

Preparation of Organometal Halide Perovskite Photonic Crystal Films for Potential Optoelectronic Applications

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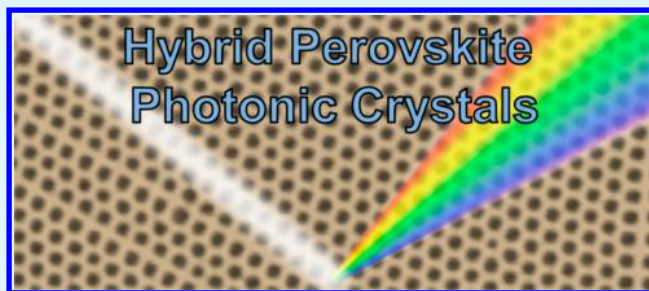
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Supporting Information

ABSTRACT: Herein, a facile method for the preparation of organometal halide perovskite (OHP) thin films in photonic crystal morphology is presented. The OHP photonic crystal thin films with controllable porosity and thicknesses between 2 μm and 6 μm were prepared on glass, fluorine-doped tin oxide (FTO), and TiO_2 substrates by using a colloidal crystal of polystyrene microspheres as a template to form an inverse opal structure. The composition of OHP could be straightforwardly tuned by varying the halide anions. The obtained OHP inverse opal films possess large ordered domains with a periodic change of the refractive index, which results in pronounced photonic stop bands in the visible light range. By changing the diameter of the polystyrene microspheres, the position of the photonic stop band can be tuned through the visible spectrum. This developed methodology can be used as blueprint for the synthesis of various OHP films that could eventually be used as more effective light harvesting materials for diverse applications.

KEYWORDS: organometal halide perovskites, inverse opals, thin films, slow-light, photonic crystal



INTRODUCTION

Over the past years, organometal halide perovskites (OHPs) have attracted great interest in the fields of photovoltaics and optoelectronics.^{1–6} The massive research activities on OHPs are due to not only their long carrier lifetimes⁷ and diffusion lengths,^{8,9} but also high absorption coefficients at energies above the bandgap.¹⁰ Furthermore, OHPs can be fabricated in a low-cost solution process and allow facile bandgap engineering by changing their composition.^{11,12}

Structures for OHP photovoltaic devices usually comprise flat and uniform thin films as the light-absorbing layer.^{13–18} However, recently structured perovskite films drew considerable attention since control over the microstructure modifies electronic properties such as lateral conductivity, ionic conductivities, charge carrier separation rates, and emission wavelengths.^{17,19–24} The fabrication of perovskite materials in well-defined structure is challenging, because of the rapid crystallization of the precursors and restructuring in the presence of trace water.²⁵ Inspired by colloidal crystal templating, our group recently published an innovative protocol for the synthesis of powdered OHPs in inverse opal (IO) morphology.²⁰ An IO is a three-dimensional (3D) photonic crystal that consists of a densely packed array of void spheres, which are surrounded by a solid material. The periodically changing refractive index creates a photonic stop band, which is similar to a semiconductor's bandgap for electrons—a region in which electromagnetic waves cannot propagate.^{26,27} By tuning the lattice parameters (i.e., the size of the spherical voids), it is possible to tune the position of the stop band over

the visible light spectrum. Since the group velocity is defined as the slope of the reduced frequency in the reciprocal space, the presence of a photonic stop band inherently implies a reduced group velocity at the edges of the photonic stop band. The reduced group velocity of photons (slow-light) can give rise to increased absorption of photons at the red edge of the photonic stop band in the high-index medium.^{26,28–32} The position of the stop band can be calculated from the modified Bragg law and is dependent on the refractive index contrast between the voids and the surrounding material, the filling fractions of the materials, the lattice constant, and also on the angle of the incoming light relative to the crystal's orientation.³³

Various studies show that the application of 3D photonic crystals of other materials such as TiO_2 ,^{29,34–36} WO_3 ,^{28,37} CuO ,³⁸ and various other metal oxides^{39–42} increases the efficiency of solar cells and photoanodes, because of the slow-light effect and the anisotropic propagation of light. Because of the angle dependence of the stop band position, it is not sufficient to deposit powdered IO particles on a film, which results in randomly distributed crystal orientations. Instead, employing the increased absorption of photons by the slow-light effect of OHP IOs in light harvesting applications requires the same photonic crystal orientation over an entire sample, or at least an area as large as the incident beam. Consequently, the direct formation of thin IO films with a defined and constant

