Formation of new perovskite nanostructures templated by porous silicon

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Introduction

A recent and promising development in solar energy involves a class of materials known as organometal halide perovskites, capable of efficiencies (>20%) comparable to the current industry standard of silicon. [1] These materials also demonstrate strong light emission, a key property associated with energy-efficient sources of lighting, suggesting potential applications in light-emitting devices such as light-emitting diodes (LED). [2] The goal of this project was to investigate the fundamental photoluminescence (PL) properties of perovskites housed in a nanoporous material known as semiconducting porous silicon (pSi). Porous silicon acts as a template for the formation of small nanostructures of perovskites; it also can possibly provide a matrix for long-term environmental stabilization of the perovskite.

Methods and Materials

In addition to acting as a template, pSi is an electrically-responsive host matrix, ideally regulating the flow of charge to/from the perovskite. Samples were prepared within the pores of surface oxidized pSi and hydride-terminated pSi, each with a mesoporous width in the 5 – 50 nm range. This research thus far has focused on methylammonium lead iodide ($MAPbI_3$) perovskite. The preparation of the perovskite precursor is described by the following chemical equation:

$$CH_3NH_3I + PbI_2 \rightarrow CH_3NH_3PbI_3$$

A precursor solution was prepared containing PbI_2 (200 mM) and CH_3NH_3I (200 mM) dissolved in dimethylformamide (DMF). The perovskite-loaded pSi was fabricated through solution-loading of the above perovskite precursor solution into warmed pSi (60ºC), removal of excess reactant solution, and drying. In a final processing step, samples were heated for 1 hr at 95ºC. Perovskite microwires were prepared by depositing perovskite precursor on a FTO glass substrate and allowing to air dry.

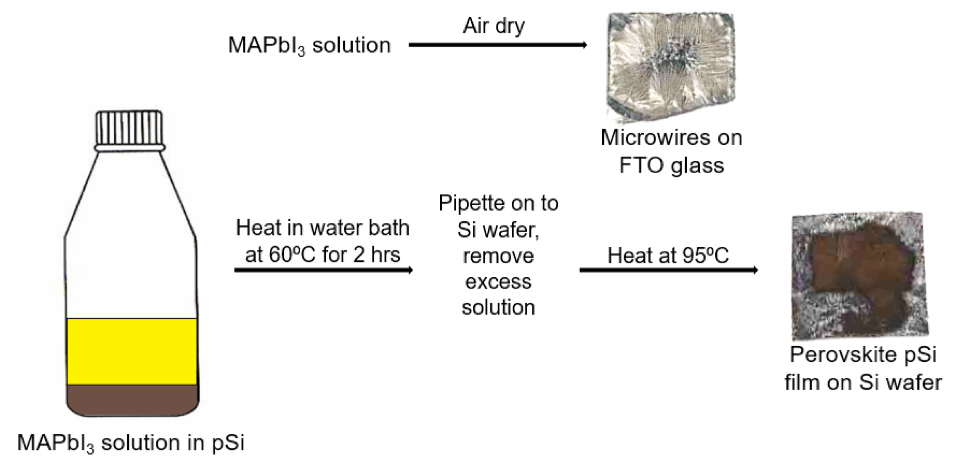


Figure 1. Visual representation of fabrication of $MAPbI_3$ perovskite microwires and loaded pSi.

Following synthesis, the stability of each prepared sample was monitored for 3 weeks through tracking its relative photoluminescence (PL) intensity at its maximum value.

