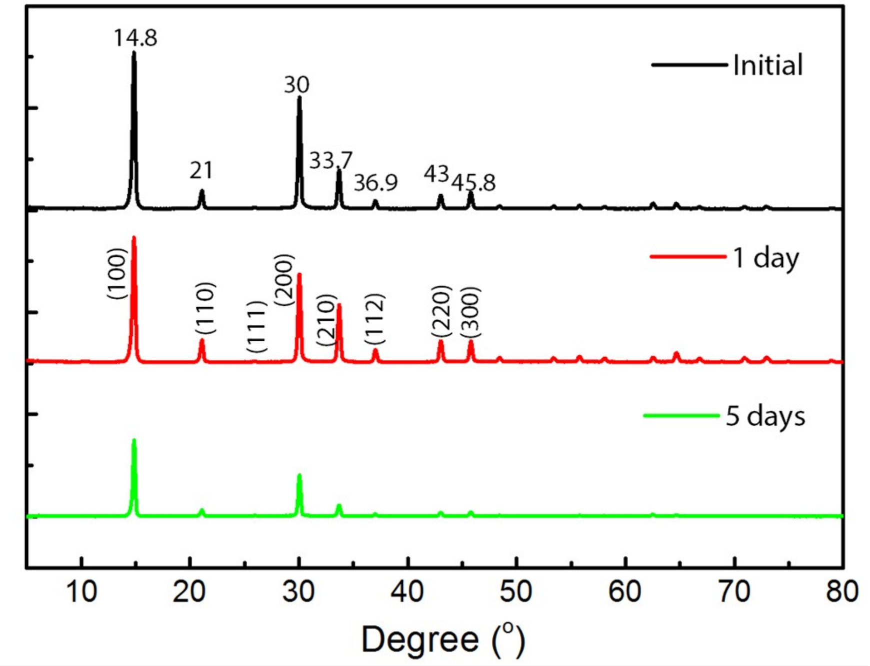

Figure S1. X-ray diffraction pattern of as-synthesized $CH_3NH_3PbBr_3$ nanocrystals (Initial), after one day aging (1 day), and after five days aging (5 days). All the diffraction patterns corresponds to $CH_3NH_3PbBr_3$ perovskite phase, and the crystal structure of $CH_3NH_3PbBr_3$ nanocrystals belongs to the space group of *Pm-3m* with a lattice spacing, a = 5.9896 Å.

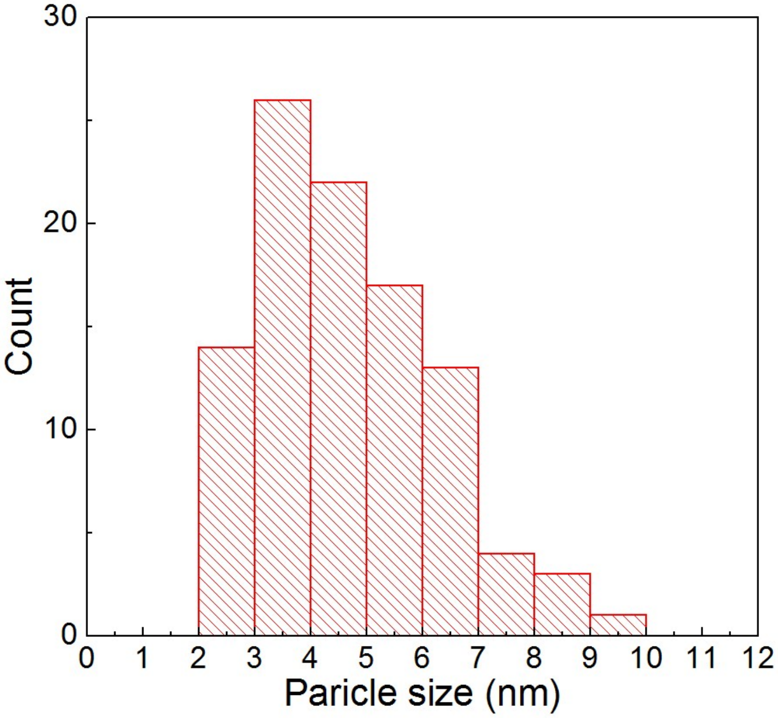

Figure S2. Particle size distribution of initial NCs.

