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TEM Analysis of $CsPbBr_3$ Nanocrystals: Challenges and Perspectives.

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$CsPbX_3$ nanostructures are among the AMX_3 (A = Cs, methylammonium, formamidium, M= Pb, Sn, X=Cl, Br, I) type perovskite materials that have attracted a high interest in multidisciplinary research communities as a promising semiconductors for optoelectronics application [1]. The optical properties of nanostructures depend on their size, shape, composition and atomic structure [2]. The morphology, size, shape and crystal structure [3] of colloidal $CsPbBr_3$ nano-crystallites produced by ligand-mediated synthesis appear to be sensitive to the synthesis conditions including temperature and organic acid, base and Cesium precursors [2] as well as on post- synthesis processing [1]. The $CsPbBr_3$ nanostructures have been often observed in cubic [4], orthorhombic [5] or mixed structures [6], where both phases exist simultaneously. Recent studies of $CsPbBr_3$ nanostructures [1-6], have used transmission electron microscopy (TEM) as one of the key structure characterization techniques despite that the radiation sensitivity of such materials may sometime give substantial challenges for their unambiguous identification [6]. Here we report TEM analysis of $CsPbBr_3$ nano-cubes where we combine different techniques including low temperature and in-situ TEM observations to overcome challenges in characterization.

We have synthesized $CsPbBr_3$ nanocubes using a modified hot injection methodology reported previously [4]. Briefly, $PbBr_2$ and octadecene (ODE) were placed in a 10 mL three-neck flask and degassed at 120 ^oC and backfilled with N_2 then oleylamine (OlAm) and of oleic acid (OA) were injected. The temperature was then raised to 180 ^oC, and 1 mL of a Cs-oleate precursor solution (125 mM in ODE) was injected. The reaction was then immediately quenched with an ice bath. The precipitate was separated by centrifugation and the resulting pellet was washed with a 4:1 mixture of toluene: acetone. The nano-cubes were stored in toluene for further analysis. The nano-sheets were produce by addition of ethyl acetate to the obtained nano-cube solutions which cause the formation of a precipitate that was collect by centrifugation. Electron Microscopy (TEM) and powder X-ray diffraction have been employed to analyze the $CsPbBr_3$ nanostructures.

Figure 1a shows XRD patterns for $CsPbBr_3$ nano-cubes and nano-sheets indicating that the nano-cubes adopts a cubic symmetry and the nano--sheets adopt an orthorhombic symmetry. The atomic models for 3 major crystal phases and typical TEM image of $CsPbBr_3$ nano-cubes are shown in Figs 1b and 1c, respectively. The representative HRTEM images of the two types of $CsPbBr_3$ nano-crystals are shown in Fig. 2. Both $CsPbBr_3$ nano-cubes (a) and nano-sheets (b) have been synthesized in similar process, but show different size, morphology, and atomic structure due to difference in post synthetic processing. The Fourier Transform Patterns in Fig. 2 evidence their difference in crystal structure. Because the nano-cube sample has more residual ligands left as compared to nano-sheet one, it has lower phase transition (orthorhombic–cubic) temperature as compared to bulk materials. Indeed, the nano-cubes with a cubic phase have an orthorhombic structure under low temperature (77K) and covert back to a cubic one under room temperature. It is also interesting to note that the orthorhombic structure of $CsPbBr_3$ nano-cubes at low temperature is radiation sensitive and degrades rapidly under electron beam making HRTEM imaging of the sample at low temperature practically impossible. Our results demonstrate that a combination of electron microscopy techniques including electron diffraction, HRTEM imaging, HRTEM contrast computer simulations, EDS analysis, as well as in-situ TEM experiments provide a comprehensive understanding of the $CsPbBr_3$ nanostructures [7].

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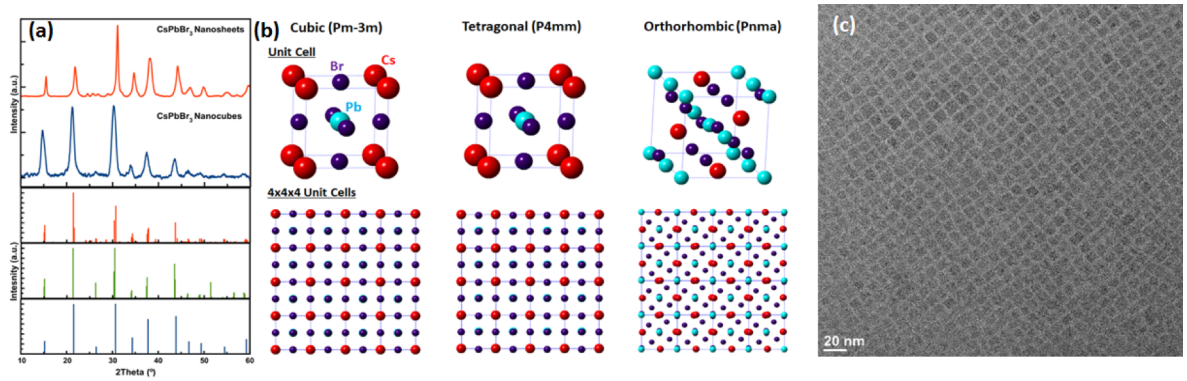

Figure 1. (a) XRD patterns for $CsPbBr_3$ nanocubes and nanosheets, (b) atomic arrangements for 3 crystal phases and (c) typical TEM image of $CsPbBr_3$ nanocubes.

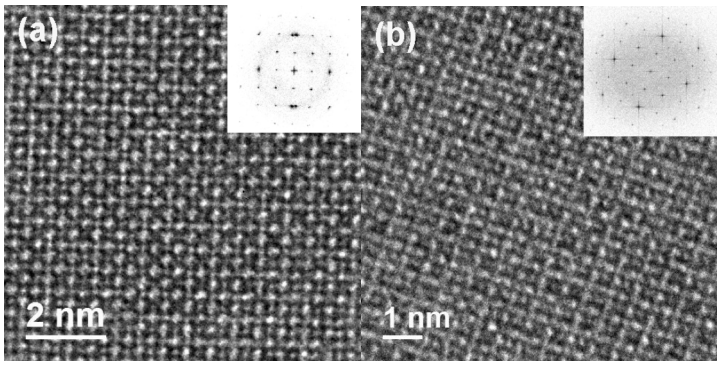

Figure 2. HRTEM images of two types of $CsPbBr_3$ nano-crystals: (a) nanocubes and (b) nano-sheets. Inserted are Fourier Transform Patterns indicating that nano-cubes (a) have a cubic structure at room temperature while nano-sheets (b) have an orthorhombic structure.

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