Morphology Dependent Growth and Absorption Coefficient in Perovskite Quantum Dots

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Introduction

A B X$_3$

A = **Cs⁺,** MA⁺ or FA⁺

B = Metal cation (**Pb²⁺**, Sn²⁺, Ge²⁺)

X = Halogen ion (**Cl, Br, I**)

CsPbI$_3$ CsPbBr$_3$ CsPbCl$_3$
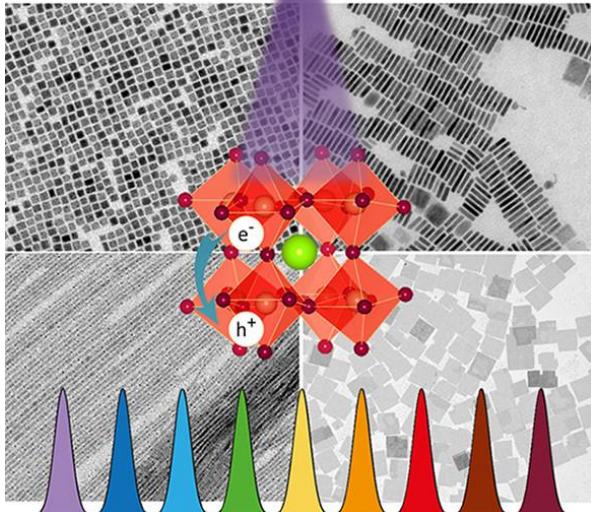
Photovoltaics

❖ High PL Quantum Yield

❖ Tunable bandgap

❖ In high demand for photovoltaics and optoelectronics applications
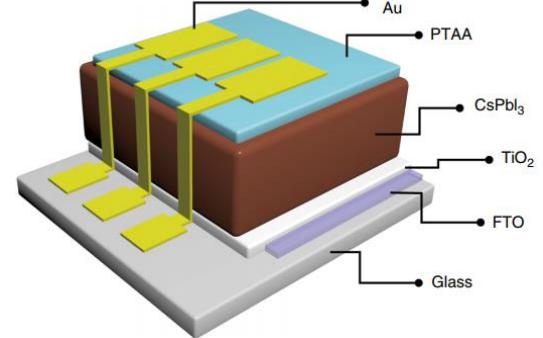
QD-LEDs and Displays

Quantum dots

Blue LED

Quantum Dot Lasing

300 μJ/cm²

190 μJ/cm²

110 μJ/cm²

30 μJ/cm²

24 μJ/cm²

PL Intensity (A.U.)

Energy (eV)

Shamsi et.al. *Chem. Rev.* 2019, 119, 5, 3296-3348

Wang et. al. *Nat. Commun.* **2018** 9, 4544

Santamaria et. al. *Nano.Lett.* **2009** 9,20, 34882-3488
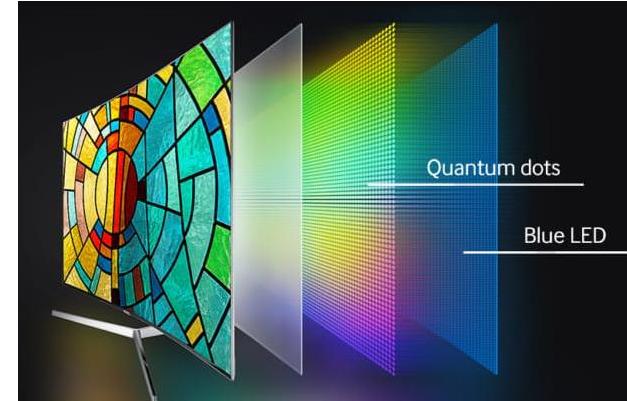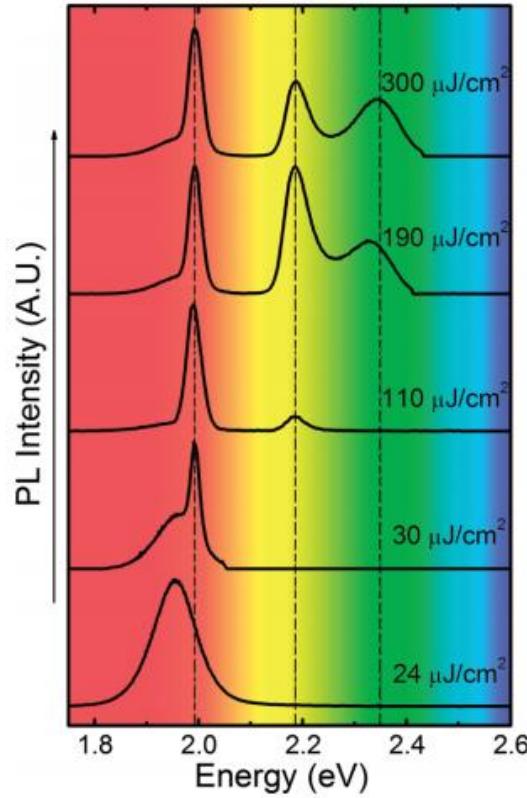
❖ Commonly observed nanocrystals are **Spherical** in shape

