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Ultrafast lattice dynamics in halide perovskite nanocrystals by reciprocal space total scattering analysis

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Recently emerging as the next generation semiconductor materials strongly impacting photovoltaics and other relevant technological sectors, lead halide perovskites, LHPs, $[\text{APbX}_3]$, $\text{A} = \text{Cs}^+$, CH_3NH_3^+ (methylammonium, MA) or $\text{CH}(\text{NH}_2)_2^+$, formamidinium, FA; $\text{X} = \text{Cl}^-$, Br^- , I^-] have also been disruptive in the field of colloiddally synthesized semiconducting nanocrystals. Bright and narrowband (< 100 meV) photoexcited emission can be easily tuned from the ultraviolet to the near-infrared ranges by playing with either mixed halide composition or nanocrystals size and shape control, through facile low-temperature synthesis. Analogously to the bulk materials, the crystal structure typically consists of a 3D framework of corner-sharing PbX_6 octahedra arranged in a cubic lattice or its slightly distorted modifications. Due to the soft nature of the lattice, these modifications imply small octahedral tilting that stabilizes lower-symmetry (tetragonal or orthorhombic) polymorphs, depending either on the chemical composition or temperature. [1]

Preserving the 3D connectivity of the PbX_6 lattice is fundamental, being it at the origin of both the electronic band structure and (together with the unique defect-tolerance and lattice flexibility) the corresponding uncommon semiconducting properties and photodynamics. Within this scenario, the role of size and surface effects in either controlling the polymorphic stability of LHP nanocrystals or inducing other structural/lattice distortions, and the nature of disorder (local or static vs dynamic) is currently poorly understood. Unveiling and quantifying these effects in below 10 nm nanocrystals is a challenging task. [1]

X-ray total scattering methods in reciprocal space are recently emerging as powerful tools for investigating ultrasmall nanocrystals, grounded on the Debye Scattering Equation pattern calculation from atomistic models of nanocrystals that simultaneously encode both relevant atomic (structure and defects) and nanometer (finite size and morphology) length scales within a unified description. Based on this approach, local octahedra tilting persistent in small subdomains at high temperature was pointed out in fully inorganic CsPbX_3 nanocrystals while they exhibited an apparent average high-symmetry cubic lattice. Cooperative halide rotations at the sub-domains twin boundaries and order-disorder phase transition were further inferred. [2] Analogously, sub-Angström Br ions displacement leading to locally tilted PbBr_6 octahedra was detected in hybrid organic-inorganic FAPbBr_3 nanocrystals, without apparently breaking the average cubic symmetry over the nanocrystals volume. [3] For these hybrid nanocrystals, phase transition to lower-symmetry polymorphs is still a matter of debate.

The microscopic origin of peculiar optical behavior and photodynamic of LHPs is currently the focus of intense research. One most debated phenomenon is the long lifetime of excitons (in the nanosecond range in NCs) and diffusion lengths. One possible explanation of such slow hole-electron recombination rate calls into question the formation and relaxation of large polarons (originating from strong exciton-phonon coupling) on a sub-picosecond timescale. [4] Ultrafast time-resolved X-ray total scattering experiments may greatly contribute to shed light on the phenomenon by directly observing related lattice/structural dynamics. Recent experiments from femtosecond-resolved, optical pump-electron diffraction probe on fully inorganic and hybrid LHP nanocrystals will be presented and will help to illustrate the potential of ultrafast X-ray Total Scattering in reciprocal space as a quantitative analysis tool of photoexcited out-of-equilibrium transient states and photodynamics in semiconductor ultrasmall nanocrystals. [5]

[1] Kovalenko et al., Science 358, 745–750 (2017)

[2] Bertolotti et al., ACS Nano 2017, 11, 3819–3831

[3] Protesescu et al., J. Am. Chem. Soc. 2016, 138, 14202–14205)

- [4] Mahata et al., J. Phys. Chem. Lett. 2019, 10, 1790–1798
[5] Yazdani et al., J. arXiv:2203.06286

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