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Full Length Article

# Infiltration of methylammonium metal halide in highly porous membranes using sol-gel-derived coating method

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ABSTRACT

Organic–inorganic halide perovskites (OIHPs) has emerged as promising optoelectronic materials for solar cells and light-emitting diodes. OIHPs are usually coated on a flat surface or mesoporous scaffold for the applications. Herein, we report a facile sol-gel-derived solution route for coating methylammonium lead iodide ($MAPbI_3$) perovskite layers onto various nanoporous structures. We found that lead-acetate solution has superior infiltration property onto surface of oxide membranes, and it can easily be converted to $MAPbI_3$ by sequential transform to PbO, $PbI_2$, and finally $MAPbI_3$. Excellent pore-filling and full coverage of the nanostructures with the final $MAPbI_3$ perovskite material are demonstrated via this sol-gel-derived solution route, using mesoporous $TiO_2$, $TiO_2$ nanorods, and high-aspect ratio nanopores in anodic aluminum oxide membranes. Given that this sol-gel-based method fills nanopores better than other conventional coating methods for OIHPs, this method may find wide applications in nanostructured OIHPs-based optoelectronic systems.



## 1. Introduction

Organic–inorganic halide perovskites (OIHPs) have been spotlighted as promising optoelectronic materials since methylammonium lead iodide ($CH_3NH_3PbI_3$; $MAPbI_3$), one of the OIHPs that has a perovskite crystal structure, was adopted as a light-absorbing (and/or charge-transport) material of organic-inorganic hybrid solar cells [1]. $MAPbI_3$ has large light-absorption coefficients ($\sim 10^5$ cm$^{-1}$ at 550 nm) owing to its direct bandgap ($\sim$1.55 eV) [2], where intramolecular charge transfer occurs between high-density orbitals in valence (Pb *s* and I *p* orbitals) and conduction (Pb *p* orbitals) band edges [3,4]. Moreover, $MAPbI_3$ easily produces free charges because of its weak exciton binding energy and has good ambipolar charge-transport characteristics, with electron and hole mobilities of $\sim$7.5 and $\sim$12.5 cm$^2$ V$^{-1}$ s$^{-1}$, respectively [5]. The outstanding optoelectronic properties of OIHPs enable their successful application in perovskite solar cells (PSCs) [6,7], solar-water splitting [8], lasing [9], and light-emitting diodes [10].

For most of these applications, nanometer-scale OIHP layers, such as nanoshells over nanoparticles (NPs) [11] or thin films filling mesoporous (mp) structures [12], are necessary. Especially in PSCs, the full surface coverage and jam-full pore filling with an OIHP over/into nanostructured electron transport layer is of great importance for the device performance [13,14]. Such nano-OIHP layers are mainly fabricated via solution processes. Various spin-coating-based solution processes, such as two-step [14–16], anti-solvent treatment [17,18], and ion-exchange methods [19,20], have been developed. However, these methods are optimized for PSCs and not for other nanostructures, such as one-dimensional nanorods (NR) or deep pores with a high aspect ratio, which may be useful for other applications in the near future. Besides, there are several vapor deposition methods, including evaporation [21] and atomic layer deposition (ALD) [22]. However, evaporation can only be used for making planar-type films, owing to the non-conformal step coverage and the shadow effect, and ALD requires considerable time and cost to form an OIHP film with a sufficient thickness, although it can produce high quality OIHP nanoshells on nanostructures. Therefore, well-established solution processes are presently considered to be the best methods for achieving high-performance devices at a low cost.

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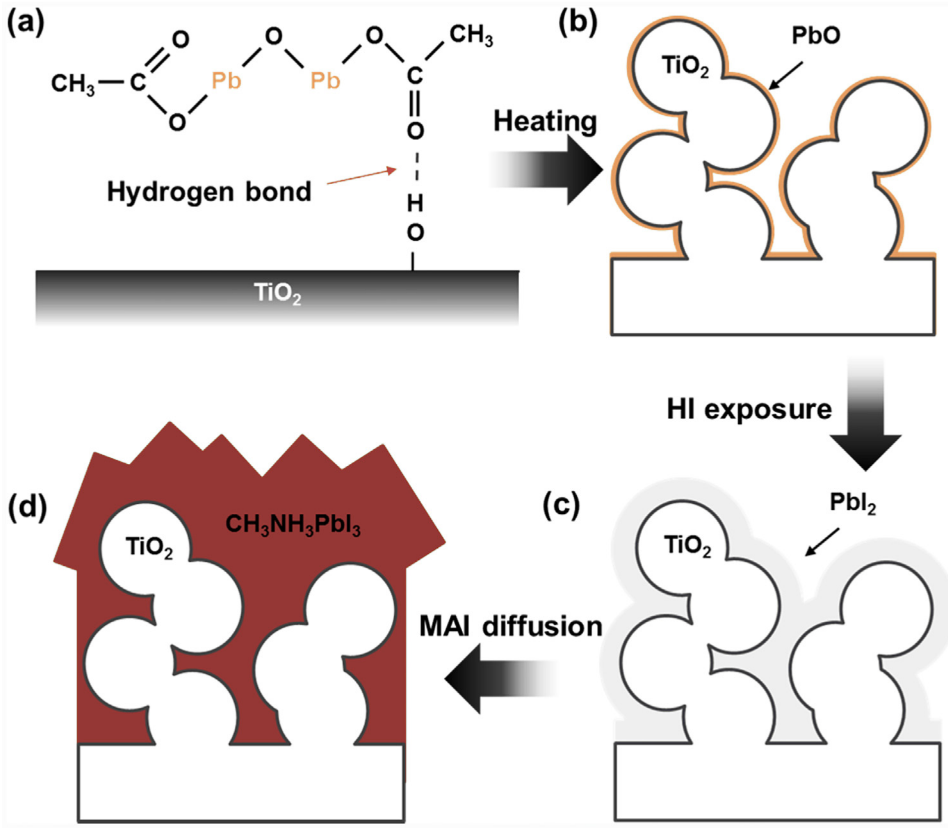