50 nm **CdSe**

5 nm

A **Cobalt NCs**

20 nm
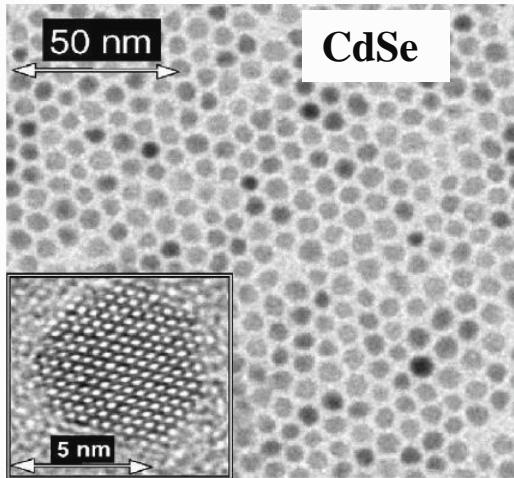
Vivien et. al. *Chem. Mater.* 2019, 31, 3, 960–968
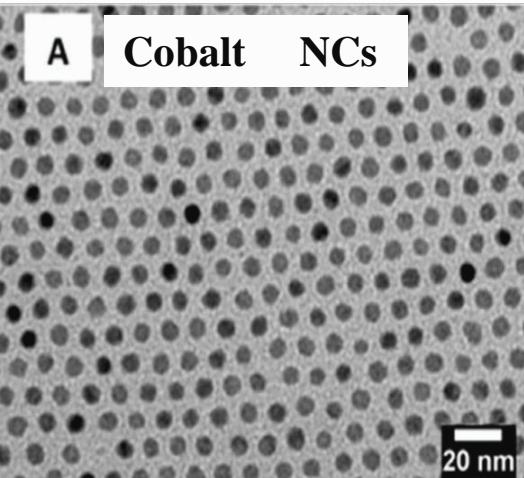
❖ Perovskite halide NCs are **Cubic.**

CsPbBr$_3$

50 nm
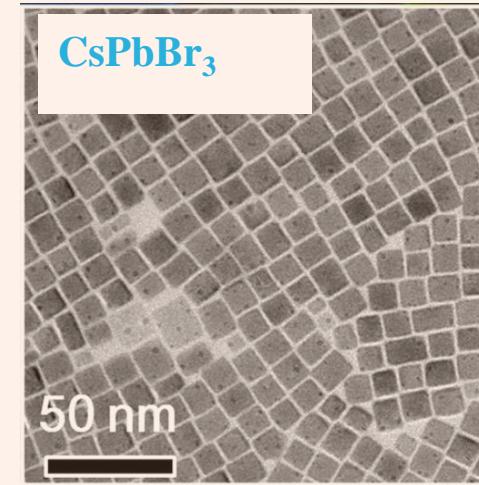
❖ **How these cubic NCs are formed?**

ε (10^5 cm^{-1} M^{-1})

CdSe

CsPbBr$_3$

ε (cm^{-1} μM^{-1})

$\sim d^3$
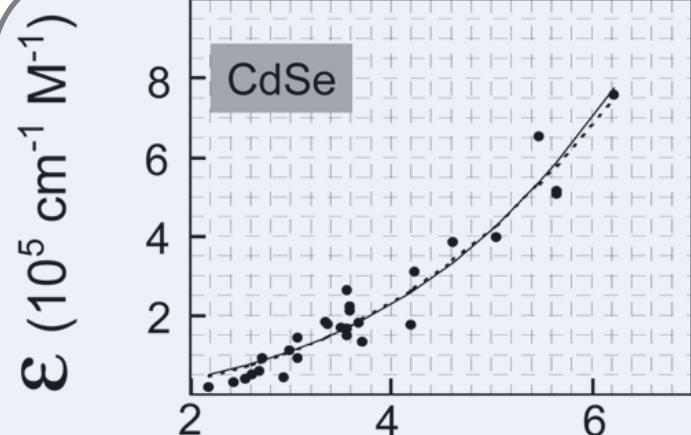
edge length (nm)

Peng et. al. *Chem. Mater.* 2004, 16, 3, 560   Maes et. al. *J. Phys. Chem. Lett.* 2018, 9, 11, 3093–3097
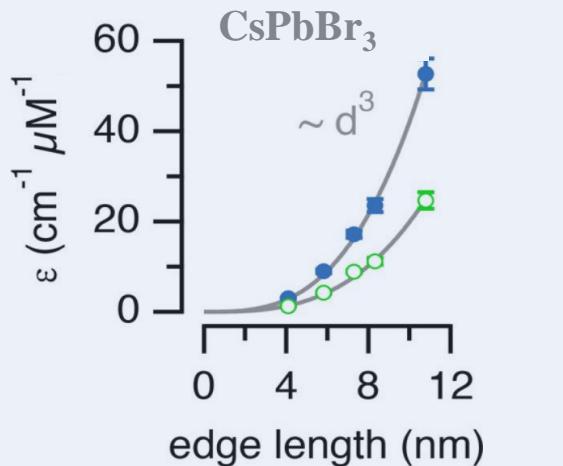
❖ ε increases with increasing size/ edge length.

