Optical Properties of Organic Perovskite Materials for Finite Nanostructures

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***Abstract*— We examine the effect of the structural confinement on optical properties of organic lead halide perovskite supercells of various shapes. With a set of 8-band tight-binding parameters that reproduce the bulk band gaps and offsets of MAPb(I/Br/Cl)$_3$ that have been known through DFT simulations, we explore the band gap of finite supercells that have homogeneous and mixed halides. This preliminary work already delivers a set of information that is useful for potential device designs because band gaps of organic lead halide perovskite supercells are rarely understood, particularly for realistically sized finite structures.**

INTRODUCTION

Halide organic perovskite materials have recently obtained huge attention due to their excellent electronic properties as optoelectronic devices [1]. Latest experimental studies have reported remarkable improvements of a crystalline quality of monocrystalline and thin film samples [2], [3], and therefore opened the possibility for device designs with nanostructures of homogeneous perovskite materials. However, effects of structural/atomic variations on optical properties of of realistically sized, finite nanostructures are not well covered in a theoretical perspective. Taking the optical gap as a focal point, this work presents a preliminary modelling study on optical properties of realistically sized, confined $CH_3NH_3PbY_3$ ($MAPbY_3$, where Y = I, Br, Cl) perovskite nanostructures.

METHODS

A 8-band, sp^3 tight-binding model is employed to simulate electronic structures with our in-house Schrödinger equation solver [4]. The set of tight-binding parameters for $MAPbY_3$ crystals is extracted to match DFT-simulated bulk dispersions [5], [6] and band alignments (offsets) [7]. As shown in Figure 1, four types of confined geometries are considered: (i) cube and (ii) sphere quantum dots, (iii) square nanowire structures that are assumed to be periodic along [100] direction, and (iv) planar quantum wall structures that are assumed to be periodic along [010]/[001] directions. The dimension of confined sides (or diameter) for all the supercells (noted as "X" in Figure 1), is set to the length of 3-30 [100] unitcells (∼2-20nm). Depending on the sizes,

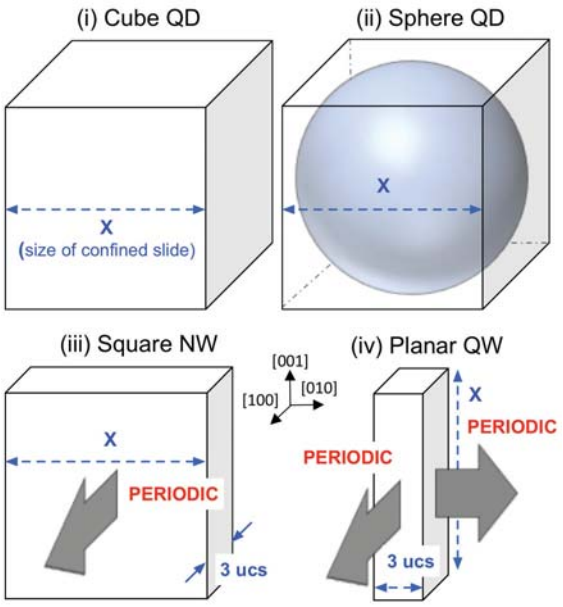

Fig. 1. **Supercell geometries considered for electronic structure simulations** Simulations are perform for the four geometries of supercells (cube quantum dots (QD), sphere QD, nanowires of square channels (1D periodic), and quantum well planes (2D periodic)). Note that "X" here is the dimension of confined slides.

supercells have 76-108K atoms, and involve (608×608)-(864K×864K) Hamiltonian matrices.

For supercells of mixed halides, three binary mixtures (I/Br, Br/Cl, I/Cl) are studied. For every size and composition, a total of 100 cases are simulated (including a few cases of extreme segregations) to consider the effect of random alloy on band gaps. Strain relaxation is not considered in this work.