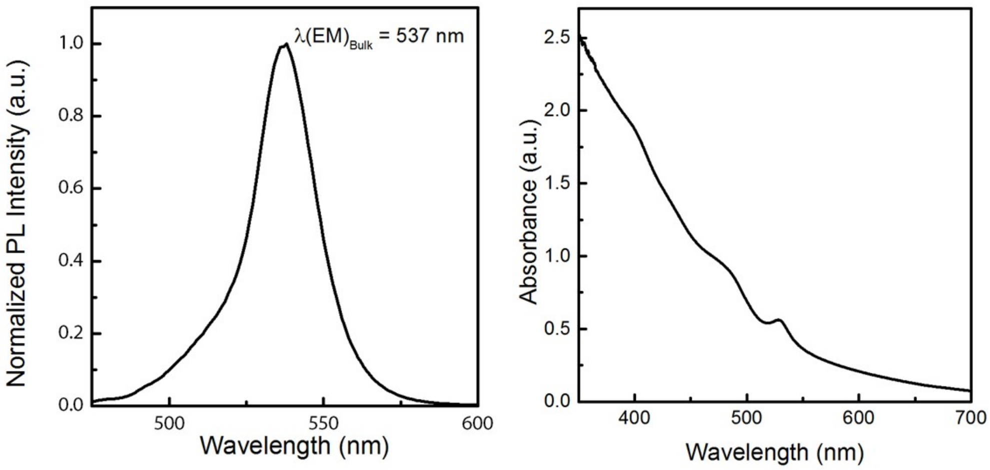

Figure S3. The PL and absorbance (λ_{Exc} = 365 nm) of bulk $CH_3NH_3PbBr_3$ perovskite.

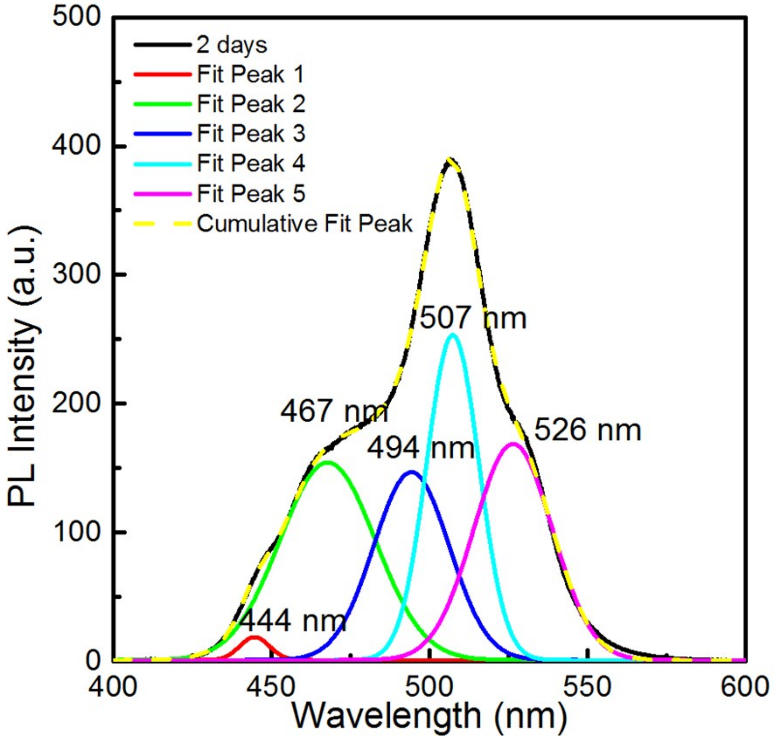

Figure S4. The PL spectra of 2 days aged sample can be fitted as a sum of several spectra centered at 444, 467, 494, 507, and 526 nm. Those values corresponds to the PL emission of layered nanoplatelets with n = 1, 2, 3, 4, 5, and etc.