❖ **Is ε depend only on size or also with bandgap/dimensionality?**

Our Approach

Cs-oleate

Ar

180 °C

30 °C

PbX2
ODE, OA, OAm

0D Dot

1D Rod

2D Nanoplatelet

3D Cube
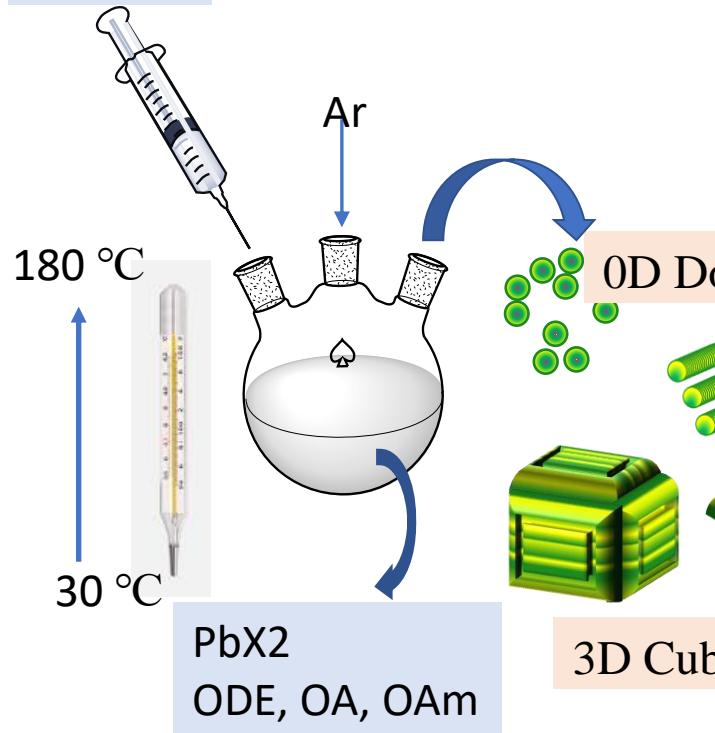
❖ **Temperature** as a parameter to modulate size and shape.

❖ Introduction of Cs–oleate precursor at various temperature to isolate the **intermediate species**.

