A hole-conductor–free, fully printable mesoscopic perovskite solar cell with high stability
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We fabricated a perovskite solar cell that uses a double layer of mesoporous TiO$_2$ and ZrO$_2$ as a scaffold infiltrated with perovskite and does not require a hole-conducting layer. The perovskite was produced by drop-casting a solution of PbI$_2$, methylammonium (MA) iodide, and 5-ammoniumvaleric acid (5-AVA) iodide through a porous carbon film. The 5-AVA templating created mixed-cation perovskite (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ crystals with lower defect concentration and better pore filling as well as more complete contact with the TiO$_2$ scaffold, resulting in a longer exciton lifetime and a higher quantum yield for photoinduced charge separation as compared to MAPbI$_3$. The cell achieved a certified power conversion efficiency of 12.8% and was stable for >1000 hours in ambient air under full sunlight.

We introduced the 5-AVA cation into the perovskite lattice with a mixture of MA and 5-AVA in the precursor solution that maintained a 1:1 molar ratio of organic ammonium cations and PbI$_2$. The optimal molar ratio of ammonium cations in (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ was determined to be between 1:20 and 1:30. The x-ray diffraction (XRD) patterns of neat MAPbI$_3$ and (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ infiltrated into the mesoporous ZrO$_2$/TiO$_2$ film are compared in Fig. 2. The newly emerging diffraction peaks arising from the (001) and (111) lattice planes for (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ are much stronger than the corresponding ones for MAPbI$_3$. And even at low 5-AVA/MA molar ratios, 5-AVA substantially increases the $b$ and $c$ lattice parameters. The large expansion of the $c$ axis induced by 5-AVA indicates its preferential alignment along this axis through contact with lead and

A schematic drawing showing the cross section of the triple-layer perovskite-based fully printable mesoscopic solar cell. The mesoporous layers of TiO$_2$ and ZrO$_2$ have thicknesses of ~1 and 2 μm, respectively, and are deposited on a FTO-covered glass sheet in blue and gray. They are infiltrated with perovskite by drop-casting from solution. (B) Energy band diagram of the triple-layer device. Energies are expressed in electron volts, using the electron energy in vacuum as a reference. The energy levels of the conduction band edges of TiO$_2$, ZrO$_2$, and MAPbI$_3$ are at ~4.0, ~3.4, and ~3.9 eV, respectively, whereas the valence band edge of the perovskite is at ~5.4 eV and that of the Fermi level of carbon is at ~5.0 eV. (C) The crystal structure of MAPbI$_3$ perovskite.
iodide ions, and the c axis becomes the dominant orientation during crystal growth. Mercier (20) used 4-ammonium-butyric acid (4-ABA) as a template for the engineering of (4-ABA)2PbI4 and mixed-cation (4-ABA)2MAPb2I7 perovskite crystals. The ABA molecules formed linear hydrogen-bonded chains that act as supramolecular synthons for layered plumboiiodide perovskite structures. We propose that the 5-AVA affects the crystal growth of (5-AVA)x(MA)1-xPbI3 in a similar fashion through the formation of hydrogen bonds between its COOH and NH3+ groups and I– ions from the PbI6 octahedra.

We applied transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to unravel differences in the morphology of the two perovskites. High-resolution TEM images (Fig. 3, A to C) reflecting the morphology of neat TiO2 particles, as well as MAPbI3 or (5-AVA)x(MA)1-xPbI3-covered TiO2 particles that were scraped off of mesoporous TiO2 films infiltrated with MAPbI3 or (5-AVA)x(MA)1-xPbI3, respectively. Substantial differences appeared between the morphologies of the samples produced from the two different perovskite precursor solutions. The observed pattern indicates that there is a much denser coverage of the TiO2 particles with (5-AVA)x(MA)1-xPbI3 as compared to MAPbI3. The (5-AVA)x(MA)1-xPbI3 appears to exhibit crystalline features on a much longer length scale than MAPbI3 covering most of the TiO2 surface in a uniform fashion. In contrast, the single-step solution precipitation of MAPbI3 only partially coated the substrate and left large areas where the perovskite absorber was completely absent.

