

Perovskites

Morphology-Controlled Synthesis of Organometal Halide Perovskite Inverse Opals

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Abstract: The booming development of organometal halide perovskites in recent years has prompted the exploration of morphology-control strategies to improve their performance in photovoltaic, photonic, and optoelectronic applications. However, the preparation of organometal halide perovskites with high hierarchical architecture is still highly challenging and a general morphology-control method for various organometal halide perovskites has not been achieved. A mild and scalable method to prepare organometal halide perovskites in inverse opal morphology is presented that uses a polystyrenebased artificial opal as hard template. Our method is flexible and compatible with different halides and organic ammonium compositions. Thus, the perovskite inverse opal maintains the advantage of straightforward structure and band gap engineering. Furthermore, optoelectronic investigations reveal that morphology exerted influence on the conducting nature of organometal halide perovskites.

Organometal halide perovskites (OHP) have attracted intense attention in the field of photovoltaics, with continuous progress on improvements to their solar-to-electric power conversion efficiency.^[1] The low cost and facile solution processing of this hybrid semiconductor has opened up bright prospects for clean and sustainable energy production using OHPs. Meanwhile, the inherent advantages of OHPs, such as band gap engineering capabilities,^[2] high fluorescence quantum yield,^[3] long carrier lifetimes, and low non-radiative recombination rates,^[4] make it promising for applications in optical and optoelectronic fields.^[5] Investigations on the properties of OHP demonstrated that the morphology and crystallinity play a central role in the device performance.^[6] For instance, the crystallinity and grain size have an effect on the carrier mobility and thus the performance of the solar cell.^[7] Consequently, exploration of novel morphologies and the development of a universal method for structure and morphology control will pave the way not only for improving the OHP performance in the aforementioned applications, but equally for exploring unprecedented applications. However, the low thermal stability of OHPs arising from its organic composition,^[8] its rapid reaction between the lead(II) halide and ammonium salts,^[9] and the restructuring in the presence of trace water,^[10] make control of the OHP morphology highly challenging. Although a few examples have been reported,^[11] OHPs with high hierarchical architecture prepared by a universal and scalable method has yet to be addressed.

Inverse opals, the replicas of opals, consist of an ordered array of regular interspace surrounded by solid materials accompanied by a uniform alternation of low and high refractive index area. This kind of material can be fabricated by colloidal crystal templating using well-defined particles as hard templates. Subsequent to assembly and infiltration of the voids of the three-dimensional(3D) template, drying and template removal steps, inverse opal structure can be obtained. The inverse opal structure provides several benefits for different applications. On one hand, the porous structure of the inverse opal provides a larger surface area than the bulk counterpart. On the other hand, the periodicity of the refractive index affects the propagation of electromagnetic waves in the material and results in a photonic band gap owing to the Bragg reflections on the lattice.^[12] Thus, the unique structure of the inverse opal increases the active sites and optical path as well as enhances the light scattering and absorption.^[13] Utilization of the inverse opal structure has displayed enhanced performance in solar cells,^[14] photocatalysis,^[15] and sensors^[16] and energy storage.^[17] Moreover, the inverse opal morphology may also increase the modulation speeds of semiconductor laser^[18] and enhance the light outcoupling in OLED device.^[19] Fabricating OHP in inverse opal morphology may improve the performance of OHP material in solar cells, lasers, and OLEDs.

Herein, we report a method for preparing OHP materials in the form of inverse opals using a colloidal crystal templating route (Scheme 1; for experimental details, see the Supporting Information). Briefly, polystyrene (PS) microspheres were centrifuged to fabricate the artificial opal template. After drying, the template was immersed into a dimethyl sulfoxide (DMSO) solution containing a 1:1 stoichiometric ratio between CH_3NH_3Br and $PbBr_2$. The



Scheme 1. Preparation route of OHP inverse opals.