RESULTS AND DISCUSSION

Homogeneous perovskite nanostructures: Figure 2 shows inter-band optical gaps of $MAPbY_3$ supercells, where we represented gaps as wavelengths to easily correlate them to the color of visible light. Here, our results indicate that confined supercells of a single material

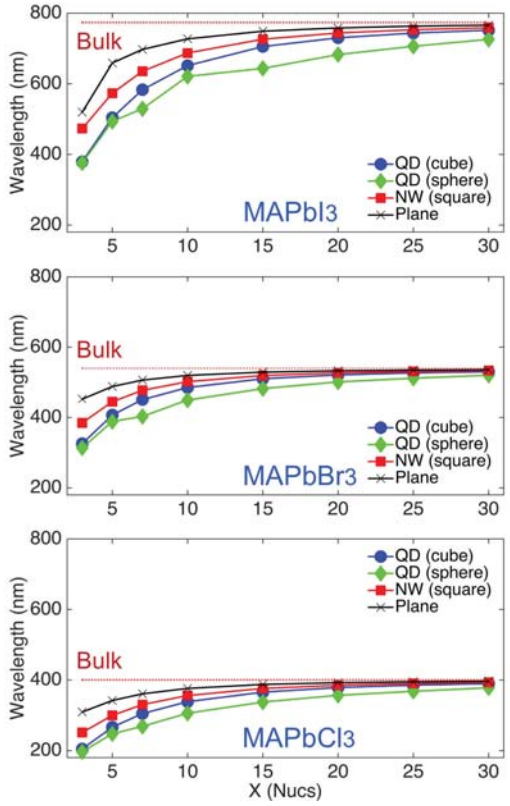

Fig. 2. **Band gaps of homogeneous material nanostructures.** Band gaps of $MAPbI_3$ (top), $MAPbBr_3$ (middle), and (d) $MAPbCl_3$ (bottom) supercells that are represented as wavelengths. The size of confined slides is represented with the number of unitcells (ucs). Wavelengths are generally smallest in sphere QDs since they have stronger structural confinements than other types of supercells. At the same dimension of confined slides, $MAPbI_3$ supercells shows largest deviation of optical gaps against their bulk values.

exhibit optical gaps of 376nm-773nm, 313nm-539nm, and 196nm-400nm for the halide anion of I, Br, and Cl, respectively. For the same confinement dimension ("X"), sphere QDs generally show smallest wavelengths regardless of material types, because they create stronger structural confinements than other three different types of supercells. For supercells of the same shape and dimension, $MAPbI_3$ is affected more heavily by quantum confinements than other two materials, so deviations of optical gaps that $MAPbI_3$ supercells show against the bulk value, are generally larger than the values obtained from supercells of other two materials.

Impacts of mixed halide anions: Effects of mixed halide anions on optical gaps of finite perovskite structures are examined. Halide mixture itself can serve as a control factor of band gaps, and random placements of atoms in halide mixtures may also affect material properties as known well from previous studies of alloy/doped structures [8], [9]. To understand the effects of halide mixtures on the optical gap, we consider three cases of binary mixtures (I/Br, Br/Cl, I/Cl) and calculate electronic structures of cube QDs. A total of 100 random cases (including several extremely segregated cases) are simulated for every combination of the dimension and composition. Results are described in Figure 3, where subfigures (a)-(c) shows the band gap of $MAPb(IBr)_3$, $MAPb(BrCl)_3$, and $MAPb(ICl)_3$, respectively. These preliminary results already present a strong evidence that the effects of random alloy in halide mixtures on inter-band optical gaps of confined supercells cannot be ignored for designs of optoelectronic devices.

As already addressed in the Methods section, this work does not consider strain relaxation, which would happen due to the lattice mismatch of $CH_3NH_3PbY_3$ and $CH_3NH_3PbY_3$ crystals. We however claim that the relaxation may not significantly change the focal message delivered by Figure 3. Mismatches in lattice constants of $MAPbI_3$, $MAPbBr_3$, and $MAPbCl_3$ crystals is $<10\%$, such that it would be safe to assume no bond-breaking, as also done in previous works based on atomistic modelling [8], [9], [10].

Conclusion

Optical properties of realisically sized, confined supercells of halide organic perovskite materials are explored with large-scale electronic structure simulations coupled to a 8-band atomistic tight-binding model. Range of inter-band optical gaps are presented for supercells of $MAPbI_3$, $MAPbBr_3$, and $MAPbCl_3$ crystals. Effects of binary mixtures of halide anions on optical gaps are also briefly investigated as a preliminary study.

