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Colloidally prepared La-doped BaSnO₃ electrodes for efficient, photostable perovskite solar cells

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Perovskite solar cells (PSCs) exceeding a power conversion efficiency (PCE) of 20% have mainly been demonstrated by using mesoporous titanium dioxide (mp-TiO₂) as an electron-transporting layer. However, TiO₂ can reduce the stability of PSCs under illumination (including ultraviolet light). Lanthanum (La)-doped BaSnO₃ (LBSO) perovskite would be an ideal replacement given its electron mobility and electronic structure, but LBSO cannot be synthesized as well-dispersible fine particles or crystallized below 500°C. We report a superoxide colloidal solution route for preparing an LBSO electrode under very mild conditions (below 300°C). The PSCs fabricated with LBSO and methylammonium lead iodide (MAPbI₃) show a steady-state power conversion efficiency of 21.2%, versus 19.7% for a mp-TiO₂ device. The LBSO-based PSCs could retain 93% of its initial performance after 1000 hours of full Sun illumination.

Fully solidified perovskite solar cells (PSCs) emerged (1, 2) after the use of methylammonium lead halide (CH₃NH₃PbX₃; X is I and Br) perovskites as dyes in dye-sensitized liquid electrolyte solar cells by Miyasaka in 2009 (3). Since then, the power conversion efficiency (PCE) of these photovoltaic (PV) devices has increased at an incredible rate (4, 5). The common device architecture for PSCs includes a mesoporous (mp) oxide layer on top of a thin oxide blocking layer as an n-type electron-transporting layer (ETL) and an organic hole-transporting layer (HTL) such as 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) and poly-triarylamine (PTAA) (6, 7). An inverted configuration has been reported by combining poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as an HTL and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) as an ETL (8). Generally, efficient PSCs are fabricated by using a mp-oxide ETL/perovskite/organic HTL configuration. In PSCs, TiO₂ is typically used as the mp-oxide; highly efficient PSCs (those exceeding a PCE of 20%) are fabricated with TiO₂ as the ETL, although the use of other oxide materials, such as SnO₂, ZnO, and Zn₂SnO₄, has been reported (9–12).

Recently, the stability of PSCs upon exposure to moisture, heat, and light has attracted interest because PSCs must be able to withstand these conditions for their commercialization. The stability of PSCs can be determined by

several factors, including the instability of the perovskite material itself and the charge transport material, such as ETL and HTL, as well as the interface in the device configuration (4, 13–17). In particular, when mp-TiO₂ is used as an ETL, it negatively affects the device stability under ultraviolet (UV) illumination (14, 15, 18). Various strategies have been considered to improve the stability of PSCs, such as the replacement of TiO₂ (15), insertion of interfacial layers between the ETL and perovskite layers (14, 19), use of a UV filter or doping of TiO₂ to reduce UV-induced photocatalysis (15, 20), and introduction of a down-converting layer (18). However, an approach that does not require additional processes is to search for a new type of ETL to replace mp-TiO₂ and fabricate stable PSCs without damaging their performance.

BaSnO₃ (BSO) is an n-type semiconducting perovskite oxide with a wide band gap of 3.2 eV. It is used in various applications, e.g., as a transparent conducting oxide (TCO) (21), thin-film transistor (22), or gas sensor (23). In particular, La-doped BSO (LBSO) exhibits an unusually high electrical mobility of 320 cm² V⁻¹ s⁻¹ at room temperature (24) and has an inferior UV photocatalytic ability because of its small dipole moment, ascribed to the cubic perovskite structure without octahedra tilting (25, 26). However, LBSO films cannot be applied onto flexible or even glass substrates because of the high crystallization temperature of the LBSO perovskite phase of >1000°C (27). An approach for obtaining

a compact, crystalline LBSO thin film below at least 500°C is to coat a desired LBSO colloidal solution that includes well-dispersed precrystalline LBSO perovskite nanoparticles (NPs) onto the substrate. Introducing amorphous precursors containing peroxo groups could reduce the crystalline temperature to 900°C; the amorphous precursors are prepared by mixing aqueous barium chloride and tin chloride solutions with a solution of hydrogen peroxide and NH_3 in water (28, 29). However, the temperature is still too high to fabricate optoelectric devices on a glass substrate. Recently, Huang *et al.* reported a peroxo-precursor synthesis method for mp-BSO at 300°C (30). However, these methods could not create a colloidal solution to fabricate the compact BSO perovskite film. Thus, the development of a mass-producible and completely dispersed precursor colloidal solution for producing BSO thin films is a challenging issue for obtaining efficient and photostable PSCs.