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DMSO was evaporated under vacuum and the obtained lightorange color composition indicated formation of CH₃NH₃PbBr₃. Finally, the polystyrene was selectively removed with toluene and the perovskite inverse opal was collected by centrifugation. The method is very flexible and can be applied to the other perovskite inverse opals, for example the methylammonium (MA) cation can be replaced by formamidine (FA) or cesium (Cs) while the bromide anion can be replaced by other single halide anions or halide mixture. As a result, the method maintains the straightforward band gap engineering properties of the OHP. Moreover, the halide perovskite opal shows a sensitive and stable photoresponse, which demonstrates its potential for applications in photovoltaic and optoelectronic devices.

The assembly of the colloidal particles and formation of the artificial opal template was accomplished with centrifugation^[20] using PS microspheres with different diameters (515, 375, and 125 nm). As seen in Figure 1 a (see the Supporting Information, Figure S1 at lower magnification for larger area), typical scanning electron microscopy (SEM) images of assembled PS spheres show 3D ordered structure and the facets of a face-centered cubic structure.^[21] In the infiltration process, DMSO was selected owing to its incompatibility with polystyrene but good compatibility with the halide perovskite at low temperatures. Because DMSO can also dissolve polystyrene and destroy the template at high temperatures, the removal of DMSO was conducted under vacuum at 60 °C for 3 h to obtain the crystallized OHP. Upon DMSO removal, a color change from white to light-orange was observed,



Figure 1. a) SEM images of artificial opal template of polystyrene (PS; 515 nm). Scale bar: $2 \mu m$. b)–d) HR SEM images of MAPbBr₃ inverse opal with b) 515, c) 375, and d) 125 nm PS microspheres as a template. Scale bars: b) 400 nm, c) 200 nm, d) 100 nm. e), f) HR cross-section images of MAPbBr₃ inverse opal with e) 515 nm and f) 375 nm PS microspheres as template. Scale bars: 200 nm in both (e) and (f).

indicating the formation of OHP. After removing the template, the perovskite inverse opal replicate with an ordered structure was obtained (Figure 1b-d). The crosssection images confirmed the topological interconnection of the inner voids (Figure 1 e,f). Moreover, the morphology directly correlated with the nature of the artificial template. As the diameter of the microsphere decreased to 375 nm, the void sizes and the wall thickness also decrease. In the infiltration process, the different concentrations of perovskite precursor (0.5, 0.9, 1.4, and 1.8M) in DMSO solution were screened to optimize the templating process. An inverse opal structure could not be obtained using the low concentration of 0.5 M, while higher concentrations of 1.4 and 1.8 M increased the fraction of non-structured solid. The best inverse opal structure was obtained with the solution containing 0.9 M PbBr₂ and MABr (Supporting Information, Figure S3). The colloidal crystal templating process for obtaining the perovskite structure has fast infiltration and crystallization steps, which probably results in polycrystalline structures since the construction of single crystalline materials needs much longer drying time.^[22] To check the polycrystallinity, the material was further investigated with TEM, where the well-organized inverse opal structure could be observed at lower magnification (Supporting Information, Figure S4). However, using higher magnification to determinate the crystallinity caused beam damage and the inverse opal structure was partly destroyed. The 3D porous structure increased the sensitivity of the perovskite structure to decomposition by the higher applied voltage. Energy-dispersive X-ray (EDX) spectra confirmed the 1:3 stoichiometric ratios between lead and bromide (Supporting Information, Figure S5). Compared with the bulk material, the MAPbBr3 inverse opal showed a circa 0.1 eV enhancement of the band gap, which can be attributed to the well-known limitation of the 3D length (Supporting Information, Figure S6).^[23]

