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Adapting a Scalable Colloidal Protocol to Perovskites for Photovoltaics to Improve Dimensionality of Formamidinium-Containing Materials

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Synthetic hybrid perovskites of general formula $APbI_3$ are taking the stage in the solar energy field for their outstanding optoelectronic properties, solution processability, limited costs of precursors and straightforward synthesis[1].
However, the fabrication of high-quality materials still suffers from reduced outputs, the use of non-benign chemicals and the need for well-controlled conditions, limiting the attractiveness and feasibility for the industry[2]. Our group designed a colloidal approach in a laboratory atmosphere, optimizing the procedure for all-inorganic $CsPbBr_3$. The method proved reliable on a multigram scale thanks to an industrial dispersing tool that manages large volumes depressing detrimental concentration and viscosity profiles. Since it relies on volatile solvents, it also opened to the recycling of waste while providing idoneous nanocrystals for ink formulation[3].
Extension of the protocol to the iodine-containing hybrid perovskites, having applications for outdoor photovoltaics, requires intensive efforts to face different solubility of the precursors, kinetics of growth of the desired crystalline phase, as well as the inherent reduced stability of iodine-rich perovskites.
As a consequence, the protocol was modified to adapt to the different behavior of each actor and mitigate thermodynamic and kinetic undesired effects. We took the first steps by formulating the injection solution with a strong excess of ligands, which are the solvents themselves. A soluble iodide extra source (the ammonium salt of the capping amine) was added to the mixture, to provide the environment with a proper concentration of halide. This is paramount to form soluble complexes of PbI_2, which are also the intermediates to avoid the thermodynamic formation of the δ inactive phase. However, formamidinium has a strong tendency to quickly nucleate in bidimensional nanosheets when the synthesis is carried out at room temperature[4,5], and that is even worsened by the presence of a large excess of amine, which can in principle alkylate the cation.
With this contribution, we explore strategies to increase the dimensionality of formamidinium-based perovskites, acting on synthesis stoichiometric ratios, formulation of the injection solution and temperature. Not all the ways we took led to satisfying enough tridimensional nanocrystals, although an effect could be detected in all cases, either in crystallographic measurements or in spectroscopical characterization. Moreover, some expedients, better than others, also allow the obtain of fairly stable nanocrystals in the form of dried powders, which can be then exploited for the preparation of inks.
In conclusion, within the campaign of trials to synthesize $FAPbI_3$ by the adjustment of the protocol optimized for all-inorganic perovskites, some samples with nanocrystals in the desired crystalline

phase, and with a satisfying resistance towards the conversion to the thermodynamic (inactive) phase, were obtained. Future efforts will be made in verifying the reproducibility and scalability of the synthesis and in the applicative in-device testing of the most interesting materials.

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