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orientation is more desirable than depositing randomly distributed IO powders. A particular challenge for the application of IOs in solar cells is the thickness control of IO films, especially when the efficiencies of OHP solar cells are strongly dependent on the thickness of the absorbing OHP layer.^{16,21,43} In two-dimensional (2D) photonic structures, such as a close-packed monolayer of spheres, a change of the lattice constant also results in a change of the thickness.²¹ In 3D photonic crystals, the lattice constant and thus the position of the photonic stop band can be varied without affecting the thickness of the photonic crystal.

To achieve enhanced solar cell efficiencies, the photonic stop band must be tuned relative to the electronic bandgap of the semiconductor, such that slow photons are present in the high-index medium (i.e., the perovskite) at wavelengths at which the semiconductor only weakly absorbs photons, i.e., close to the bandgap energy. Thus, the photonic stopband must be at wavelengths slightly lower than the band edge.^{26,29} In addition to the advantage of the reduced group velocity of photons close to the photonic stop band, the colloidal crystal templating approach to fabricate structure-controlled OHP films offers advantages such as large surface area and short transport distances that could result in more-efficient movement of charge carriers through the film, opening the possibility for new applications.²¹ Furthermore, inverse opals and comparable photonic structures of other materials were also shown to increase the light extraction efficiency of various types of light-emitting diodes by diffraction of waveguided light.^{44–48} Since IO photonic crystals can either enhance or suppress spontaneous emission by modifying the density of electromagnetic modes, such structures are also applicable as distributed feedback lasers,^{19,49–54} which have not yet been achieved for OHPs. In analogy to the directed flow of electrons through a wire, the waveguiding properties of IOs can also be applied to fabricate circuits for communication and processing.^{32,55} To the best of our knowledge, 3D organometal halide perovskite photonic crystal in thin film morphology have not yet been realized.

In this study, we report, for the first time, the fabrication of thickness-controlled methylammonium lead halide 3D photonic crystal thin films by a colloidal crystal templating route comprising polystyrene (PS) opal formation via drop-casting, OHP infiltration via spin-coating, and template removal in toluene (Figure 1). By tuning the size of the polystyrene spheres hard template and the halide anions, a range of OHP photonic crystal films on various substrates with pronounced photonic stop bands could be fabricated.

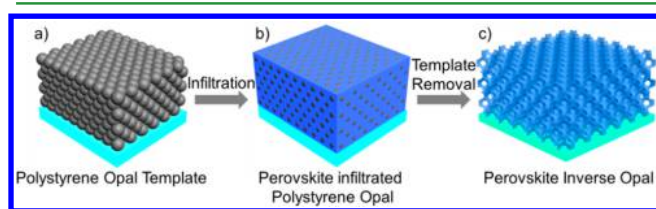


Figure 1. Schematic preparation route of OHP IO thin films including self-assembly of polystyrene (PS) spheres via (a) drop casting, (b) perovskite infiltration via spin-coating, and (c) template removal with toluene.

MATERIALS AND METHODS

Methods. All chemicals were analytical grade and used as received without further purification. Conductive fluorine-doped tin oxide (FTO) substrates were purchased from Sigma–Aldrich (8 Ω/sq).

Polystyrene (PS) Synthesis. Polystyrene (PS) spheres were synthesized by a surfactant-assisted emulsion polymerization approach modified from the literature.⁵⁶ Briefly, 190 mL of water was added to a 500 mL two-necked round-bottomed flask equipped with a reflux condenser and argon inlet. The water was stirred for 10 min at 80 °C and purged with argon before 20 mL of styrene (previously extracted three times with 1 M NaOH and three times with deionized water) were added. After the mixture reached a stable temperature of 80 °C, 617 mg of sodium persulfate and 92.0 mg of sodium dodecyl sulfate dissolved in 10 mL of water were rapidly added to the mixture. The mixture was stirred for 5 h under an argon atmosphere. Subsequently, the white suspension was sedimented by centrifugation (30 min, 16 500 rpm). The supernatant liquid was removed and the polystyrene spheres were redispersed in water via sonication. This process was repeated three times. Finally, the suspensions were diluted to 0.5 wt % polystyrene. By adjusting the stirring speed during polymerization, PS spheres with diameter of 205, 220, and 260 nm (from SEM) were obtained.

