Perovskite Metamaterials

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Abstract: We report the first dielectric metamaterials nanostructured from solution-processed organolead halide perovskite thin films. Metamaterials exhibit strong resonances tunable by design across the visible spectrum, aiming applications in enhanced photovoltaics and light-emitting devices.

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Metal halide perovskites are increasingly attracting interest as solution-processable materials with outstanding optoelectronic properties [1,2] for applications beyond photovoltaic energy conversion, such as water splitting, light-emitting diodes and tunable, electrically pumped lasers, owing to their cost-effectiveness and ease of processing. To obtain the wide range of colours required for these applications, chemical tuning by varying the perovskite composition has been the strategy adopted so far, thus limiting the choice of materials to the natural colour variation of unstructured perovskite films.

Concurrently, the field of metamaterials has developed significant interest in all-dielectric platforms, which are showing similar or better performances with respect to plasmonic metamaterials while not suffering from losses which are inherent in their metallic counterparts [3]. Nonetheless, the design of metamaterials resonant in the visible part of the spectrum has proved very challenging, which is attributed mainly to the choice of available unstructured media [4].

Here we show that through nanopatterning of an organolead halide perovskite thin film (~150nm) we obtain a two-fold benefit: we generate all-dielectric metasurfaces with high-quality optical resonances in the visible part of the electromagnetic spectrum and, at the same time, we demonstrate color tuning of the perovskite film, achieved via nanostructuring of its surface rather than via the usual bandgap engineering approach.

We selected a methylammonium lead iodide perovskite, $CH_3NH_3PbI_3$ ($MAPbI_3$), which has proven to be an exceptional light harvester for hybrid organic-inorganic solar cells with remarkable performances in a variety of device architectures. Perovskite films of thickness 150 nm were deposited on quartz substrates by spin-coating. The optical constants of these films were estimated experimentally from ellipsometry measurements as well as by first principle calculations, which were in turn used to design metasurfaces composed of nanogratings and nanoslit metamolecules. (Fig. 1a and 1b).

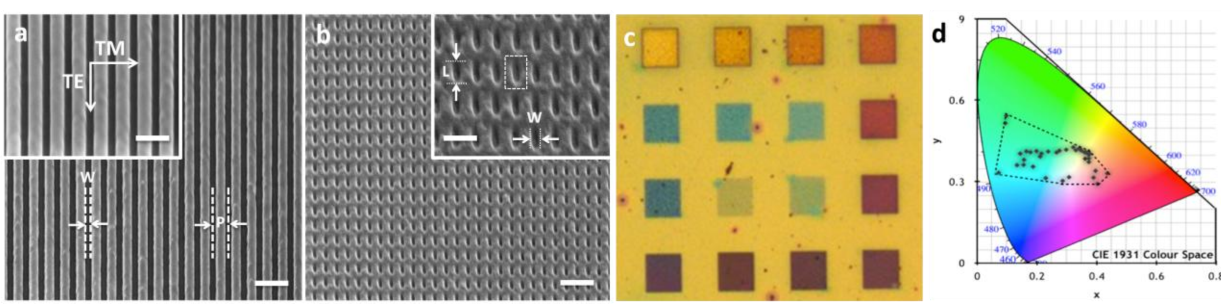

Fig. 1: Nanostructuring of an organolead halide perovskite 150nm thin film by Focused Ion Beam milling with (a) gratings and (b) slits metasurfaces designs. Geometrical changes in the design lead to structural coloring of the thin film that (c) is directly observable under a microscope and (d) which gives access to a very large color gamut.

We observe that small changes in the geometrical features of the metamolecule, its size, period and milling depth allow us to achieve a very rich spectral response from the film that manifests itself in a very broad range of colors from violet-blue to green (Fig. 1c and 1d).

We fabricated nanograting and nanoslit metamaterial arrays of 20 µm × 20 µm area by focused ion beam (FIB) milling, with a fixed groove width (W) of ~100 nm, periods ranging from 300 to 450 nm and gradually increasing milling depth (from 20 to 150 nm). The metasurfaces were measured under normal incidence across the entire visible spectrum both in reflection and transmission, with light polarised both parallel and orthogonal to the grating length. We could clearly observe narrow reflection/transmission resonances introduced by the subwavelength structuring of the films due to the interaction of the interference in the thin film with the grating modes (Fig 2). Figure 2 shows the spectral response of both nanograting and nanoslits metasurfaces, where the typical red shift of the resonances with increase of the period is clearly visible (Fig 2a and 2c). We used the optical constant extracted by ellipsometric measurements to model our metasurfaces (Fig 2b and 2d) and we found a fairly good agreement with the experimental spectra.

