

Review

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Synthesis and Optical Properties of Water-Durable Lead Halide Perovskite Nanocrystals

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Abstract

Metal halide perovskite nanocrystals (MHP NCs) show promise as next-generation optical and electronic materials. Surface passivation of MHP NCs to improve polar solvent stability is essential for exploiting their optoelectronic properties. Our group sought to develop novel surface modification methods to improve the chemical and dispersion stabilities of MHP NCs. This short review summarizes our recent reports on the synthesis and optical properties of lead-based perovskite CsPbBr₃ NCs passivated with a cationic oligomeric (gemini, 12-*n*-12; trimeric, 12-*n*-12-*n*-12) ligand. Dynamic light scattering experiments revealed excellent dispersion properties following surface passivation using 12-*n*-12 ligands with longer spacer groups more than hexylmethylene; other ligands allowed aggregation and precipitation of nanoparticles. Fluorescence spectroscopy showed that CsPbBr₃ NCs passivated with 12-*n*-12 had fluorescence efficiency comparable to that of didodecyldimethylammonium bromide (DDAB), and that they exhibited water stability. We also elucidated the surface chemistry of CsPbBr₃ NCs passivated with the oligomeric ligands using hard X-ray photoemission spectroscopy (HAXPES).

Key-words: Perovskite, Nanocrystal, Luminescence, Water durability, Ligands

1. Introduction

Organic-inorganic hybrid crystals featuring intriguing optoelectronic properties and compositional modularity are emerging replacements for traditional ceramics in functional materials. In particular, metal halide perovskites (MHPs)¹⁻³ with the general formula of ABX₃ (A is a monovalent cation, B is a divalent cation, and X is a halogen anion) demonstrate exceptional optoelectronics. MHPs offer excellent light absorption, band gap tunability, intriguing excitation behavior, and efficient photoluminescence quantum yields (PLQYs).^{4,5} In addition, MHPs can crystallize readily from solution under ordinary temperatures⁶ to form bulk single crystals,⁷ thin films,^{8,9} and colloidal nanocrystals (NCs).¹⁰⁻¹² Near-unity PLQYs of MHP NC light emitters¹³ foreshadowed advances in various photophysical fields, such as color filters for light-emitting diodes (LEDs),¹⁴ lasers,¹⁵ photovoltaics,¹⁶ and photocatalysis.¹⁷

Colloidal nanoparticle surface chemistry can control their photophysical properties, dispersion, and chemical stability, because of their large surface area-to-volume ratios. X or A-type ions dissociate from strongly ionic MHP NC surfaces to yield ionic defects¹⁸ responsible for excited state deactivation. In addition, strong surface ionicity promotes the incorporation of strongly polar solvent molecules such as water,¹⁹ dimethylformamide (DMF),²⁰ and dimethyl sulfoxide (DMSO),²⁰ which decompose the perovskite three-dimensional framework.

To passivate surface defects and prevent the decomposition of MHP NCs, various types of surface modifications have been investigated.¹⁸ Our group also investigated new surface modification methods applicable to lead-based halide perovskite (e.g., CsPbX₃ and (CH₃NH₃)PbX₃, X = Cl, Br, I) NCs and recently reported some successful results from the viewpoint of the surface and ligand chemistry.^{21,22} In this manuscript, we overview our recent studies on the synthesis and properties of polar- and water-durable colloidal MHP NCs, particularly focusing on the ligand chemistry-based approach.

2. Surface modification of MHP NCs

2.1 Ligand exchange

Fig. 1 shows the origin of the surface defects in MHP NCs with the general formula ABX₃ and their passivation with surface-capping ligand molecules. The major origin of the surface defects in MHP NCs is assumed to be the ionic vacancies formed by the dissociation of the A- and X-sites,¹⁸



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