Methylammonium Bromide.²⁰ 48 wt % hydrobromic acid (20.4 mL, 180 mmol) was slowly added to a 33 wt % methylamine solution in ethanol (20.0 mL, 161 mmol) at 0 °C and stirred for 2 h in a 100 mL round-bottomed flask. The solvent was removed by rotary evaporation at 60 °C. The obtained solid was washed with diethyl ether for 30 min and recrystallized from ethanol. Finally, the crystals were dried at 50 °C in a vacuum oven for 24 h.

Methylammonium Iodide.²⁰ 57 wt % hydroiodic acid (23.8 mL, 180 mmol) was slowly added to a 33 wt % methylamine solution in ethanol (20.0 mL, 161 mmol) at 0 °C and stirred for 2 h in a 100 mL round-bottomed flask. The solvent was removed by rotary evaporation at 60 °C. The obtained solid was washed with diethyl ether for 30 min and recrystallized from ethanol. Finally, the crystals were dried at 50 °C in a vacuum oven for 24 h.

Methylammonium Chloride.⁵⁷ 37 wt % hydrochloric acid (15 mL, 180 mmol) was slowly added to a 33 wt % methylamine solution in methanol (20.0 mL, 161 mmol) at 0 °C and stirred for 2 h in a 100 mL round-bottomed flask. The solvent was removed by rotary evaporation at 60 °C. The obtained solid was washed with diethyl ether for 30 min and recrystallized from ethanol. Finally, the crystals were dried at 0 °C in a vacuum oven for 24 h.

TiO₂ Substrates.¹⁸ FTO substrates were cleaned by sonication in acetone, isopropanol and water for 20 min each. Subsequently 0.15 M titanium diisopropoxide bis(acetylacetonate) (Sigma–Aldrich, 75 wt % in isopropanol) in 1-butanol was spin-coated on an FTO glass substrate at 700 rpm for 8 s, 1000 rpm for 10 s, and 2000 rpm for 40 s. Subsequently, the films were dried for 5 min at 125 °C and then calcined for 1 h at 550 °C.

PS Opal Films. PS opal films were prepared on 25 mm × 25 mm glass and FTO/TiO₂ substrates previously cleaned by sonication in acetone, isopropanol, and water for 20 min each. Hydrophilicity was achieved by immersing the clean glass slides in a freshly prepared piranha solution for at least 1 h. Subsequently, the glass slides were placed on a hot plate at 60 °C and 200 μL of a 0.5% PS solution was dropped on the glass slide. Evaporation of the solvent leads to the self-assembly of the PS spheres in a closest packed array with the (111) surface parallel to the glass surface and a mean thickness of 2 μm. PS opal films with thicknesses of 3 and 6 μm were prepared by adjusting the volume of the polystyrene suspension to 300 and 600 mL, respectively. For comparison, a disordered opal such as the PS template was fabricated by mixing the three PS suspensions in equal volumetric amounts before drop casting.

Methylammonium Lead Halide Inverse Opal Films. 150 μL of a 1 M methylammonium lead halide solution consisting of 1 M methylammonium halide and 1 M lead(II) halide in dimethylsulfoxide (DMSO) was deposited dropwise on the as-prepared PS opal films and spun at 2000 rpm for 10 s. After drying at 60 °C for 1 h, the PS

template was removed by immersing the film in toluene for 1 min at room temperature.

Electron Microscopy. Scanning electron microscopy (SEM) images were taken with Hitachi TM3030 and S-3500N electron microscopes.

X-ray Diffraction. Wide angle X-ray diffraction patterns (XRD) were recorded at room temperature under grazing incidence on a Stoe theta/theta diffractometer in Bragg–Brentano geometry (Cu $K\alpha_{1/2}$ radiation). The measured patterns were evaluated qualitatively by comparison with entries from the ICDD-PDF-2 powder pattern database or with calculated patterns using literature structure data.

