

Excitonic properties of hybrid organic perovskite crystals for photovoltaics and lasers

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Since 2012, hybrid organic perovskites (HOPs) represent a “material breakthrough” for photovoltaics, HOP-solar cells reaching an efficiency record of 21%, competing with the efficiencies of the silicon-based cells. The explanation of such a success is related to a combination of good transport properties for both electrons and holes and appropriate excitonic properties. More broadly, HOPs have also high potentialities for light-emitting devices such as electroluminescent diodes and lasers. Thus, it seems that HOPs combine strengths of the inorganic semiconductors and organic semiconductors, likely to solve the contradiction that high charge carrier mobility and large stimulated emissions are required for lasing devices but can't be found, in general, in the same material.

A decisive advantage of the HOPs crystals, allowing the access to this wide range of applications, come from the ability to tune the excitonic effects. In fact HOPs can be arranged in such a way that carriers are able to move at 3, 2, 1 or 0 dimensions. In particular, the exciton binding energy in 3D HOPs has been shown to be of the order of tenth of meV, well suited for an electron-hole separation at room temperature. When HOPs are arranged in two dimensions, they can be considered as hybrid multi-quantum wells in which both quantum and dielectric confinements lead to a huge exciton binding energy of several hundreds of meV stable at room temperature, presenting oscillator strengths one order of magnitude larger than in GaAs/(Ga,Al)As heterostructures.

We will discuss here about the optical properties of HOPs single crystals and compare them to those of thin polycrystalline films. In particular, the main feature in CH₃NH₃PbI₃ crystals is the appearance, in the low temperature luminescence spectra, of a sharp emission line (FWHM ~ 5 meV) at high energy which is attributed to the free exciton signature [1]. Experiments performed as a function of temperature confirm the existence of a strong electron-phonon coupling both in 3D and 2D HOPs [1, 2].

We will report also on ultrafast pump-probe experiments performed on (C₆H₅C₂H₄NH₃)₂PbI₄ thin layers at room temperature [3]. The exciton dynamics is fitted with a bi-exponential decay with a free exciton lifetime of ~100 ps. The presence of a long tail in the pump/probe signal is attributed to trapped excitons on dark states, while an ultrafast intraband relaxation ($\tau_{\text{intra}} \leq 150$ fs) is reported. The analysis of the transient broadening and loss of oscillator strength demonstrates that 2D HOPs share common behaviours with standard semiconductors quantum wells despite their huge exciton binding energy that is closer to the one reported for organic semiconductors.

[1] H. Diab et al, J. Phys. Chem. Lett., 2016, 7 (24)

[2] K. Gauthron et al, Optics Express **18** (2010) 5912

[3] K. Abdel-Baki et al, J. Appl. Phys. **119**, 064301 (2016).

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