We first demonstrate a crystalline superoxide-molecular cluster (CSMC) colloidal solution containing well-dispersed CSMC NPs in 2-methoxyethanol (2ME) that was prepared by the reaction of BaCl_2 , SnCl_2 , $\text{La}(\text{NO}_3)_3$, and H_2O_2 in an NH_4OH aqueous solution at 50°C. We determined that the crystalline LBSO perovskite phase developed below 300°C from CSMC via an intermediate peroxo-complex by using extended x-ray absorption fine structure (EXAFS) analysis and density functional theory (DFT). The compact and uniform perovskite LBSO layer was successfully fabricated from the CSMC colloidal solution by spin-coating onto a fluorine-doped SnO_2 (FTO) substrate. To fabricate PSCs with the LBSO as an ETL, we used methylammonium lead iodide (MAPbI_3) as a light harvester, because MAPbI_3 , which has a higher conduction band edge than formamidinium lead iodide (FAPbI_3), is more suitable for the energy level of the LBSO electrode. The best-performing PSC exhibited a PCE of 21.2% (the highest value reported for MAPbI_3 -based PSCs) and a very high photostability below a 10% change for the PCE after 1000 hours of full-Sun illumination [including UV radiation, air mass (AM) 1.5G, 100 mW cm^{-2}].

The crystalline phase of LBSO (used as an electrode in this study) is the same as that of pure BSO, as shown in fig. S1 (31), and we used undoped BSO as a model system to investigate the formation of LBSO at a low temperature. For the colloidal solution, Ba and Sn precursors were dissolved in a hydrogen peroxide (H_2O_2) aqueous solution (30% H_2O_2) at 50°C and room temperature (RT). A mass-producible white powder (>92% yield) was obtained by adjusting the pH from 1 to 10 by addition of NH_4OH at 50°C, and the as-prepared powder was well dispersed in 2ME (fig. S2) (31). Figure 1A shows a representative scanning electron microscopy (SEM) image of the as-prepared powder synthesized at 50°C. The SEM image exhibits highly dispersed and defined NPs whose size distribution is shown in fig. S3 (31). The col-

loidal solution is highly transparent because individual discrete NPs (versus aggregates) form by a self-condensation reaction in the H_2O_2 -assisted process. Figure 1B shows x-ray diffraction (XRD) patterns, measured in air, of the as-prepared and annealed powders. The spectrum for the as-prepared powder obtained via the CSMC route contains crystalline XRD peaks, whereas the conventional route (at RT) produces an amorphous powder (Fig. 1B).