Microscale Reflectance and Transmittance/Scattering.⁵⁸ Microscale reflectance and transmittance/scattering measurements were made using a home-built optical setup. The sample was illuminated with modulated monochromatic light, and the incident, reflected, and transmitted/scattered beams were measured via lock-in detection (Stanford Research Systems, Model SR830) on three different amplified photodetectors (Thorlabs PDA100A). A super-continuum light source (Fianium WL-SC390-3) was sent through an acousto-optic tunable filter (Fianium AOTF-V1-N1) to produce monochromatic (full width at half maximum (fwhm) = 3 nm) light tunable from 400 nm to 750 nm. The wavelengths were measured using an OceanOptics USB4000 spectrometer. Light from the laser was rotated to vertical polarization using a half-wave plate and sent through a beamsplitter (Thorlabs, CM1-BS013): one branch went directly to a photodetector to measure the incident power, and the other branch was focused down onto the sample using an objective with low chromatic aberration (Mitutoyo M Plan Apo NUV 50X, NA 0.42). The sample was mounted inside a 2-in. integrating sphere. The light reflected from the sample passed back through the objective and was directed by the beamsplitter to the reflectance photodetector. The light transmitted and scattered by the sample was collected by the photodetector mounted on the integrating sphere and screened from direct incidence by a baffle. The photodetectors used to measure reflectance and incident power were adjusted at slight angles to the incident beam avoid any back-reflections within the optical system. Calibration of the reflectance photodetector was performed using a protected silver mirror (Thorlabs, PF10-S303-P01) and assuming the company's reflectance values published on their website. Because of the small size of the integrating sphere and high absorptance of the samples, measurements of the transmitted and scattered light were corrected⁵⁹ for absorption of the diffuse light within the integrating sphere by measuring the absorbance (a) when the laser missed the sample inside the integrating sphere and using the following formula:

$$T_{\text{corrected}} = \left(\frac{1}{1 - a} \right) T_{\text{measured}}$$

The total absorbance (A) is then given as $A = 1 - R - T_{\text{corrected}}$.

Angle-Dependent Transmittance. Angle-dependent transmittance of polystyrene opal films at different angles were recorded with a Varian Cary 4000 spectrometer equipped with a home-built sample holder, which allows rotation of the films in 5° increments.

Diffuse Reflectance. Ultraviolet–infrared (UV-vis diffuse reflectance spectra of MAPbBr₃ IOs prepared on different substrates were conducted on a Varian Cary 4000 spectrometer that was equipped with a Praying Mantis setup. MgO nanoparticles were used as a reference.

Angle-Dependent Reflectance. Angle-dependent reflectance spectra were recorded from 0° to 60° in steps of 2.5° in theta/theta geometry.

RESULTS AND DISCUSSION

OHP inverse opal thin films were prepared by a colloidal crystal templating method, using PS spheres as a hard template which was self-assembled by a facile drop casting method, followed by infiltration with the OHP precursor in DMSO and subsequent template removal in toluene.²⁰ To elucidate the effect of the photonic stopband's position on the optical properties of

MAPbBr₃, PS opals with various sphere diameters of 205, 220, and 260 nm were prepared on glass substrates. The PS diameters were chosen to give photonic stop bands of the MAPbBr₃ inverse opals above, overlapped with, and below, the bandgap energy of MAPbBr₃, respectively. The prepared opals are close-packed with the (111) surface parallel to the glass surface and possess large ordered domains with dimensions of tens of micrometers \times 10 μm , as representative SEM images show (see Figure S1 in the Supporting Information). Unlike most reported protocols for preparing PS opals that either are very time-consuming⁶⁰ or yield thick films⁶¹ (between tens and hundreds of micrometers with large thickness modulations),^{60,62} our protocol, which is a modification from the literature,⁵⁶ employs surfactant-assisted polymerization of PS and allows the formation of homogeneously thin films with controllable thicknesses between 2 μm and 6 μm within minutes via drop casting. The thickness of the opal can easily be tuned by adjusting the volume of the PS suspension used for drop casting (see Figure S2 in the Supporting Information).

To elucidate the effect of periodic contrast of the refractive index on the optical properties of the IO perovskite films, a disordered opal-like PS film was synthesized by drop casting a PS suspension consisting of equal amounts of the three PS suspensions with differently sized PS spheres. In the following, the PS opal films are named 205-PS, 220-PS, 260-PS, and Mix-PS, according to the PS diameter.

