

Engineering the Synthesis and Properties of Two-Dimensional Colloidal Perovskite Nanoplatelets

by

Seung Kyun "SK" Ha

Submitted to the Department of Chemical Engineering on June 22nd, 2021 in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Abstract

Colloidal semiconductor nanocrystals are among the leading material platforms for a wide range of optoelectronic applications including photovoltaics, displays, photodetectors, and thermoelectrics. Their colloidal stability enables facile device fabrication by providing solution processability, and tunability of the bandgap with particle size opens up the opportunity to independently optimize nanocrystal properties for specific applications. Recently, colloidal lead halide perovskite nanoplatelets (chemical formula: $L_2[ABX_3]_{n-1}BX_4$, L: alkylammonium, A: methylammonium or formamidinium or cesium, B: lead, X: halide, n : number of $[BX_6]^{4-}$ octahedral layers in the direction of thickness) have emerged as a promising class of novel semiconductor nanocrystals capitalizing on their strong absorption, bright emission with high color purity, strong quantum- and dielectric-confinement, and anisotropic transition dipole moment orientation. This dissertation seeks to establish a robust synthetic protocol for the preparation of colloidal perovskite nanoplatelets and further engineer their desirable properties, which will be crucial for the fabrication of next-generation devices.

First, I briefly review the history of perovskite nanoplatelets and introduce a protocol for the facile synthesis of colloidal perovskite nanoplatelets at room-temperature. Monodispersity of the nanoplatelets is confirmed by optical and structural characterizations. Photoluminescence and absorption spectra reveal strongly-confined excitonic features which can be tuned in the visible range by changing nanoplatelet thickness and varying the composition of halide anions. Furthermore, I show that multiple species of surface-bound alkylammonium ligands can be introduced while using the same synthetic protocol. This demonstrates the possibility of further optimizing the surface properties of nanoplatelets which can hugely impact the charge transport behavior inside the device as well as the operating stability.

Then I focus on lead bromide nanoplatelets, which is considered as one of the leading light-emitting platforms for the next-generation displays owing to their desirable deep-blue luminescence. I systematically investigate key factors that determine the stability of the nanoplatelets under UV excitation, which effectively mimics the condition of hot-carrier injection into an operating device. It is shown that the freshness of the perovskite precursor solution is

crucial in maintaining the stability and efficient luminescence. Then I show that the decrease in photoluminescence intensity upon UV irradiation primarily results from intrinsic instability of the perovskite lattice against UV irradiation in nanoplatelets, whereas transformation of nanoplatelets into thicker nanostructures results from extrinsic factors, primarily moisture. Then substitution of the organic cation from formamidinium to methylammonium and the addition of excess alkylammonium bromide ligands during the synthesis are shown to be effective stabilization strategies.

Lastly, doping of manganese (Mn^{2+}) ions — a powerful method for manipulating excited state dynamics and altering semiconductor nanocrystal properties — in colloidal perovskite nanoplatelets is demonstrated along with in-depth kinetic studies. Substitutional doping of manganese for lead introduces bright and long-lived mid-gap Mn^{2+} atomic states, and the doped nanoplatelets exhibit dual emission from the band edge and the dopant state due to facile band edge-to-dopant excitation transfer. I show that photoluminescence quantum yields and band-edge-to-dopant photoluminescence intensity ratios exhibit strong excitation power dependence that cannot be explained by the saturation of long-lived dopant states. By developing a kinetic model combined with time-resolved spectroscopic studies, it is demonstrated that the annihilation of dopant-site excitons by interacting with band-edge excitons is responsible for the observed power dependence. Then I discuss significantly faster band edge-to-dopant excitation transfer in methylammonium-containing nanoplatelets compared to the transfer in formamidinium-containing nanoplatelets.

Thesis Supervisor: William A. Tisdale

Title: ARCO Career Development Professor of Chemical Engineering