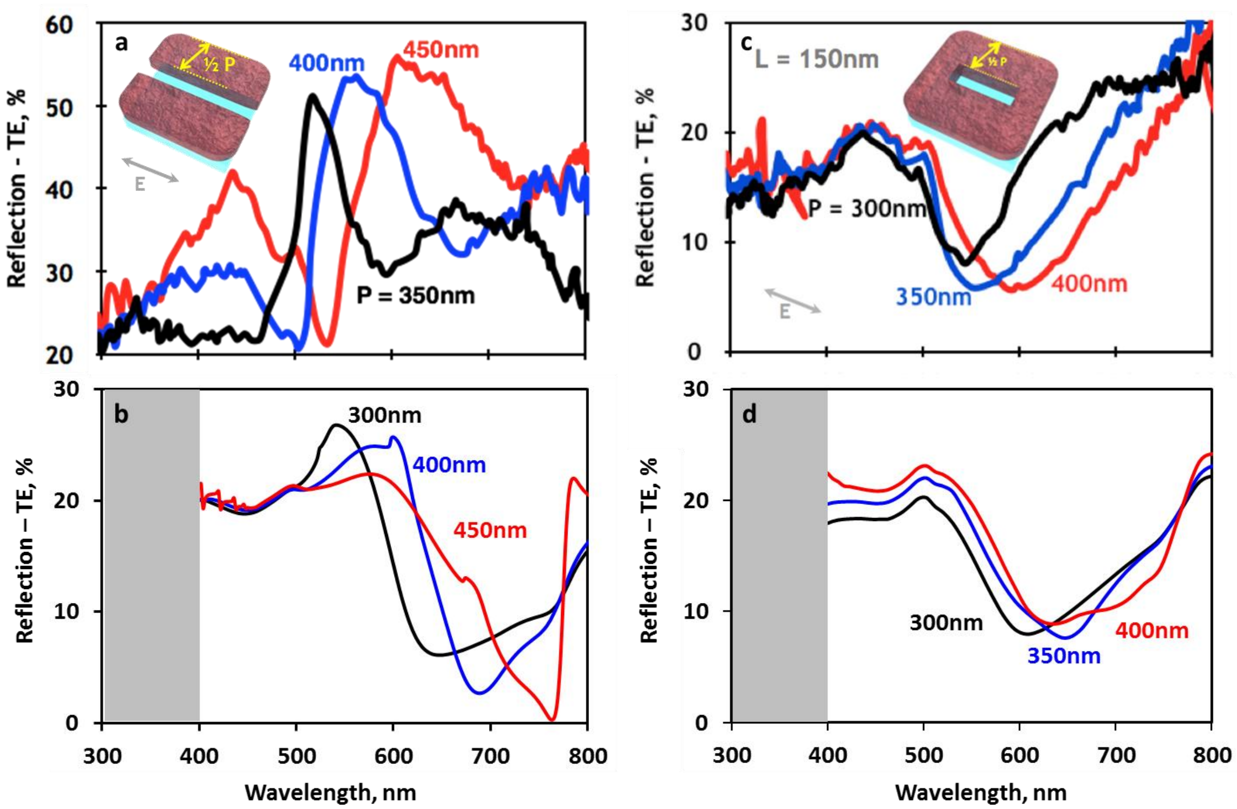

Fig. 2: Tunabilty in the spectral response of the nanostructured organolead halide perovskite thin film by change in period for (a) experimental and (b) simulated nanograting metasufaces and (c) experimental and (d) simulated nanoslits metasufaces.

In conclusion, we report for the first time, an experimental demonstration of all-dielectric, solution processed perovskite metasurfaces, with highly tunable optical response. We show that nanostructuring of perovskite films with metasurface designs, provides a simple and versatile mechanism to engineer the optical response of perovskite subwavelength films. With this novel approach, we are able to tune the colour response of the perovskite across the entire visible spectrum, which if implemented, for instance, with large-area nanoimprint lithography, may accelerate their deployment in large area photovoltaic energy conversion and light-emitting devices and displays.

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