

Intrinsic quantum confinement and charge-carrier localization in metal halide semiconductors

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Metal halide semiconductors have emerged as attractive materials for solar cells with power-conversion efficiencies now exceeding 25%.

Here we discuss intrinsic quantum confinement effects [1] in the lead halide perovskite FAPbI₃, which has recently been implemented in highly efficient solar cells. We have estimated the length scale of confinement to be 10–20 nm [1], and suggest that such domains may be detrimental to charge extraction in solar cells, but advantageous in light emitting devices. We observe photon emission from quantum-confined regions, highlighting their potential usefulness to light-emitting devices and single-photon sources [2]. We show that these nanoscale electronic effects can be controlled through partial replacement of the FA cation with Cs [2]. Overall, this intriguing quantum electronic phenomenon in a nominally bulk semiconductor offers intrinsic nanoscale optoelectronic properties without necessitating cumbersome additional processing steps.

We further report ultrafast charge-carrier self-trapping in lead-free low-toxicity silver-bismuth semiconductors [3,4]. We examined the ultrafast evolution of photoexcited charge carriers in the double perovskite Cs₂AgBiBr₆ observing rapid decays in terahertz photoconductivity transients that reveal an ultrafast localization on the time scale of 1.0ps into an intrinsic self-trapped small polaronic state. We further demonstrate the novel semiconductor Cu₂AgBiI₆ which exhibits several advantages over Cs₂AgBiBr₆, namely a much lower exciton binding energy and a lower and direct band gap near 2.1 eV [4] making it a significantly more attractive lead-free material for solar cells. However, charge carriers in Cu₂AgBiI₆ are found to exhibit similarly strong charge-lattice interactions to those in Cs₂AgBiBr₆, suggesting a link with the presence of AgBi. The presence of such self-trapping therefore emerges as a serious challenge for this class of materials.

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