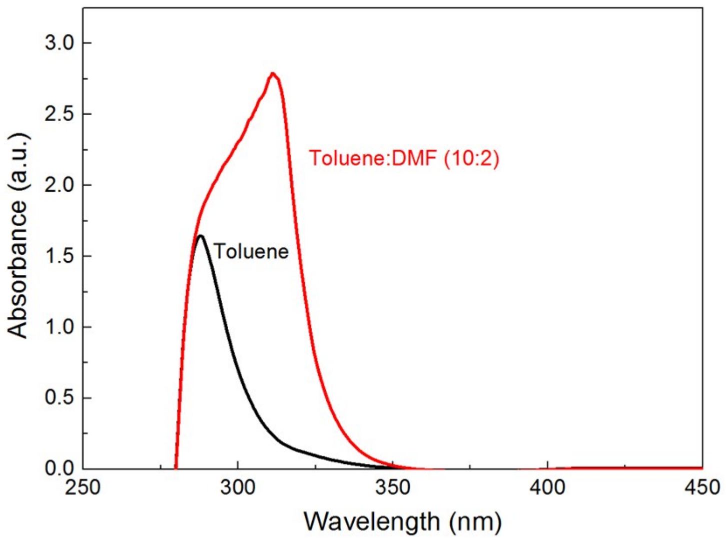

Figure S5. Absorbance of $PbBr_2$ dissolved in toluene and toluene-DMF mixture with 10:2 ratio indicates the solubility of $PbBr_2$ in aforementioned solvents.

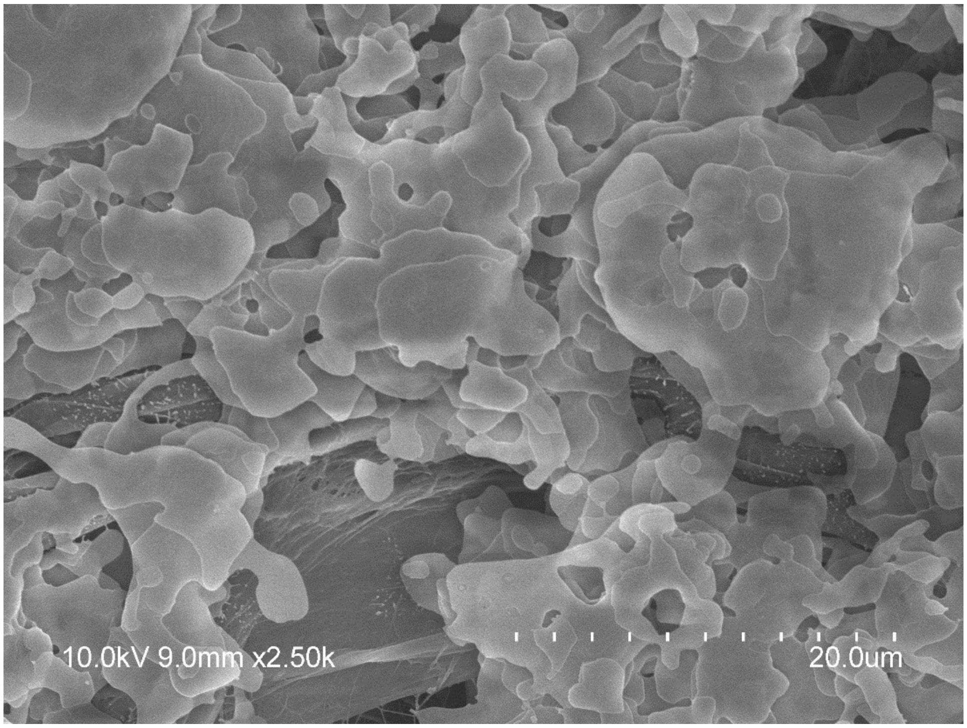

Figure S6. Aggregate of $CH_3NH_3PbBr_3$ perovskite nanoparticles obtained by intense centrifuging of as-synthesized sample. This micrograph shows the typical appearance of perovskite nanoparticle aggregates, we did not observe such aggregates in our samples, this act excludes particle growth process by aggregation.

