

Anion Exchange in Lead Halide Perovskites: An Overview

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Precise tuning of the bandgap of lead halide perovskites by the postsynthetic anion exchange reaction has been considered as one of the best methods to customize their optical/electronic properties. The anion exchange reaction of lead halide perovskites is very fast and occurs at room temperature. The crystal structure of the lead halide perovskites is soft, and hence it facilitates diffusion of the halide ions through the crystal lattice. Through this anion exchange reaction, emission of lead halide perovskites can be tuned in the entire visible range, by varying the amounts of chloride, bromide, and iodide ions from the same synthesis in a cost-effective manner. Herein, the mechanism involved in the anion exchange reactions and the factors influencing the same are discussed. Also, the discussion is extended to demonstrate how anion exchange process can make lead halide perovskite a more promising candidate for various applications.

1. Introduction

In the last decade, lead halide perovskites have emerged as one of the most promising semiconductor materials owing to their excellent optoelectronic properties.^[1–17] The properties like strong optical absorption, tunable bandgap with size and composition, broad band emission, high photoluminescent quantum yield, etc. make them a promising candidate for photovoltaic and optical devices.^[6,18,19] Lead halide perovskites have a generic formula ABX_3 where A can be Cs^+ , $CH_3NH_3^+$, $C_2H_5NH_3^+$, etc.; B is Pb; and X can be any halide ions like bromide, chloride or iodide (Figure 1A).^[20–22] As a result of the soft crystal structure, the exchange of A type cation and X anions are possible.^[23–26] Both the processes can alter the band positions of the

perovskite.^[23,27–29] In the case of cation exchange reactions, the changes in size and electro positivity of the cations result in the modification of band gap.^[30–33] In this review we focus on the anion exchange process of lead halide perovskites for band gap engineering. Anion exchange reactions are very rapid at room temperature, and it is easy to perform.^[34–36] A schematic representation of the post-synthetic anion exchange reactions of $CsPbBr_3$ nanocrystal is presented in Figure 1B. In the presence of chloride ions, anion exchange reaction occurs in the bromide analogue of the lead halide perovskite resulting in the shift of absorption and emission spectra towards the blue region.^[34] At the same time, a red shift was observed in the absorption/

emission spectra of the same perovskite nanocrystal in the presence of iodide ions.^[34] The shift in the emission spectrum from its normal position (bromide analogue has the emission peak centered ≈ 500 nm), for chloride ion to the shorter wave length is due to the increase in the bandgap. The iodide analogue shows an emission spectrum toward the longer wave length, due to the decrease in the bandgap.^[34,37–39] From the same synthesis, by varying the proportions of chloride, bromide, and iodide ions, perovskites emitting in the whole visible region can be obtained in a cost-effective manner.^[34,40] The shift in the band positions of perovskites in the presence of different halide ions can be attributed to the size and the electronegativity of the anion.^[41] Band gap is directly proportional to the electronegativity of the halide ion. All these processes are completely reversible (Figure 1B).

2. The Anion Exchange Process

Kovalenko and co-workers first reported the anion exchange taking place in perovskite nanocrystals.^[34,42] By varying the halide ion precursor concentrations ($PbBr_2:PbI_2:PbCl_2$), perovskites having emissions in the entire visible region were obtained.^[34,42] Following this, many modifications were proposed.^[43,44] Among them, the most interesting method is the anion exchange, taking place between two perovskites nanocrystals having different halide ions (Figure 2A).^[45] The reaction continues, until it reaches an equilibrium concentration of the halide ions in each

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