Results

(I.) Scanning Electron Microscopy (SEM) Analysis of porous Si

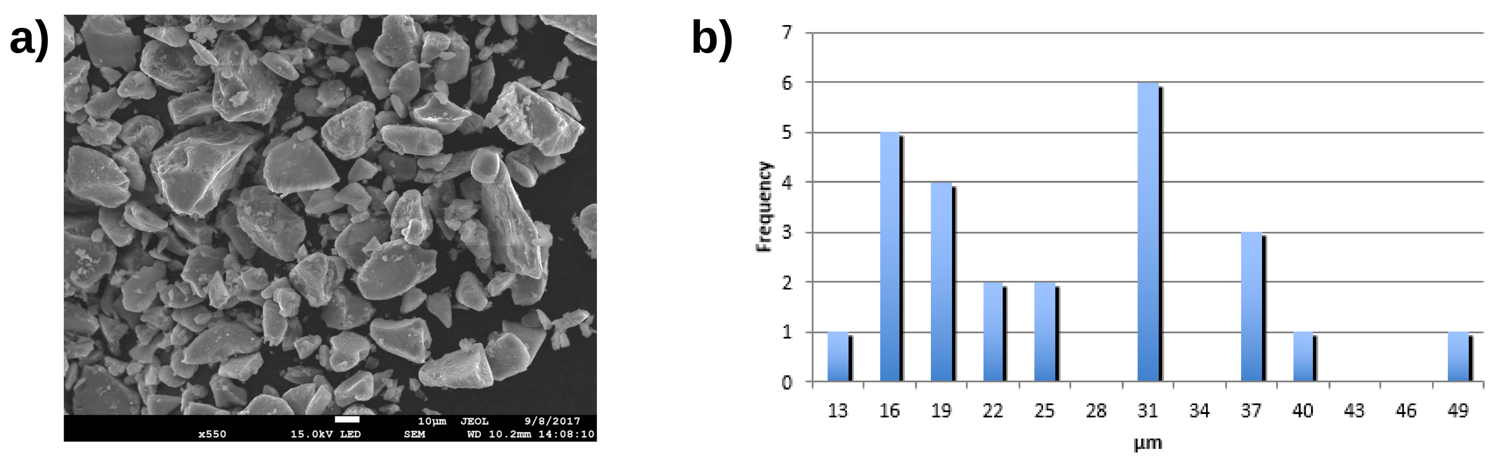
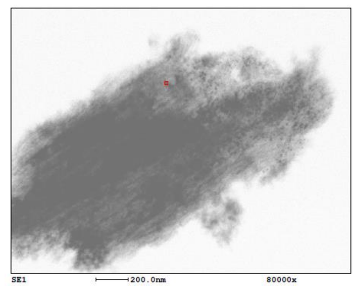


Figure 2. (a) Representative SEM image of porous silicon host morphology in surface hydride-terminated pSi (scale bar = 10 µm) and its (b) corresponding particle size distribution (µm).

(II.) Energy-Dispersive X-Ray (EDX) Spectroscopy Analysis



a)

b)

EDS Quantitative Results		
Element	Wt%	At%
O (K)	25.99	46.62
Si (K)	48.19	49.25
Pb (M)	19.51	2.70
I (L)	6.31	1.43

c)

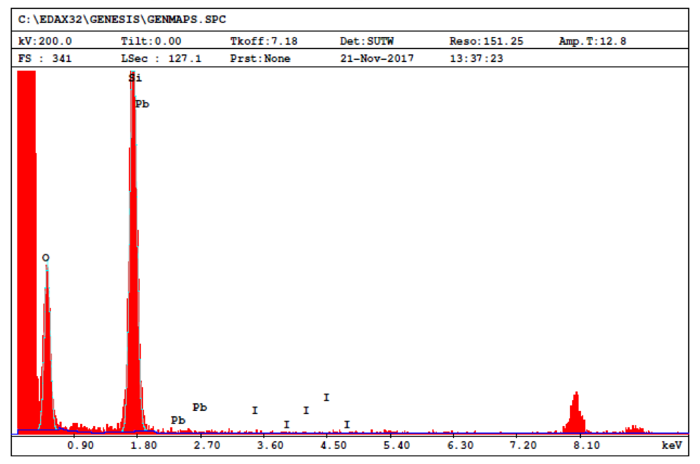


Figure 3. (a) TEM of $MAPbI_3$ perovskite in oxidized pSi imaged to calculate (b) associated Wt and At % of O, Si, Pb, and I in a typical sample, and (c) EDX spectrum for the sample.