**Fig. 1.** Schematic illustration of the sol-gel-based process for $MAPbI_3$ coating. Process: (a) precursor coating, (b) PbO nanoshell formation, (c) transformation of PbO to $PbI_2$ via ion exchange, and (d) formation of $MApbI_3$ via reaction of MAI and $PbI_2$.

To fabricate nano-OIHP layers on nanostructured membranes via a solution process, sufficient infiltration of precursor materials into the nanostructures must be achieved before the reaction among the materials. In this aspect, the sol-gel method, a facile classical solution process, is a suitable process to produce a full-filling OIHP layer. The sol-gel method is a low-cost process and is suitable for mass production via large-area coating [23–26]. Moreover, large variety of choice for solute and solvent guarantees the successful setup of an efficient route.

Herein, we report a sequential solution route, starting from a sol-gel-processed PbO coating, to fabricate a uniform $MAPbI_3$ film that fully covers and completely fills various nanostructured membranes, such as a $TiO_2$ mp film, $TiO_2$ NRs, and porous anodic aluminum oxide (AAO). Excellent pore filling of the sol-gel-processed films compared with films fabricated via other solution processes is confirmed by compositional and morphological analyses.

## 2. Experiments

### 2.1. Chemicals and materials

Lead acetate trihydrate (99%) and 2-methoxyethanol (2ME, ≥99%) were purchased from Duksan and Acros, respectively. Ethanol (99.5%) and 2-propanol (99.5%) were purchased from Dychemi and Sigma-Aldrich, respectively. Monoethanolamine (MEA, ≥98%), hydroiodic acid (HI, 57 wt% in $H_2O$) and titanium tetra-isopropoxide (TTIP, 97%) were purchased from Sigma–Aldrich. $TiO_2$ NP (20 nm) paste for the mp-$TiO_2$ film was purchased from Dyesol and diluted with ethanol before use. Methylamine iodide (MAI, 99.5%) and $PbI_2$ (99.99%) were purchased from Xi'an and Alfar Aesar, respectively. *N,N*-Dimethylformamide (DMF,

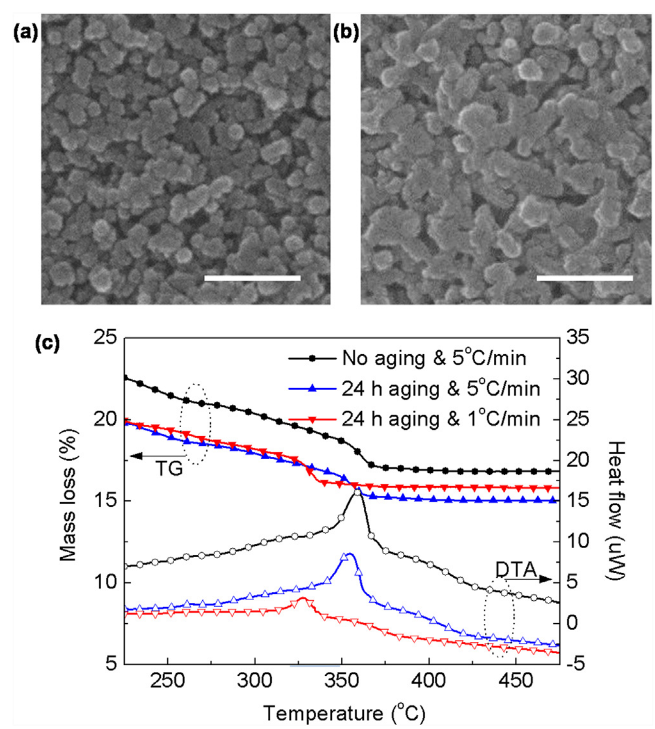


**Fig. 2.** Scanning electron microscopy (SEM) images for (a) pristine and (b) PbO-coated mp-$TiO_2$. Scale bars: 200 nm. (c) Thermogravimetric analysis (TGA, left axis) and differential thermal analysis (DTA, right axis) results for lead acetate-based films.