The close-packed array of PS spheres results in a periodic contrast of the refractive index with a periodicity on the order of half a wavelength of visible light, which, according to the modified Bragg law,⁴² results in a photonic stop band in the visible light. The UV-vis transmittance spectra of the PS opal films (Figure 2), 205-PS, 220-PS, and 260-PS, show reduced transmittances at \sim 455, 490, and 580 nm at normal incidence,

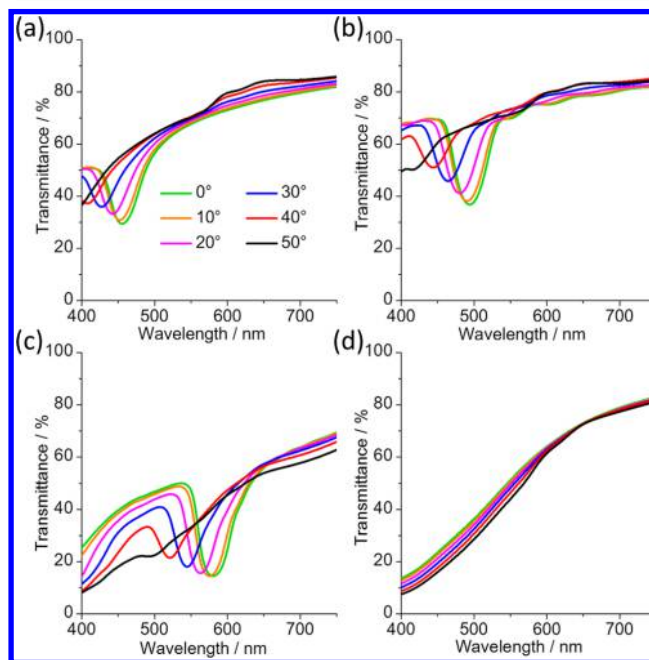


Figure 2. Transmittance spectra of (a) 205-PS, (b) 220-PS, (c) 260-PS, and (d) Mix-PS at different angles of the incident light normal to the film surface. Insets show the square of the wavelength at the stop band maximum as a function of the square sine of the incident light (black circles), together with linear regression lines (red line).

respectively. The observed dips in transmittance are the result of the photonic stop band of the (111) plane of the PS opals.

The stop band position of the (111) plane of close-packed photonic structures such as opals and IOs can be calculated according to the modified Bragg law,⁴²

$$\lambda_{\max} = \frac{2\sqrt{6}}{3} D \sqrt{f_1 n_1^2 - (1 - f_1) n_2^2 - \sin^2 \theta} \quad (1)$$

where D is the diameter of the PS spheres, f_1 is the filling fraction of component 1, which, in the case of close-packed structures, is 0.76. n_1 and n_2 are the refractive indices of the components and θ is the angle of the incident light perpendicular to the (111) surface. Transmittance measurements at different angles of the incident light (θ) show a hypsochromic (blue) shift of the stop band position (Figure 2). Figure S3 in the Supporting Information shows the linear relationship between the square of the stop band maximum wavelength λ_{\max}^2 and $\sin^2 \theta$, which is in accordance with the modified Bragg law (eq 1). For comparison, an opal-like sample (Mix-PS), consisting of equal amounts of PS spheres with sizes of 205, 220, and 260 nm, also was prepared. The different sizes of the PS spheres inhibit the formation of an ordered array of PS spheres (Figure S1), which in turn inhibits the formation of a photonic stop band. Figure 2d shows the angle-dependent transmittance spectra of Mix-PS which, as expected, does not possess a photonic stop band, because of the absence of ordering in the structure. Instead, the transmittance of Mix-PS is strongly reduced at short wavelengths, because of scattering by the disordered structure.