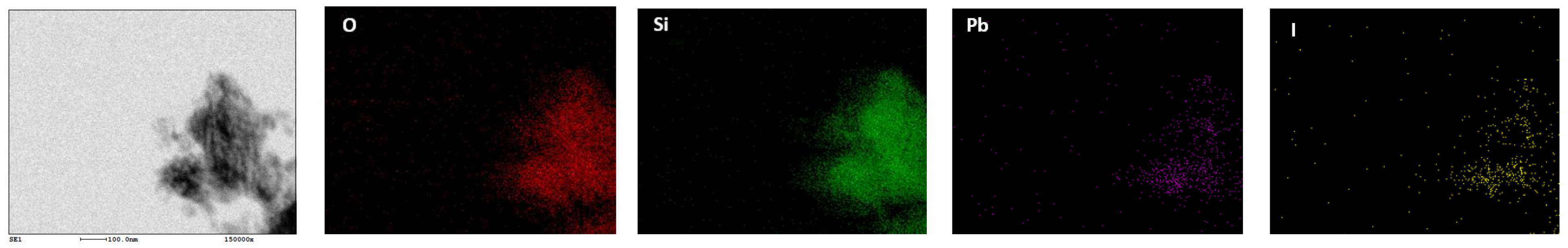


Figure 4. TEM image with corresponding EDX maps of O, Si, Pb, and I.

(III.) X-Ray Powder Diffraction (XRD) Analysis

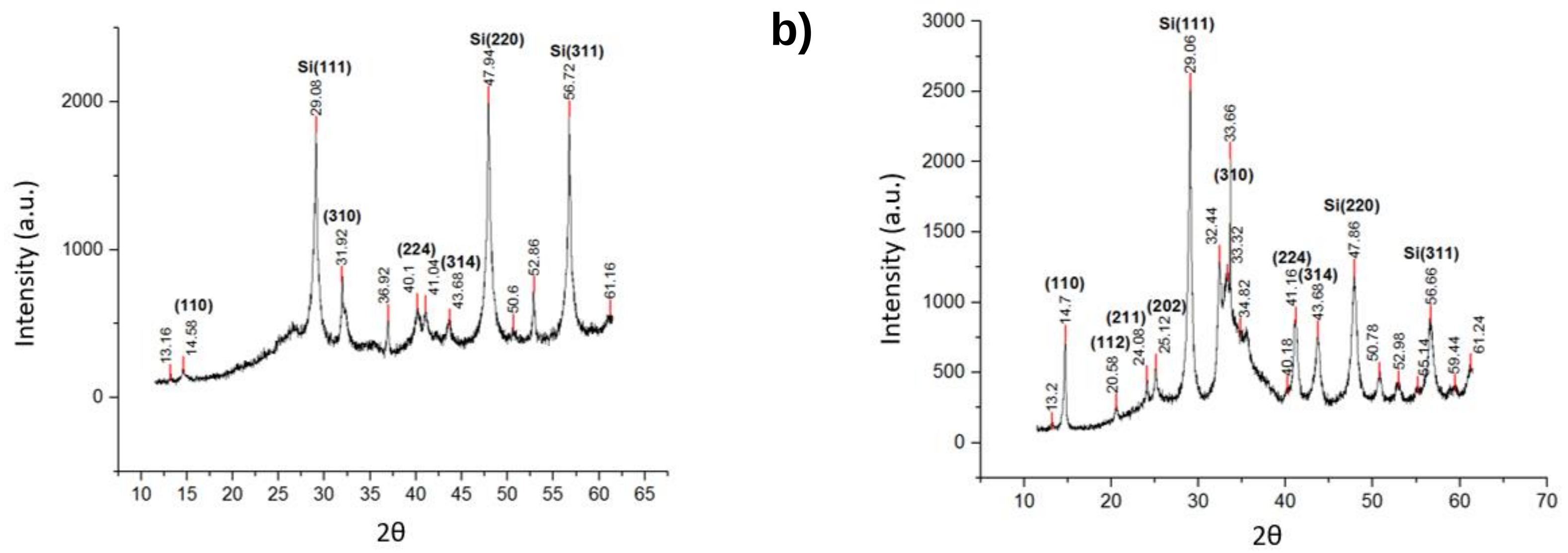


Figure 5. XRD spectra of $MAPbI_3$ perovskite in (a) hydride-terminated pSi and (b) oxidized pSi with corresponding tetragonal crystal structures for the perovskite.