The improvement of the perovskite crystal quality and the higher loading of the mesopores of the oxide scaffold in the presence of 5-AVA cations probably resulted from the templating action of the AVA affecting the perovskite crystal nucleation and growth within the mesoscopic oxide scaffold. The COOH groups of 5-AVA anchor a monolayer of the amino acid to the surface of the mesoporous TiO2 and ZrO2 film by coordinative binding to the exposed Ti(IV) or Zr(IV) ions. In the adsorbed state, the terminal -NH3+ groups of 5-AVA face the perovskite solution and hence serve as nucleation sites. This role we attribute to AVA is confirmed by recent work (21) showing that protonated amino acids of the AVA type indeed template the crystal growth of plumbohalide perovskites in mesoscopic TiO2 films, improving the crystalline network and charge-carrier lifetime of the CH3NH3PbI3 inserted into the porous metal oxides.

We performed photoluminescence (PL) decay measurements in order to extract quantitative information on the yield of light-induced charge separation. Excitons generated by light excitation of MAPbI3 dissociate into free charge carriers within 1 ps (22). We infiltrated mesoporous TiO2 and ZrO2 films with MAPbI3 or (5-AVA)x(MA)1-xPbI3 and measured the PL decay; ZrO2 serves as a reference because its conduction band is not accessible for electron injection. The PL decay of the MAPbI3 perovskite contained in ZrO2 films exhibits a time constant of $\tau_0 = 8.14$ ns.

**Fig. 2. Diffraction data.** XRD patterns of mesoscopic ZrO2/TiO2 film on FTO glass infiltrated with the perovskites (5-AVA)x(MA)1-xPbI3 (red trace) and MAPbI3 (blue trace), as well as a blank ZrO2/TiO2 film (black trace).

**Fig. 3. Microscopy images.** (A to C) TEM images of (A) TiO2 and mixtures of (B) MAPbI3 and (C) (5-AVA)x(MA)1-xPbI3, with TiO2 particles scraped off of a mesoporous film infiltrated with perovskites. (D and E) SEM images of the cross section of (D) MAPbI3– and (E) (5-AVA)x(MA)1-xPbI3–based perovskite mesoscopic solar cells.
overlap integral of the IPCE spectra with the AM 1.5 solar emission are also shown. The integrated photocurrent of the (5-AVA)\(_x\)MAPbI\(_3\)–based photoelectricity is 17.8 mA cm\(^{-2}\), which agrees closely with the photocurrent density of 18.4 mA cm\(^{-2}\) measured at the beginning of testing, which rose to 21.1 mA cm\(^{-2}\) after 3 min of light soaking.

whereas for the (5-AVA)\(_x\)MAPbI\(_3\), \(\tau_c\) is 23.7 ns [fig. S1 (29)]. The longer charge-carrier lifetime observed with (5-AVA)\(_x\)MAPbI\(_3\) indicates a much lower defect concentration. With the TiO\(_2\) scaffold, \(\tau_c\) for MAPbI\(_3\) and (5-AVA)\(_x\)MAPbI\(_3\) were similar, 1.71 and 1.36 ns, respectively; and from the branching ratios, led to calculated quantum efficiencies of 94 and 80%, respectively.

Cross-sectional SEM views of the (5-AVA)\(_x\)MAPbI\(_3\)– and MAPbI\(_3\)–based mesoscopic solar cells, which confirm the different extent of pore filling by the two perovskites are shown in Fig. 3, D and E. Thus, for (5-AVA)\(_x\)MAPbI\(_3\), most of the mesopores of the ZrO\(_2\)/TiO\(_2\) double layer are fully loaded with the perovskite, whereas for the device with MAPbI\(_3\), the pore filling is less complete, with a substantial amount of voids remaining within the mesoporous ZrO\(_2\)/TiO\(_2\) double-layer film. Optical studies also confirmed the higher perovskite loading in the presence of 5-AVA [figs. S2 and S3 (23)].