The prepared PS opal films were used as templates to prepare methylammonium lead halide photonic crystal thin films, which are also expected to possess a photonic stop band. For this, the templates 205-PS, 220-PS, 260-PS, and Mix-PS were infiltrated with a 1 M MAPbBr₃ precursor solution consisting of 1 M methylammonium bromide and 1 M PbBr₂ in DMSO via spin-coating, followed by drying at 60 °C in an ambient atmosphere. After drying and crystallization, the PS templates were removed selectively by immersing the samples in toluene at room temperature in air. The obtained MAPbBr₃ IO films are labeled as 205-MAPbBr₃, 220-MAPbBr₃, 260-MAPbBr₃, and Mix-MAPbBr₃, based on the size of the PS spheres. Representative SEM images (Figure 3) show the well-ordered IO structures of 205-MAPbBr₃, 220-MAPbBr₃, 260-MAPbBr₃, and the disordered structure of Mix-MAPbBr₃ (lower magnifications are given in Figure S4 in the Supporting Information). The 3D opal structure of the PS template is well-replicated by the perovskite material, which forms a honeycomb-like IO lattice in three dimensions. The cross-sectional SEM image of 220-MAPbBr₃ in Figure 3e shows that PS is completely removed in all layers of the IO upon treatment in toluene.

For photovoltaic application of OHP IO films, it is essential to fabricate IO films on conductive substrates such as FTO and TiO₂ deposited on FTO. Therefore, we also fabricated 220-MAPbBr₃ via an identical method on these substrates. Cross-sectional SEM images of 220-MAPbBr₃ prepared on FTO and TiO₂ deposited on FTO show a well-ordered IO structure and good contact to the substrates (Figure S5 in the Supporting Information). Furthermore, the IO films prepared on these substrates possess a pronounced photonic band gap with, compared to IO films prepared on glass, similar position and reflectivity, as diffuse reflectance spectra show (Figure S6 in the Supporting Information). The high reflectivities of ~55%

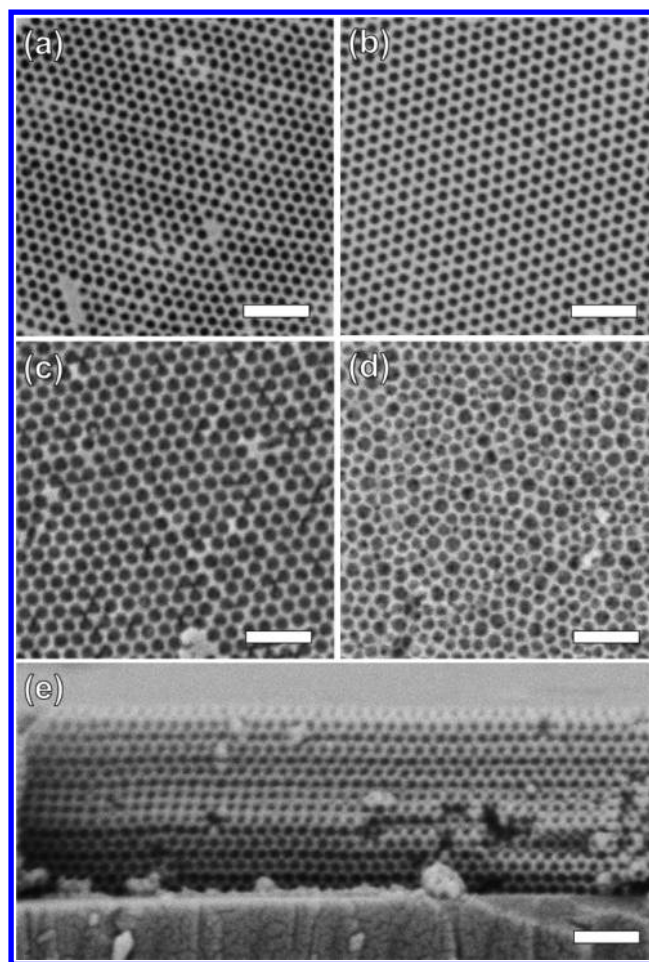


Figure 3. Representative SEM images of (a) 205-MAPbBr₃, (b) 220-MAPbBr₃, (c) 260-MAPbBr₃, and (d) Mix-MAPbBr₃; (e) cross-sectional image of 3- μm -thick 220-MAPbBr₃. Scale bar in each image is 1 μm .

indicate the presence of well-ordered IO domains for all three substrates.