Results (cont.)

(IV.) Photoluminescence (PL) Analysis

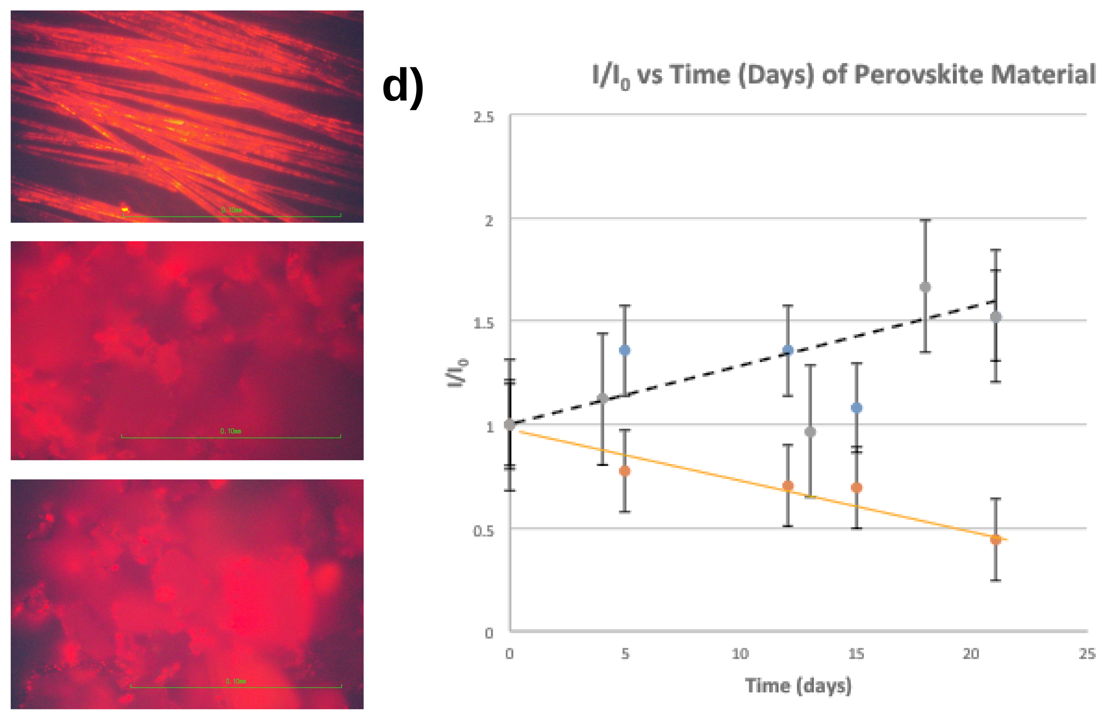


Figure 6. Fluorescence imaging at 60X of (a) perovskite microwires, (b) perovskite in hydride-terminated pSi, and (c) perovskite in oxidized pSi. Figure 6d shows normalized fluorescence intensity of perovskite in microwires, hydride-terminated pSi, and oxidized pSi as a function of time.

Conclusions

In this study, TEM imaging showed the presence of small perovskite nanocrystals whose composition was consistent with the formation of perovskite within the porous Si matrix (EDX spectroscopy). It was also found that the emission intensity for $MAPbI_3$ formed within hydride-terminated pSi (at ~730 nm) and oxidized pSi (at ~740 nm) were relatively stable over a 3 week period, but the emission intensity for perovskite microwires formed in the absence of any pSi template actually decreased over time.

Future Work

More detailed measurements of the long term stability of these new nanoscale materials are currently under evaluation. A range of porous silicon materials along with variation in perovskite composition will be measured.

References

[1] S.D. Stranks, H.J. Snaith, Nat. Nanotechnol. **10**, 391 (2015).

[2] N. Aeineh, E.M. Barea, A. Behjat, N. Sharifi, and I. Mora-Seró, ACS Applied Materials & Interfaces **9**, 13181 (2017).

Acknowledgements

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