CLB-180
CLB-150
CLB-120
CLB-90
CLB-60
CLB-30

CLB-180

CLB-30

(a) CLB-30   1.8 nm   10 nm
(b) CLB-60   2.3 nm   CsPbBr$_3$ 10 nm
(c) CLB-100   5.7 nm   10 nm
(d) CLB-120   8.2 nm   20 nm
(e) CLB-150   9.3 nm   20 nm
(f) CLB-180   11.6 nm   20 nm
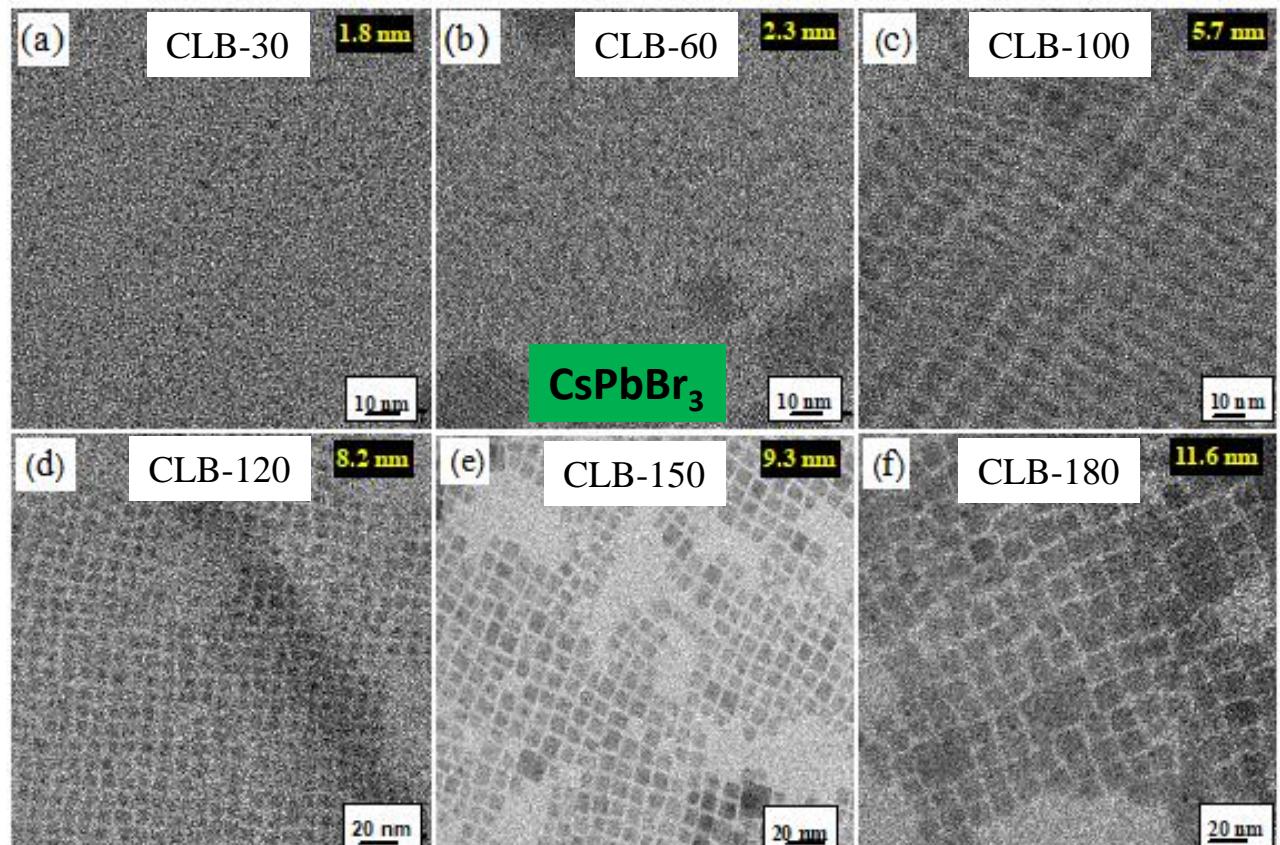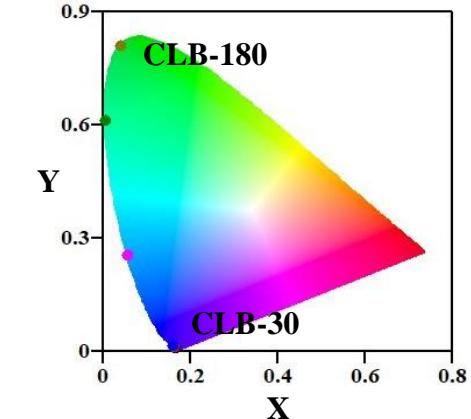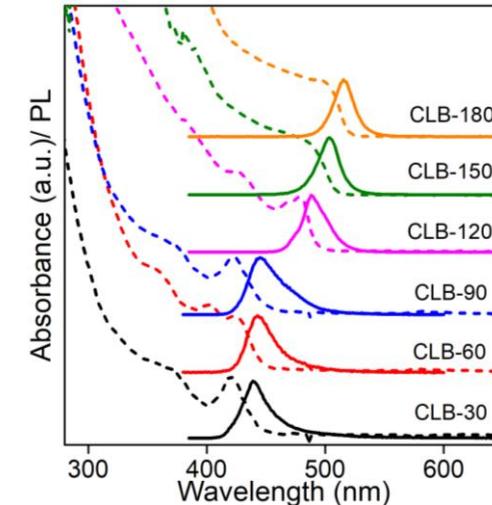
Optical, Microscopic and Crystal Structure Studies for Growth Mechanism