The crystalline white powder was successfully converted into a pure perovskite BSO phase by annealing for 30 min at 200°C, which requires a much shorter time and lower temperature than a conventional route such as a solid-state reaction and sol-gel process for the pure BSO perovskite phase (32). By contrast, the amorphous powder produced at RT did not convert to the perovskite phase even at a much higher temperature (500°C). Thus, the initial crystalline phase in the as-prepared powder plays a key role in the formation of the BSO perovskite phase at 200°C. The XRD pattern of the as-prepared powder shown in Fig. 1B indicates that the initial crystalline phase is not an ideal cubic BSO perovskite phase. Infrared (IR) spectroscopic analysis was performed to identify the constituents in the as-prepared crystalline powders. Figure 1C shows Fourier transform (FT) infrared (IR) spectra of the as-prepared powders synthesized at 50°C and RT. The amorphous powder synthesized at RT shows stretching frequencies at 856 cm^{-1} and 1400 to 1500 cm^{-1} , which are assigned to $\nu(\text{O-O})$ and $\delta(\text{O-O-H})$ vibrations (33), respectively, revealing that the powder includes hydroperoxo (O-O-H) ligands. The hydroperoxo ligands were previously observed for amorphous or crystalline peroxo-precursors in H_2O_2 -assisted methods (30, 33–35). The amorphous peroxo complexes exist as $\text{AM}_2(\text{O}_2) \cdot 3\text{H}_2\text{O}$ (A is Ca, Sr, or Ba; M is Ti or Sn), which can be rewritten as $\text{A}[\text{M}(\text{OH})_5(\text{OOH})]^{2-}$ (35). Therefore, these compounds are assumed to exist in the amorphous phase when prepared at RT. In addition, the crystalline structures consisting of alkaline metal cations and the hexahydroperoxostannate anion ($[\text{Sn}(\text{OOH})_6]^{2-}$) have been reported through the substitution of the hydroxo ligands of the hydroxostannate precursor ($[\text{Sn}(\text{OH})_6]^{2-}$) by a reaction with concentrated H_2O_2 (33, 34). However, for the crystalline powder prepared at 50°C, the broad absorption related to the hydroperoxo ligand at 1400 to 1500 cm^{-1} decreased and new IR absorption peaks at 1054 and 1098 cm^{-1} are observed, which are ascribed to vibrations of the superoxo (O_2^-) ligand with a shorter O–O bond length than the peroxo ligand (36). The powder is different from previously reported amorphous and crystalline peroxo-precursors for BSO perovskite (28, 30, 34, 35).

On the basis of controlled experiments examining the effects of temperature and H_2O_2 concentration (fig. S4) (31), a schematic formation map for the superoxide precursor col-

loidal solution is shown in Fig. 1D. In the precipitates of $\text{Sn}(\text{OOH})_x(\text{OH})_{4-x}$ formed from H_2O_2 and NH_4OH mixture in aqueous solution, the value of x will increase with increasing amount of H_2O_2 (33). The decomposition of H_2O_2 is affected by various environmental conditions such as heat, catalysis, concentration of H_2O_2 , and pH (37). As shown in Fig. 1D, the formation of superoxide (SnO-OSn) will be more favorable at a higher x value and at a mild temperature below 90°C via the condensation reaction between $-\text{OOH}$ ions. According to previous reports (37), the decomposition of H_2O_2 was limited below 30°C at pH 10 to 11, whereas the increase in temperature from 30° to 40°C accelerated the decomposition rate of H_2O_2 up to 3.3-fold at pH 10 to 11. Indeed, we observed that the crystalline superoxide complex appears at solution temperatures between 40° and 70°C (fig. S4A) (31), whereas reaction temperatures above 90°C decrease crystallinity (fig. S4A) (31). Furthermore, the crystalline phase is formed only at H_2O_2 concentrations above 15% (fig. S4B) (31). Under these specific conditions (50°C and 30%), CSMC can be rapidly formed even within 10 min (fig. S4C) (31). An adequate temperature and high concentration of H_2O_2 accelerate the formation of superoxide during the reaction that then forms the CSMC. The superoxo groups at surface of CSMC NPs tend to efficiently repel each other via surface charge, which lead to the stable colloidal solution. However, the CSMC phase formed at 90°C does not create colloidal solution because a sizable fraction of superoxide decomposes to form oxygen.

To elucidate the initial crystalline phase of CSMC and the phase-converting procedure from the initial phase to the BSO perovskite phase at low temperatures, we performed in situ EXAFS analysis for the initial crystalline powder in air as a function of temperature. Figure 2A shows the temperature-dependent radial distribution functions (RDFs) of Fourier-transformed (FT) Sn K-edge EXAFS spectra for the as-prepared CSMC powder. The initial powder showed a single strong peak at 1.58 \AA , corresponding to the first oxygen shell. No meaningful peak intensity was observed for the higher radial space regions until heating to 150°C . The distinct singlet RDF feature means that the Sn-O bonds did not have long-range order in the initial crystalline powder, reflecting the existence of single molecular clusters of Sn-O_x . However, a small FT peak at 4.17 \AA developed at 160°C and gradually increased until 180°C . Considering the uncorrected phase shift (r_{eff} is higher than $\sim 0.4 \text{ \AA}$), the FT peak is not attributed to the BSO perovskite phase but might result from $\text{Sn-O}_2^{2-}\text{-Sn}$ in the intermediate phase that includes the peroxo anion (O_2^{2-}) because the initial crystalline powder includes superoxo ligands. After the complete disappearance of the FT peak at 190°C , new doublet FT peaks evolved at 3.31 and 3.84 \AA at 200°C . The FT peaks correspond to the characteristic overall RDF feature of Sn-Ba and corner-