The PS sphere sizes that were employed in this study were chosen to match the bandgap energy of MAPbBr₃ to make use of the slow-light effect at the bandgap region of MAPbBr₃. However, the synthetic protocol can generally be applied to other OHPs. To show the applicability of this method for the preparation of other OHP IO films, 220-PS was infiltrated with 1 M solutions of MAPbCl₃, MAPbCl_{1.5}I_{1.5}, and MAPbI₃ in DMSO, using the same aforementioned method. As SEM images (Figure S7 in the Supporting Information) show, these perovskites also form well-ordered IO films with large ordered domains. Grazing-incidence X-ray diffraction (GIXRD) analyses confirm the cubic phase of 220-MAPbBr₃ and 220-MAPbCl₃ and the tetragonal phase of 220-MAPbI₃. The diffractogram of 220-MAPbCl_{1.5}I_{1.5} shows a superposition of 220-MAPbCl₃ and 220-MAPbI₃, which indicates the coexistence of both species in the sample (see Figure 4).

The fabrication of IOs of most semiconductor materials as TiO₂,⁶³ WO₃,²⁸ and BiVO₄,⁴⁰ requires high-temperature treatment, which leads to shrinkage of the structure and, consequently, destruction of the periodic arrangement of the IO structure, which, in turn, strongly inhibits the formation of a photonic stop band. However, the crystallization of OHPs does not require treatment at high temperatures and the template

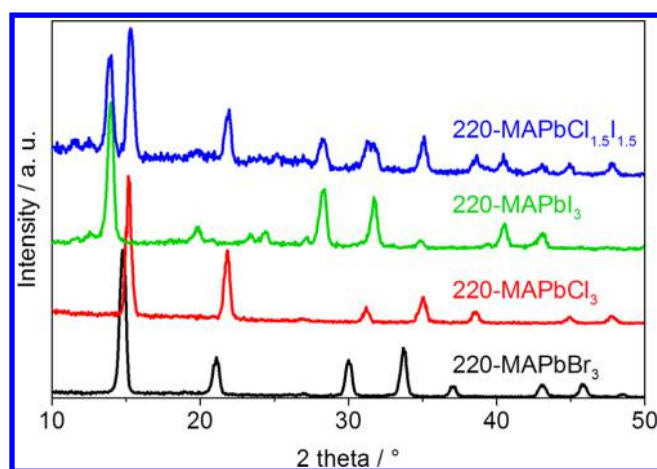


Figure 4. Grazing-incidence X-ray diffraction (GIXRD) patterns of 220-MAPbBr₃, 220-MAPbCl₃, 220-MAPbI₃, and 220-MAPbCl_{1.5}I_{1.5}; the spectra are offset along the y-axis for clarity.

can be efficiently removed by a solvent at room temperature. Consequently, no shrinkage of the structure occurs. This is evident from the linear shrinkage of the sphere diameter, which is <1%.

The absence of shrinkage yields highly ordered IOs displaying pronounced photonic stop bands above, overlapped with, and below the bandgap energy of MAPbBr₃ at ~435, 545, and 640 nm, respectively (see Figures 5a–c). In contrast, Mix-

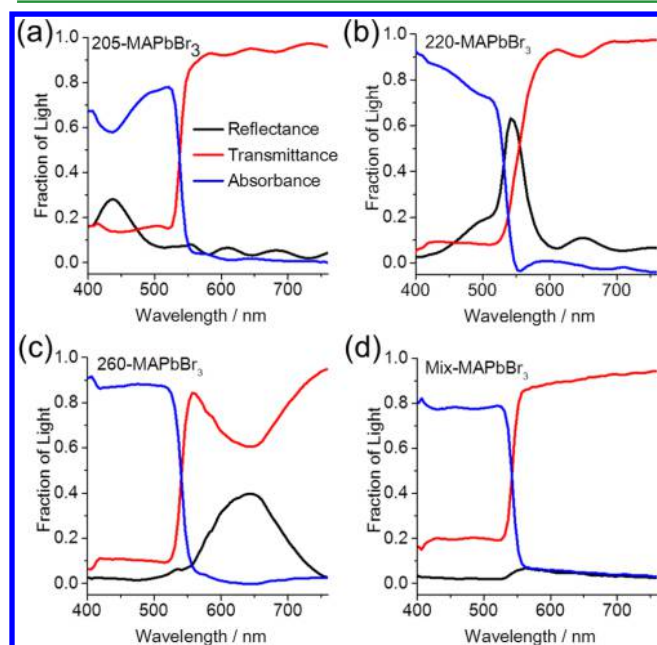


Figure 5. Microscale reflectance, transmittance/scattering, and absorbance spectra of (a) 205-MAPbBr₃, (b) 220-MAPbBr₃, (c) 260-MAPbBr₃, and (d) Mix-MAPbBr₃ measured in an integrating sphere.