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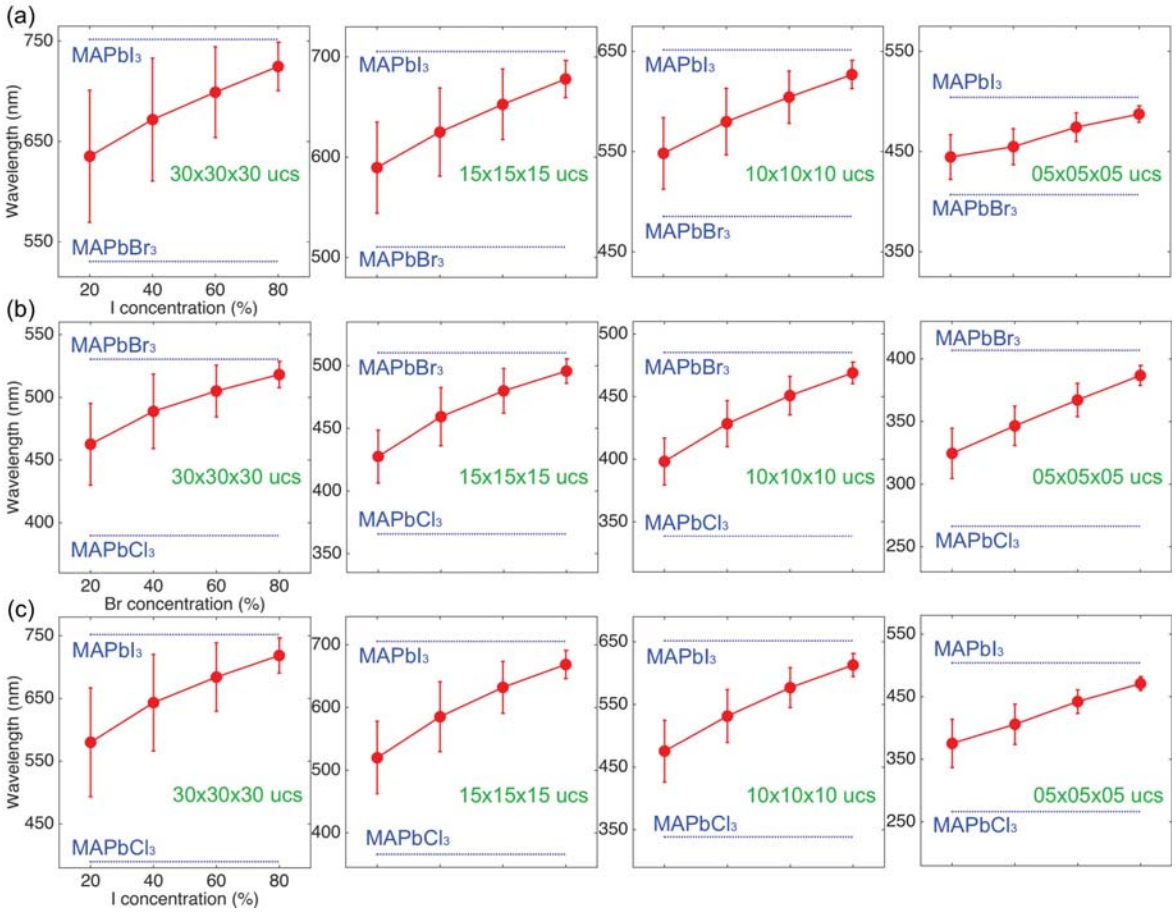

Fig. 3. **Effects of mixed halide anions on the optical gap of confined supercells.** Band gaps of box QD are simulated for three binary mixtures of halide anions. Results are shown for the confinement dimension of 5/10/15/30 unitcells (ucs) for the mixture of (a) I/Br, (b) Br/Cl, and (c) *I*/*Cl*. A total of 100 random cases are tested for each combination of the size and the composition, where median values are plotted with error bars. Results of this simple preliminary test already indicates that effects of random alloy on optical gaps cannot be ignored for designs of optoelectronic devices.

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