shared Sn-(O)-Sn distributions for the BSO perovskite crystal structure, respectively, revealing that the as-prepared white powder was effectively converted to the pure perovskite phase during the in situ experiment at 200°C . Thus, the formation of a superoxide molecular cluster with a perovskite frame can facilitate the synthesis of well-dispersed perovskite BSO NPs, even below 500°C .

On the basis of the XRD, IR, and temperature-dependent RDF results, we performed a first-principles calculation using DFT to elucidate the origin of the phase evolution to BSO perovskite below 200°C (crystal structures are shown in Fig. 2B). The CSMC has structural deformations from cubic symmetry because the octahedral consisting of Sn and six O_2^- molecules maintain their local geometries but have randomly distributed orientations. This long-range-ordered single cluster consisting of Ba^{2+} cations and the hexasuper-oxostannate anion, $[\text{Sn}(\text{O-O})_6]^{2-}$, in the as-prepared powder initially formed cross-linked Sn-[O-O]-Sn octahedra with the removal of O_2 during heating; the higher temperature promotes long-range-ordered development of corner-shared Sn-(O)-Sn octahedra by way of O_2 removal, finally revealing the pure cubic BSO perovskite structure. We hypothesized that the formation of the long-range-ordered single cluster as a precursor requires lower energy and presents a faster pathway to the thermodynamically stable cubic perovskite BSO phase, as compared to starting from the amorphous phase.

The phase evolution from CSMCs to pure BSO perovskite makes it possible to fabricate a LBSO film as an n-type layer for PSCs on a transparent conductive oxide (TCO) glass substrate below 500°C by coating with the CSMC colloidal solution. Figure 2C shows a SEM image of an LBSO film deposited by a spin-coating method using the CSMC colloidal solution with sequential annealing. The film is crack-free and provides uniform, continuous coverage of the substrate with densely packed LBSO NPs. Moreover, the surface roughness of the film is very low ($\sim 5 \text{ nm}$ root-mean-square roughness) as measured by atomic force microscopy (AFM). The XRD spectra for as-coated and annealed LBSO films are shown in fig. S5 (31). Analyses confirmed that La cations were successfully doped into BSO perovskite to form the final LBSO film for use as an ETL in PSCs (fig. S6) (31).

Figure 3A shows a cross-sectional SEM image of the PSC fabricated by a solvent-engineering process (38) with MAPbI_3 as a halide perovskite material and PTAA as an HTL. The PSC consisted of uniform layers of a LBSO perovskite oxide layer ($\sim 120 \text{ nm}$ in thickness) and a uniformly deposited upper layer ($\sim 440 \text{ nm}$ in thickness) of MAPbI_3 . In Fig. 3B, photocurrent density-voltage (J - V) characteristics of the PSC fabricated with LBSO as an ETL are presented and compared with those of a control device by using mp-TiO_2 , which is a typical ETL for fabricating highly efficient PSCs.