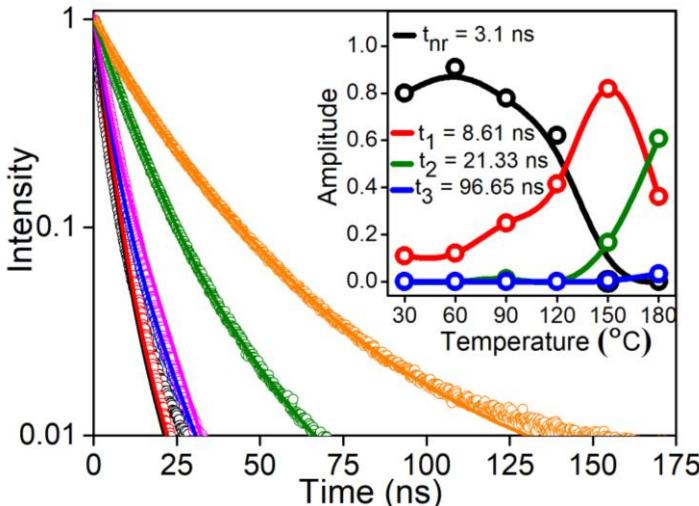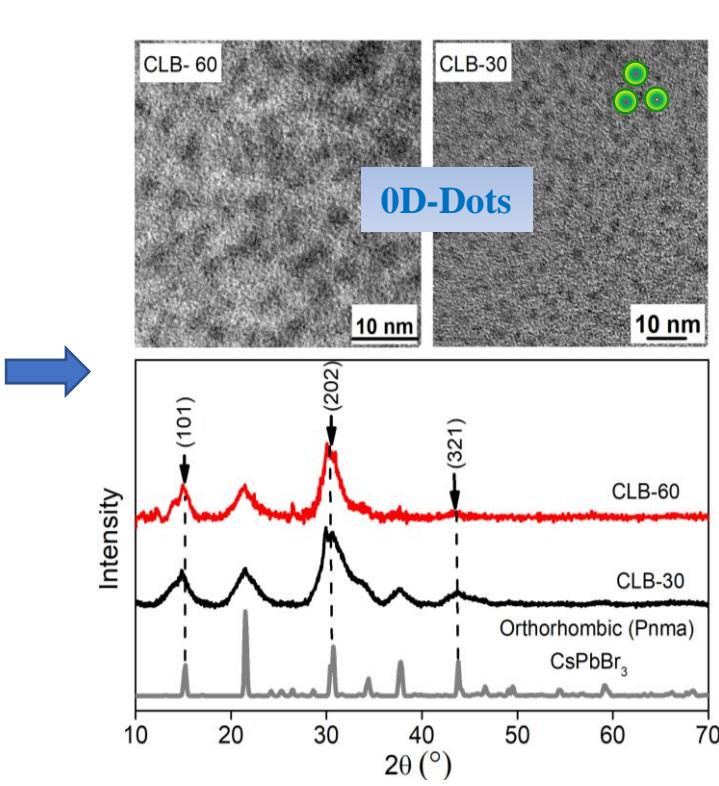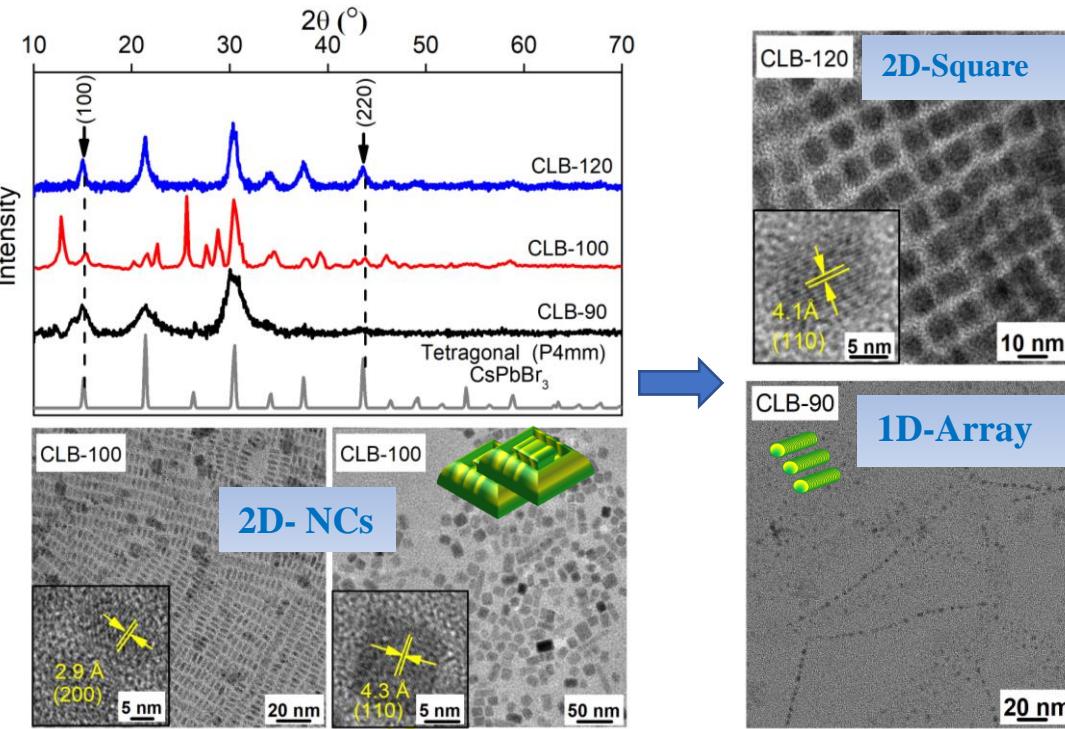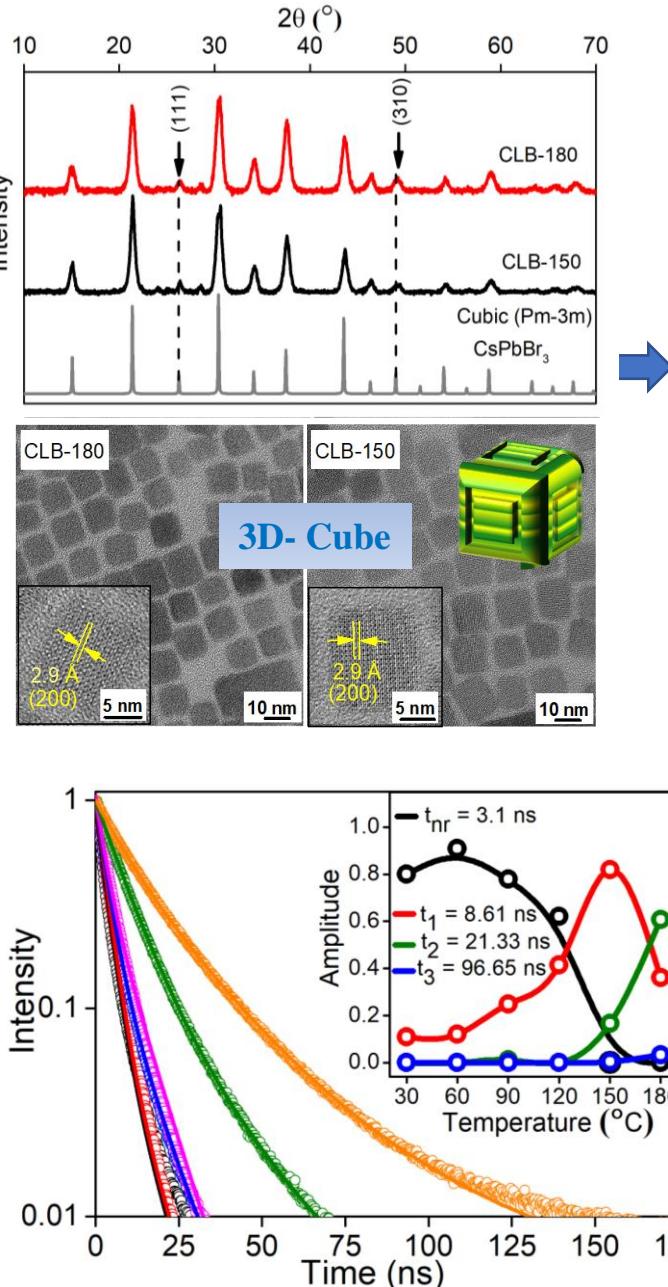
❖ Three probable life time for **rod, sheet and cube** corresponds to **1D, 2D and 3D** NCs
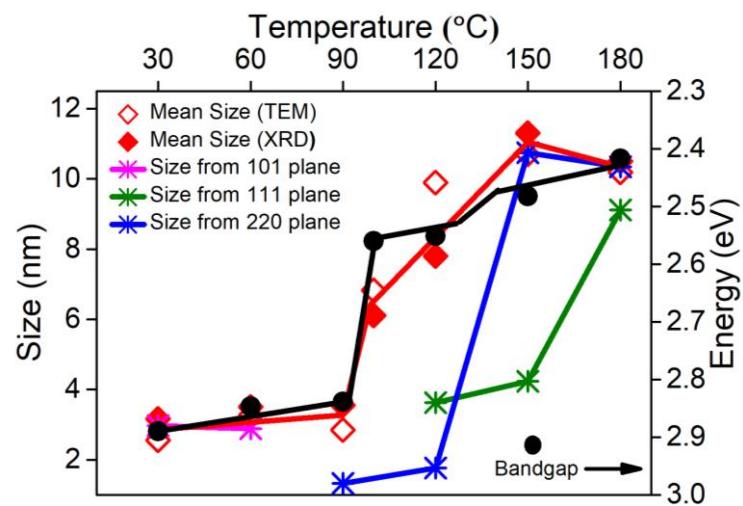
❖ Jump in bandgap **90 to 100 °C & 120 to 130 °C** correlated with phase transition.