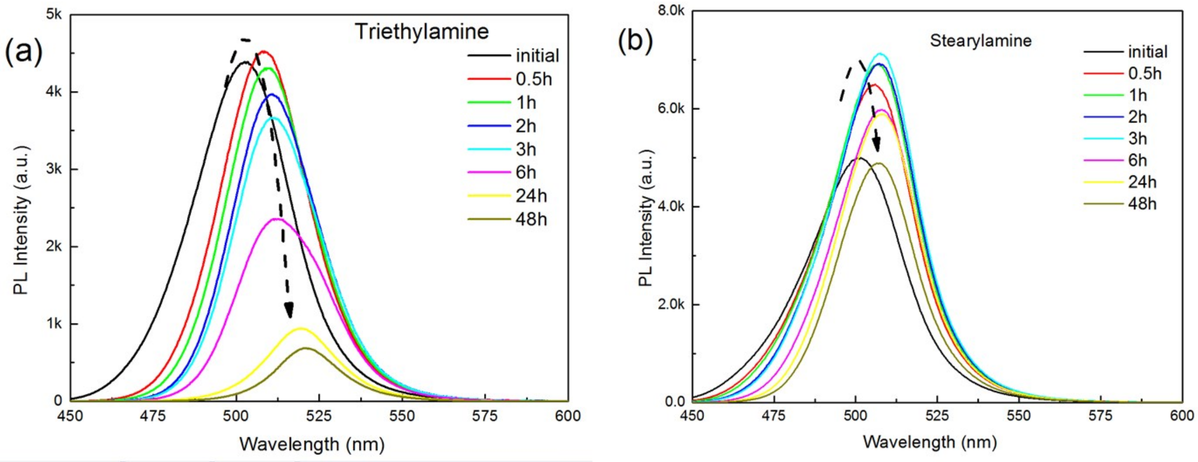

Figure S7. Photoluminescence spectra of triethylamine (a) and stearylamine (b) treated samples over aging process. Samples are based on 5 drops of precursor solution and 12 drops of surfactant solution.

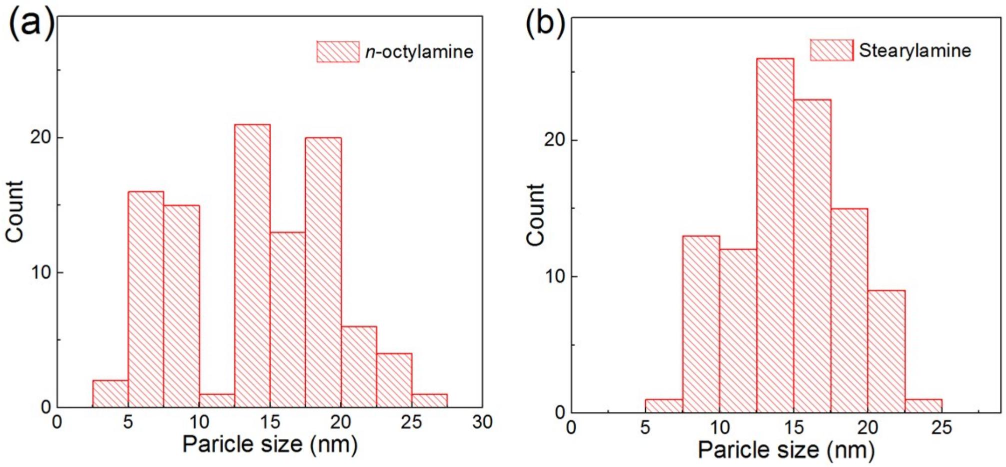

Figure S8. Particle size distribution demonstrating *n*-octylamine (a) and stearylamine (b) capped NCs size after two days of aging.