The band gap of the halide perovskite can be easily manipulated by adjusting the halide composition, which is very important for using OHP as light absorber and emitter materials. To test the compatibility of our method with this advantage, the perovskite materials with single halides or halide mixture were prepared. Because lead iodide can form a stable complex with DMSO,^[9] the perovskite with iodide composition needed to be annealed at 100 °C to obtain the crystalline material. Typical SEM images provided direct evidence for the feasibility of preparing OHP inverse opal with other halides and mixtures of halides (Supporting Information, Figures S7, S8). EDX spectra confirmed the composition of OHP with different halides (Supporting Information, Figure S9). X-ray powder diffraction (XRD) patterns (Figure 2a,b) confirmed the cubic phase of MAPbCl₃, MAPbBr₃, MAPbBr_{1.5}Cl_{1.5}, and MAPbBr_{1.5}I_{1.5}. MAPbI₃ showed a mixture of cubic and tetragonal phases. For MAPbBr_{1.5}Cl_{1.5} and MAPbBr_{1.5}I_{1.5}, the diffraction peaks were in the middle of the peaks observed for the two end members MAPbCl₃ and MAPbBr₃, or MAPbI₃ and MAPbBr₃, respectively, indicating the solid-solution formation. However, the diffraction peaks of MAPbI₁₅Cl₁₅ displayed a superposition of the individual MAPbCl₃ and MAPbI₃ patterns, indicating this composition was a mixture

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Figure 2. a) XRD patterns of OHP inverse opals with different composition of halides; b) The enlarged XRD pattern between 13° and 17°; c) diffuse reflectance spectra and Tauc plots of OHP inverse opals with different compositions of halides.

of these phases, rather than a solid solution. To further confirm the coexistence of different phases, the perovskite inverse opal with different Cl/I composition ratios were prepared and XRD patterns exhibited that the intensity of the same lattice plane depends on the Cl/I composition (Supporting Information, Figure S10). This observation can be attributed to the unstable structure when chloride replaces the equatorial iodine in the PbI₆^{4–} block.^[24] Moreover, the diffuse reflectance spectra also corroborated the XRD observations. The spectra of MAPbI1.5Cl1.5 showed two humps near to MAPbCl₃ and MAPbI₃, respectively, confirming the mixture of different phases (Figure 2c). Using the Kubelka-Munk equation to determine the band gap, the band gaps for MAPbBr_{1.5}Cl_{1.5} and MAPbBr_{1.5}I_{1.5} were in between the two individual species respectively, which demonstrates that the morphology-control method is compatible with the straightforward engineering of the OHP band gap (Figure 2d).

To demonstrate the universality of the preparation method, other perovskite inverse opals were also prepared. Formamidine perovskites have high thermal stability and have the optimum band gap for single-junction solar cells.^[8] Cesium perovskites were recently exhibited as novel optoelectronic materials owing to their high quantum yield and wide color spectrum.^[25] The SEM images and EDX spectra exhibited that our method was feasible when formamidine or cesium replaced methylammonium (Supporting Information, Figures S9 and S11). XRD patterns confirmed the cubic phase of FAPbBr3 and orthorhombic phase of CsPbI3 (Supporting Information, Figure S12).^[26] The band gap of FAPbBr₃ is smaller than MAPbBr3 owing to the larger size of formamidine than methylammonium (Supporting Information, Figure S13). The yellow color of CsPbI₃ also indicated the presence of the orthorhombic phase.^[27] Meanwhile the absorption onset of the Tauc plot (Supporting Information, Figure S14) was at 1.70 eV, which is consistent with the known value.^[26]

One of the main bottlenecks of OHP materials is their instabilities. The stability of the OHP inverse opal was also investigated. After their preparation, the samples were stored in covered glass vials for one month at room temperature under ambient conditions and characterized using several analytic techniques. The SEM image and diffuse reflectance spectra of MAPbBr₃ inverse opal did not display any significant change in morphology and absorption properties. However, XRD patterns of fresh and stored samples displayed a slight change between different peak intensity ratios (Supporting Information, Figures S15, S16). The iodide counterpart showed a more pronounced change in morphology, diffuse reflectance spectrum, and XRD patterns (Supporting Information, Figures S17, S18). Our observation is consistent with that of the OHP material with high content of bromide showing higher stability than the iodide counterpart both under ambient atmosphere and in the presence of moisture.^[28] The sample should be kept in dry inert atmosphere for longer storage times. The different stability between MAPbBr₃ and MAPbI₃ is related to the difference in bond strength and crystalline forms.^[29]