Mandal et.al., *Nanoscale Adv.*, 2020, 2, 5305-5311

❖ Bandgap vs size plot help us to determine the size of a NCs from known absorbance.

Equation 1: $E_g(l) = E(\infty) + \dfrac{1}{\alpha + \beta l + \gamma l^2}$

Where E_g = Bandgap of the nanocrystals (in eV)

$E(\infty)$ = Bandgap of the bulk (in eV), l = Size of the nanocrystals (in nm)

❖**Beer-Lambert's law,**

$$A \;=\; \varepsilon C L$$

A = Absorbance, C = Nanocrystal concentration and L = path length ε = Molar absorption coefficient

EXAFS Study

(a) CsPbI$_3$ QDs / Ref. cubic / CsPbBr$_3$ QDs / Ref. cubic / CsPbCl$_3$ QDs / Ref. cubic

Intensity (normalized) vs 2θ (°)

(b) CsPbCl$_3$ / Fit / Pb-Cl — $|\chi(R)|$ (Å^{-4}) vs R (Å)

(c) CsPbBr$_3$ / Fit / Pb-Br — $|\chi(R)|$ (Å^{-4}) vs R (Å)

(d) CsPbI$_3$ / Fit / Pb-I — $|\chi(R)|$ (Å^{-4}) vs R (Å)
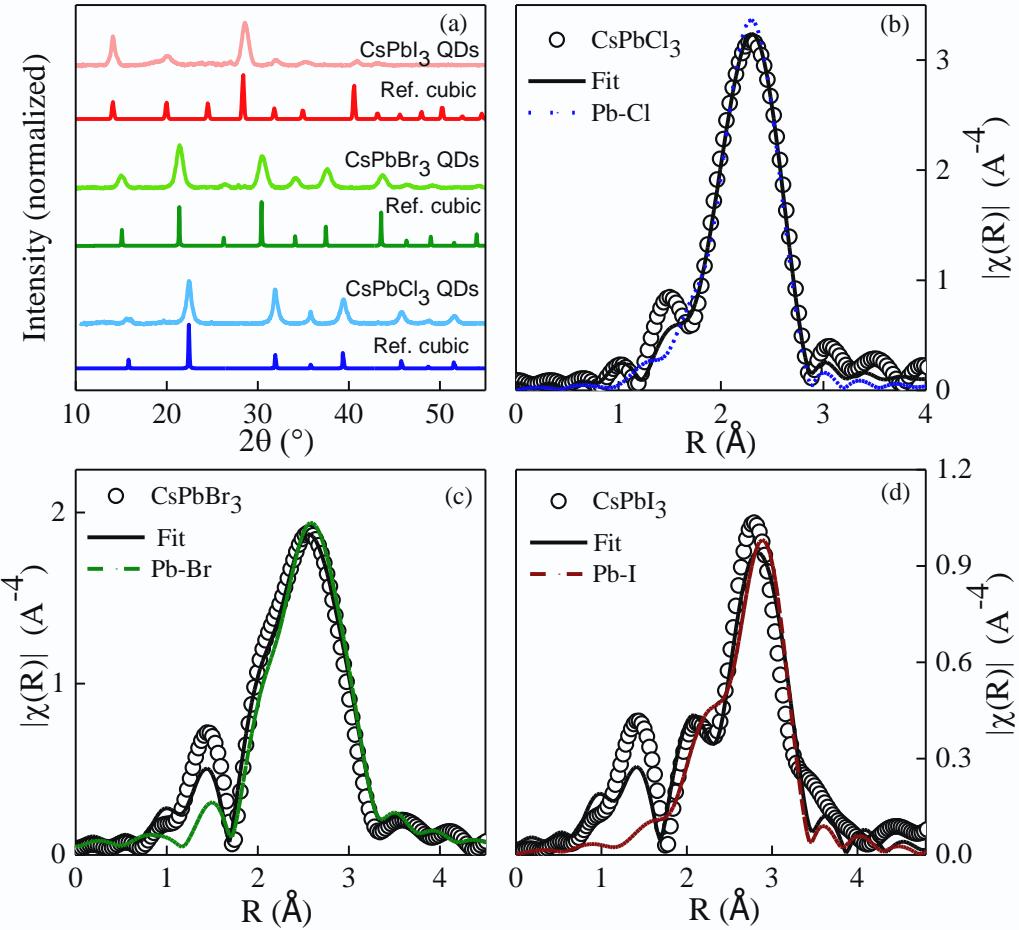
❖ XRD confirm phase purity of the nanocrystals.
❖ Pb LIII edges fitted with the corresponding Pb-X path indicating purity of the nanocrystals.

