**The Role of Surface-Ligand Interactions in Stability of All Inorganic Cesium Lead Halide Perovskite Nanocrystals.**

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**Highlights**

* CsPbX3 NCs prepared in typical synthetic procedure is unstable under air.
* The stability of CsPbX3 NCs can be considerably enhanced by modifying the synthesis.
* Origin of enhanced stability of CsPbX3 NCs can be interpreted in the context of modified surface.

**1. Introduction**

Recent drastic increase of interest in colloidal all inorganic cesium lead halide perovskite (CsPbX3, X is Cl, Br, and/or I) nanocrystals have derived from their extremely bright photoluminescence (PL), narrow full width at half maximum (FWHM) of PL spectrum, band gaps which are tunable over entire visible spectrum, defect tolerance, and highly dynamic interaction between ligands and atoms on NC surfaces (surface-ligand interactions).1,2 However, the NCs are significantly unstable under air, hence further investigation is strongly hampered.2 Here we present new synthesis of CsPbX3 NCs with modified surfaces, thus considerably enhanced air stability. Also, the origin of instability (and stability) of CsPbX3 NCs is revealed in the context of surface-ligand interactions.3

**2. Methods**

The synthesis are described in previously reported studies.1,2 For the synthesis of typical CsPbBr3 NCs, hot Cs-oleate solution is injected into degassed mixture solution of PbBr2, oleic acid (OA), and oleylamine (OLA) in 1-octadecene (ODE) at 170 ºC. The NCs are immediately formed upon the injection and the flask containing reaction mixture is rapidly cooled in an ice bath. For the synthesis of surface modified and air-stable CsPbBr3 NCs, the mixture solution is formed by adding additional metal bromides (e.g., ZnBr2) to PbBr2, OA, and OLA in ODE. And other procedures are carried out identically with typical CsPbBr3 NCs. After the synthesis, the NCs are purified by multiple centrifugations with or without polar antisolvent (e.g., methyl acetate). Finally the CsPbBr3 NCs are dispersed in organic solvents such as hexane and toluene, or stored in the form of films for further characterizations.

**3. Results and discussion**

The typical CsPbBr3 NCs prepared without additional metal halides fused along (110) direction when the NCs were exposed to air in the form of films. Also, the PL QY of typical CsPbBr3 NCs decreased drastically under air condition possibly due to relaxed confinement of exciton upon fusion of the NCs.4 In contrast, CsPbBr3 NCs synthesized with additional of additional metal bromide are highly stable without nearly no sign of fusion in air. In addition, the PL QY of the NCs relatively well retained compared to typical NCs (Figure 1).2

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**Figure 1.** Schematic illustration and TEM images of typical (bottom) and modified (upper) CsPbBr3 NCs.

**4. Conclusions**

In conclusion, we successfully present CsPbX3 NCs with dramatically enhanced stability under air by adding additional metal halides in the synthesis.2 Further study will be presented to reveal the origin of instability (stability) of CsPbX3 NCs in the context of modified surface-ligand interactions with the addition of additional metal halides during the synthesis.

**References [Calibri 10]**

1. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, Nano Lett. 15 (2015) 3692−3696.
2. J. Y. Woo, Y. Kim, J. Bae, T. G. Kim, J. W. Kim, D. C. Lee, S. Jeong, Chem. Mater. 29 (2017) 7088−7092.
3. J. De Roo, M. Ibanez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. Van Driessche, M. V. Kovalenko, Z. Hens, ACS Nano 10 (2016) 2071−2081.
4. H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee, Science 350 (2015) 1222-1225.