Photoconductivity is one of the most crucial properties of OHP materials for the applications in solar cells, lasers, lightemitting diodes, photodetectors, and other optoelectronic devices. Thus, the optoelectronic performance of the MAPbBr₃ and MAPbI₃ inverse opals were investigated. Upon illumination with a solar simulator lamp, the MAPbI₃ inverse opal displayed a linear relationship under scanning from -2 V to 2 V. Clear enhancements in current with light intensity are observed (Figure 3 a). The slope of the *I-V* curve represents the transconductance (g_m) of the OHP layer.^[30] The ratios of transconductance obtained at different light intensities (25.5, 17.1, 13.8, and 6.9 mWcm⁻²) and that in darkness for MAPbI₃ inverse opals was 57.8, 47.8, 45.0, and



Figure 3. a) Typical *I-V* curves and b) photocurrent of MAPbI₃ inverse opal under different light intensities with 1 V applied bias. c) Typical *I-V* curves of crushed inverse opal and d) the plot of transconductance ratio (g_m/g_d) versus light intensity. g_m , transconductance under the light intensity *m*; g_d , transconductance in darkness.

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31.8. The *I-V* curves of MAPbBr₃ inverse opal also displayed a linear relationship (Supporting Information, Figure S19). The transconductance ratios for MAPbBr₃ inverse opal were 17.8, 13.6, 11.2, 4.2, indicating a less sensitive to illumination than MAPbI₃ (Figure 3d).

Both MAPbBr₃ and MAPbI₃ generated stable photocurrents under light illumination (Figure 3b; Supporting Information, Figure S19b). When the cycles were repeated 50 times, the photocurrents displayed excellent reproducibility (Supporting Information, Figure S20). Even when the time was extended to 3 h, the OHP inverse opal still showed a stable response (Figure S21), which demonstrated the good photostability of the perovskite inverse opals. To test the morphology effect on the optoelectronic properties, the OHP inverse opal was pressed to crush the 3D ordered porous structure (Figure S22). The I-V curves of crushed samples displayed the nonlinear relationship of semiconductor diode (Figure 3c; Supporting Information, Figure S23). The nonlinear relationship was even more pronounced in the bulk counterpart (Supporting Information, Figure S24). OHPs possess mixed ionic/electronic conducting nature.^[31] OHP inverse opal exhibited electronic conductivity, while the crushed sample and also the bulk material exhibited predominantly ionic conductivity from halide vacancies. Such a difference can be attributed to the morphology effect. Previous studies found that when oxygen is incorporated into OHPs to fill halide vacancies, the material displayed Ohmic behavior.^[31] Owing to the higher surface area of the OHP inverse opal, trace oxygen can be more effectively incorporated into the material, giving rise to predominantly electronic conductivity in the OHP inverse opals.

In summary, a facile colloidal crystal templating method has been established for preparing organometal halide perovskites (OHP) in inverse opal morphology. Our method is not only feasible with a series of OHP compositions, but it also satisfies the requirement for scalable fabrication (Supporting Information, Figure S25). In principle, the method can also be applied to other morphologies by controlling the structure of the polystyrene-based template. The OHP inverse opal is compatible with the advantage of straightforward band gap engineering and keeps the sensitive photoconductivity properties. Combining the advantages of OHP and inverse opal, the novel OHP inverse opals could be attractive materials in the field of heterogeneous photocatalysis and perovskite solar cell. The construction of devices for the perovskite solar cell is in progress.

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