Absorption Coefficient

(a) CsPbCl$_3$ / Fit — $\varepsilon \times 10^6$ (L mol^{-1} cm^{-1}) vs $E_{g(NCs)} - E_g$ (Bulk) (meV)

(b) CsPbBr$_3$ / Cs$_4$PbBr$_6$ / Fit — $\varepsilon \times 10^5$ (L mol^{-1} cm^{-1})

(c) CsPbI$_3$ / Fit — $\varepsilon \times 10^6$ (L mol^{-1} cm^{-1})

(a) CsPbCl$_3$ — $\varepsilon \times 10^6$ L mol^{-1} cm^{-1} vs Size (nm)

(b) Cs$_4$PbBr$_6$ / CsPbBr$_3$ — $\varepsilon \times 10^5$ L mol^{-1} cm^{-1}

(c) CsPbI$_3$ — $\varepsilon \times 10^6$ L mol^{-1} cm^{-1} vs Size (nm)
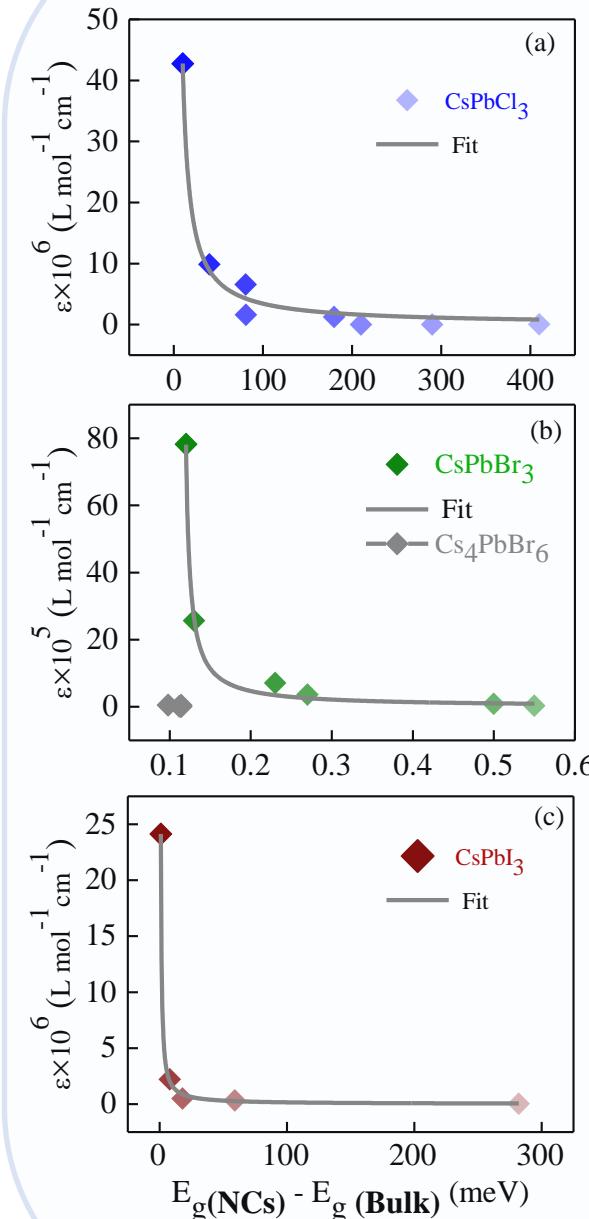
Electronic structure and dimensional Effect
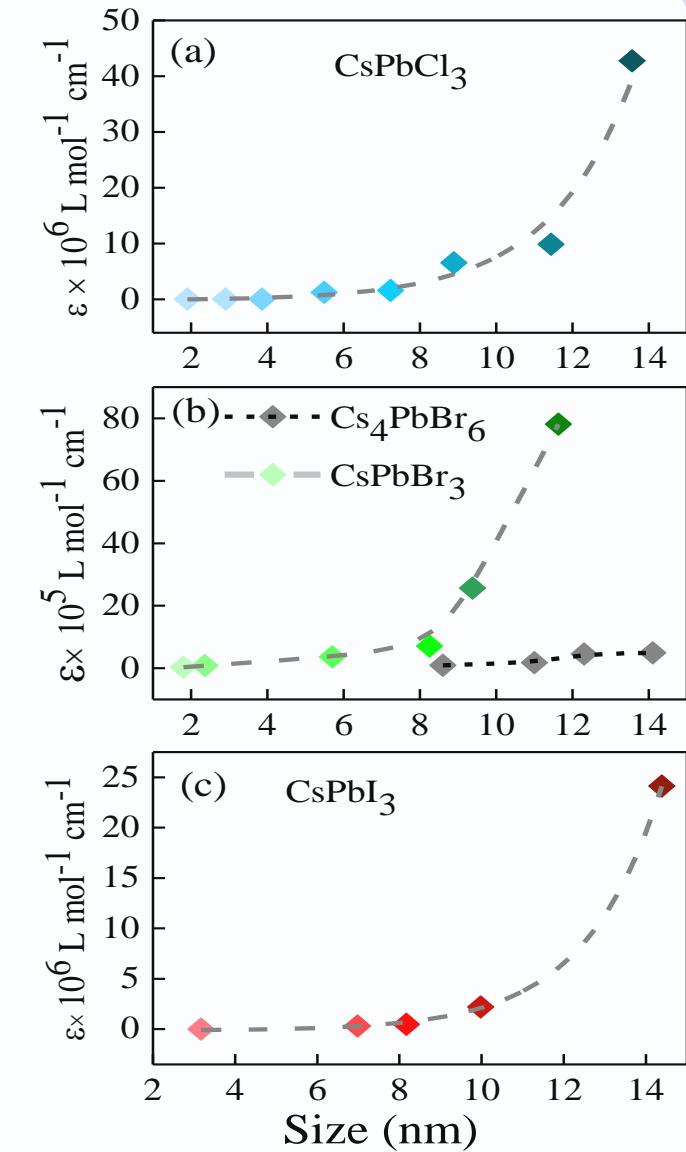
Size Effect