We measured the photocurrent density as a function of forward bias voltage \((J-V)\) curves of the (5-AVA)\(_x\)MAPbI\(_3\)– and the MAPbI\(_3\)–based mesoscopic solar cells under standard reporting conditions [air mass 1.5 (AM1.5) solar light at 100 mW cm\(^{-2}\) and room temperature]. Figure S4 \((23)\) presents the temporal evolution of the device performance for (5-AVA)\(_x\)MAPbI\(_3\)–based mesoscopic solar cells during the initial phase of illumination. The four key photoelectric parameters; i.e., the open-circuit voltage \(V_{oc}\), short-circuit photocurrent \(J_{sc}\), fill factor \(FF\), and PCE, increased to a stable value within the first 3 min and then exhibited excellent stability during exposure to full AM 1.5 simulated sunlight over 1008 hours. The final PCE increased slightly during this period, which is more remarkable given that the test was performed with an unsealed device, the perovskite being protected by the 10-μm-thick carbon layer back contact acting as a water-retaining layer.

A hysteresis effect often appears during measurement of the \(J-V\) curves of perovskite solar cells. For a mesoscopic triple-layer solar cell with perovskite (5-AVA)\(_x\)MAPbI\(_3\) under standard 1 sun irradiation with the scanning rate of 3 mA cm\(^{-2}\)s\(^{-1}\), there was no substantial effect [fig. S5 (29)]. However, a hysteresis effect appeared at higher scan rates unless the cell was subjected to light soaking for a few minutes, which eliminated the hysteresis effects even at scan rates as high as 250 mV s\(^{-1}\) (blue curve). The \(J_{sc}\) measured at the beginning of testing, which rose to 21.1 mA cm\(^{-2}\) after 3 min of light soaking.

In the absence of ZrO\(_2\), the performance of the perovskite photovoltaic is poor, with \(J_{sc} = 12.51\) mA cm\(^{-2}\), \(V_{oc} = 592\) mV, \(FF = 0.56\), and PCE = 4.18% [fig. S7 (23)]. This confirms that ZrO\(_2\) is blocking the flow of photogenerated electrons to the back contact, preventing recombination with the holes from the perovskite at the back contact.

**REFERENCES AND NOTES**

**Applied Optics**

**Dielectric gradient metasurface optical elements**

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Gradient metasurfaces are two-dimensional optical elements capable of manipulating light by imparting local, space-variant phase changes on an incident electromagnetic wave. These surfaces have thus far been constructed from nanometallic optical antennas, and high diffraction efficiencies have been limited to operation in reflection mode. We describe the experimental realization and operation of dielectric gradient metasurface optical elements capable of also achieving high efficiencies in transmission mode in the visible spectrum. Ultrathin gratings, lenses, and axicons have been realized by patterning a 100-nanometer-thick Si layer into a dense arrangement of Si nanobeam antennas. The use of semiconductors can broaden the general applicability of gradient metasurfaces, as they offer facile integration with electronics and can be realized by mature semiconductor fabrication technologies.