MAPbBr₃ does not show a photonic stop band (see Figure 5d). Compared to the other IOs, 205-MAPbBr₃ possesses a less-pronounced reflectance peak, which can be attributed to the strong absorbance of MAPbBr₃ in this spectral region, which prohibits light propagation through deeper layers of the IO structure. Furthermore, light reflected by the photonic stop

band at 435 nm is being absorbed by MAPbBr₃ before it can exit the material.

In devices, enhanced incident photon-to-current efficiency (IPCE) is expected when the photonic stop band is slightly blue-shifted from the bandgap energy so that slow-light is present at the weakly absorbing bandgap region of the high-index medium. The bandgap energy of MAPbBr₃ is 2.2–2.3 eV (i.e., 565–540 nm). Thus, at normal incidence, 220-MAPbBr₃ possesses a photonic stop band within the bandgap energy. Angle-dependent reflectance measurements of this sample were recorded between 0 and 60° at 2.5° intervals and show the expected blue-shift of the photonic stopband at increasing angles of the incident light (Figure 6a). The stop band position

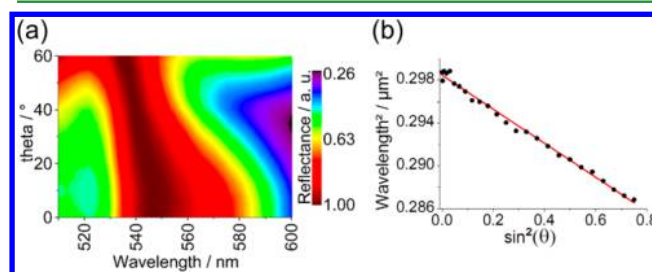


Figure 6. (a) Angle-dependent reflectance of 220-MAPbBr₃ (normalized to the reflectance at the stopband maximum), and (b) linearized plot of the stop band maximum between 0° and 60° with a linear regression line (shown in red).

hypsochromically shifts from 547 nm at normal incidence to 535 nm at an angle of 60°, meaning that the stop band shifts through the bandgap energy of MAPbBr₃. Figure 6b shows the linear dependence between the square of the stop band wavelength and the square sine of the incident angle, as expected from the modified Bragg law.

CONCLUSION

In summary, we have demonstrated a facile protocol to fabricate methylammonium lead halide inverse opal thin films with controllable thicknesses comparable to that relevant for organometal lead halide solar cells on glass, fluorine-doped tin oxide, and TiO₂ substrates. The prepared three-dimensional (3D) photonic crystals possess large ordered domains and pronounced photonic stop bands, whose position can be tuned by adjusting the diameter of the polystyrene spheres employed as the template and by changing the angle of the incident light, as angle-dependent reflectance measurements show. By changing the halide groups, the composition, crystal structure, and bandgap of the perovskite photonic crystal thin films could be also straightforwardly tuned. The prepared IO organometal halide perovskite photonic crystal films could lead to improved perovskite-based solar cells by replacing the dense perovskite layer by an IO structured layer to employ the slow-light effect for light harvesting applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b09227.

SEM images of 205-PS, 220-PS, 260-PS, and Mix-PS; cross-sectional SEM images of 220-PS with different thicknesses; angle-dependent stopband maximum position of PS opal films; representative SEM images of

MAPbBr₃ inverse opals; cross-sectional SEM images of 220-MAPbBr₃ on FTO and TiO₂/FTO substrates; diffuse reflectance UV-vis spectra of 220-MAPbBr₃ on glass, FTO, and TiO₂/FTO; XRD patterns of 220-MAPbBr₃, 220-MAPbCl₃, 220-MAPbI₃, and 220-MAPb-Cl_{1.5}I_{1.5} (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PS, polystyrene; MA, methylammonium; IO, inverse opal; OHP, organometal halide perovskite

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