Discussions and Conclusions

Spherical dot

Oriented attachment of spherical dots

Cube

Nanorods

Oriented attachment of nanorods

Nanoplatelets
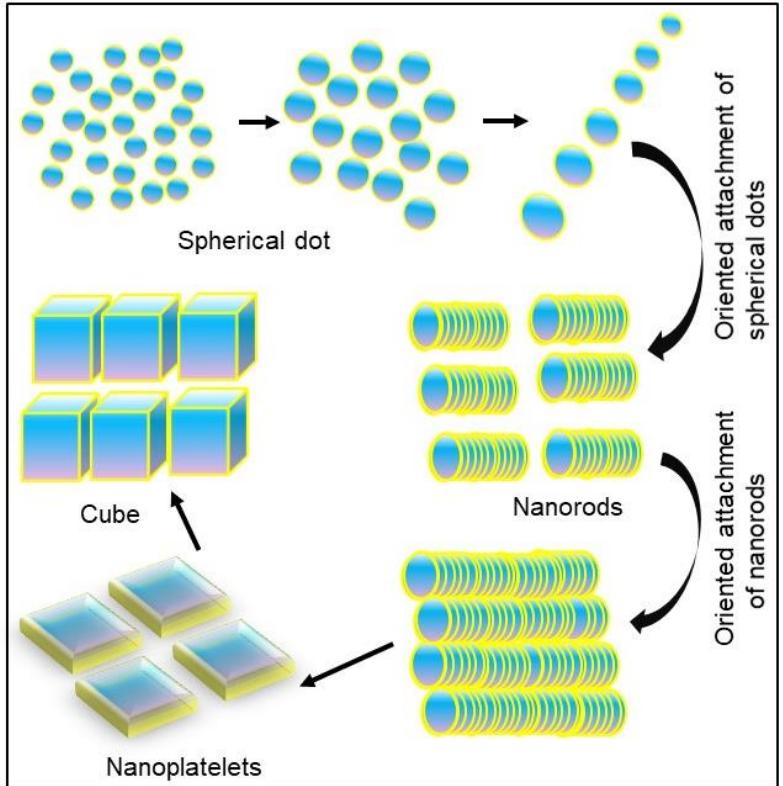
❖ Dimensionality-based exploration of anisotropic growth via asymmetrically coordinated oriented attachment.

❖ Experimental determination of absorption coefficient will help in calculation of direct concentration of nanocrystals.
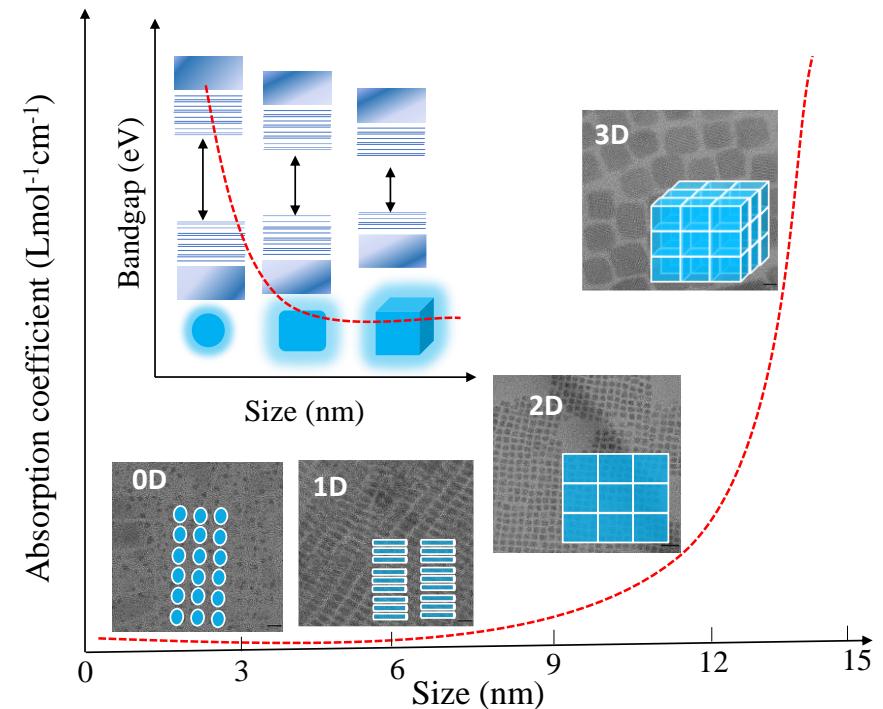
Abs. coefficient (ε) of perovskite NCs depends on size, dimensionality along with the bandgap.

Thank you !!