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**Supplementary Materials**

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**Materials and Methods**

Supplementary Text Figs. S1 to S9

**References**

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The field of nanophotonics has started to facilitate the replacement of bulky optical components by ultrathin, planar elements (1–5). Such elements can be realized by nano-pattern thin films and can benefit from a more natural integration into electronic and mechanical systems. They can also provide entirely new functions that capitalize on the rapid developments in the field of metamaterials (6). The recent realization of metasurfaces, or metamaterials of reduced dimensionality (7), is of particular relevance as it is opening up new opportunities to realize virtually flat optics (8, 9). Metasurfaces consist of dense arrangements of resonant optical antennas. The resonant nature of the light-matter interaction with such structures affords substantial control over the local light scattering amplitude and phase. These scattering properties can be manipulated through choices of the antenna material, size, geometry, and environment. By arranging antennas with distinct scattering properties on a surface, space-variant metasurfaces are created that offer tremendous freedom in manipulating optical wave-fronts. Metasurfaces constructed from high-index antenna arrays are used as anti-reflection coatings (10), as well as to enhance absorption (11), create structural color (12), and manipulate the state of polarization (13, 14). However, space-variant metasurfaces for beam steering and focusing have thus far been constructed from nanoscale metallic antennas only (7). Ohmic losses in the metal and the limited scattering cross sections of the antennas have limited high device efficiencies to reflection mode (15, 16). We leverage recent advances in the realization of high-index dielectric antennas (12, 17, 18) and Pancharatnam-Berry phase optical elements (PBOEs) (19, 20) to realize easy-to-fabricate and highly efficient transmissive devices. Si-based gradient metasurfaces capable of serving as optical gratings, lenses, and axicons are demonstrated.

Figure 1 shows a dielectric gradient metasurface optical element (DGMOE) serving as an axicon. Whereas conventional glass axicons are a few millimeters in size (Fig. 1A), the DGMOE features a 100-nm-thick layer of poly-silicon deposited on a quartz substrate (Fig. 1B) generated in a single patterning step (21). Figure 1D shows a scanning electron microscopy (SEM) image of the fabricated DGMOE composed of thousands of Si nanobeam antennas.

When illuminated with a collimated Gaussian left circularly polarized (LCP) light beam at a 550-nm wavelength, the DGMOE creates a non-diffracting Bessel beam on the transmission (Fig. 1, C and E, and section S2 of the supplementary materials). The intensity distributions along and across the center of Bessel beam are shown as insets to Fig. 1E. The ratio between the high-intensity central beam spot and the first ring is 6:1, a signature of a Bessel beam. The operation of the lens could be analyzed by understanding all of the coherent far-field and near-field interactions between the Si nanobeam antennas. Here, we describe the behavior of the optical element based on an understanding of the Pancharatnam-Berry (PB) phase.

The PB phase is a geometric phase achieved by space-variant polarization manipulations (22, 23), as opposed to a propagation phase. PBOEs are constructed from wave plate elements for which the orientation of the fast axes depends on the spatial position. Well-defined algorithms exist for realizing specific optical functions. By tilting a surface with half-wave plates with their fast-axes orientations according to a function $\theta(x,y)$, an incident circularly polarized light beam will be fully transformed to a beam of opposite helicity and imprinted with a geometric phase equal to $\varphi(x,y) = \pm2\theta(x,y)$ (21, 24). By controlling the local orientation of the fast axes of the wave plate elements between 0 and $\pi$, phase pickups can be achieved that cover the full 0-to-2$\pi$ range while maintaining equal transmission amplitude for the entire optical component. This provides full control over the wavefront. A continuous desired phase function can be approximated using discrete wave plate orientations. We use eight orientations with which a high theoretical diffraction efficiency of 95% can be achieved (25). The realization of wave plate elements represents a crucial step in crafting PBOEs.

In designing ultrathin nanobeam-based wave plates, it is important to first understand the optical resonances of individual semiconductor nanobeams. Top-illuminated single beams support resonances under transverse electric (TE) illumination (with the electric field polarized normal to the length of the structure) and the orthogonal transverse magnetic (TM) polarization (12, 18). The thickness of the resonant structures can be small compared with the free-space wavelength due to the high refractive index of semiconductors. A 120-nm-wide and 100-nm-high Si nanobeam supports a strong resonance and a substantial phase retardation in our target wavelength range of interest. We chose this beam as the basic building block for our wave plate (Fig. 2A) in anticipation that its resonant behavior and the accompanied phase retardation between the orthogonal polarizations would persist in the beam array. Finite element simulations indicate that the wavefront for a TE-polarized light beam at 550 nm is delayed by 0.14$\pi$ as compared with the wavefront in the absence of the nanobeams. The wavefront for TM-polarized light is delayed even further to 1.15$\pi$ (Fig. 2B). As a result, the phase retardation between the two orthogonal polarizations...