As shown in the J - V curves, the LBSO cell exhibited an open-circuit voltage (V_{oc}) of 1.12 V, a short-circuit current density (J_{sc}) of 23.4 mA/cm², and a fill factor (FF) of 81.3%, giving an overall PCE of 21.3%, whereas the control device showed an overall PCE of 19.6% with a V_{oc} of 1.07 V, a J_{sc} of 23.3 mA/cm², and a FF of 78.6%. The superior performance of the LBSO PSC is mainly attributed to a higher V_{oc} and FF , which are associated with beneficial effects such as a higher conduction band minimum and electron density of LBSO, and reduced carrier recombination compared to mp-TiO₂. Because the PSCs using LBSO as the ETL exhibited a large hysteresis in their J - V curves with reverse and forward sweeps (fig. S7) (31), the stabilized PCEs were estimated to determine the real power output of the device by measuring the steady-state photocurrent with an applied voltage at the maximum power point under simulated solar illumination (100 mW cm⁻², AM 1.5G). The LBSO PSC showed a stabilized power output of 21.2% near the maximum power point (0.96 V), which closely matched the values extracted from the J - V curve with a reverse sweep (Fig. 3B, inset), whereas the TiO₂-based device showed a stabilized PCE of 19.7%. The reverse-sweep J - V curve for the LBSO PSC is notable, although the underestimated forward-sweep J - V curve requires further study. Figure S8 shows the time-correlated single-photon counting (TCSPC) results for perovskite samples on different substrates (glass, TiO₂, and LBSO) to investigate the photoinduced carrier kinetics inside the perovskite layer (31). The LBSO sample provides faster emission quenching than the TiO₂ sample, which seems to be caused by a more efficient electron injection. In addition to the efficient electron injection, the high electron density created by La-doping in BSO might cause a large built-in potential at the junction between perovskite and the n-type layer (12), which seems to result in a superior PV performance. That the high electron density contributes to the improvement of V_{oc} and FF becomes clearer in comparison with the undoped BSO (fig. S9) (31), because optical properties of 5 mol % La-doped BSO are only changed by a small amount (39), indicating a widely constant position of the conduction band edge. Figure 3C shows the external quantum efficiency (EQE) spectrum and integrated J_{sc} values for one of the LBSO PSCs. The high J_{sc} value is attributed to a very broad EQE plateau above 85% between 400 and 750 nm. The J_{sc} value obtained by integrating the EQE spectrum is 23.2 mA cm⁻², which agrees with the measured value of 23.4 mA cm⁻² in Fig. 3B. Figure 3D presents the histogram for PCEs extracted from the stabilized PCEs at the maximum power point. High-efficiency solar cells with average stabilized PCE of 20.3% (maximum and minimum values of 21.2 and 19.7%, respectively) could be achieved with a high degree of reproducibility by using the LBSO electron collection layer.

One of the most important requirements for PSCs is pho-

tostability under light illumination, including UV. The marked UV-induced degradation in PCEs for TiO₂-based PSCs presents a serious problem (14, 15, 18) for their practical use under natural sunlight. So far, PSCs claiming photostability have been tested with white light-emitting diode or UV-filtered solar simulators (40, 41). We conducted a light-soaking experiment by monitoring the J - V characteristics under AM 1.5G illumination with a xenon or metal-halide lamp, including UV radiation to estimate the photostability under 1-sun illumination for the LBSO- and TiO₂-based PSCs. Figure 4A shows the monitored PCEs of the unencapsulated FTO/LBSO/MAPbI₃/PTAA/Au and FTO/TiO₂/MAPbI₃/PTAA/Au devices in a nitrogen-filled chamber with a constant device temperature of 25°C and constant AM 1.5G illumination with a xenon lamp. The LBSO cell showed a greater resistance against photodegradation than the TiO₂ cell; the latter showed an abrupt decrease in PCE upon initial illumination.

However, a cell architecture that includes organic hole-transport materials (HTMs), such as PTAA or spiro-OMeTAD, is inappropriate for estimating the influence of n-type materials on the photostability for long-term measurements (~1000 hours) because organic HTMs can degrade the PV performance by morphological deformation, metal diffusion, movable additives, and so forth. To exclude the influence of organic HTMs on the photostability test, we fabricated a two-sided glass-encapsulated architecture using an inorganic p-type NiO layer instead of the organic HTM layer, which is glass/FTO/n-type oxide/MAPbI₃/NiO/FTO/glass, by lamination of two half cells (glass/FTO/n-type oxide/MAPbI₃ and MAPbI₃/NiO/FTO/glass). The fabrication procedure and initial photovoltaic performance for the laminate cell are described in fig. S10 (31). PCEs in encapsulated BSO and TiO₂ cells were monitored by measuring J - V curves in air under AM 1.5G illumination with a metal-halide lamp, including UV radiation; a spectrum is presented in fig. S11 (31). The LBSO cell retained 93.3% of its initial performance after 1000 hours, whereas the TiO₂ cell completely degraded within 500 hours (Fig. 4B). The development of the n-type BSO perovskite moves us a step closer to PSC commercialization by eliminating the requirement of the additional UV filter for previous TiO₂ PSCs.

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SUPPLEMENTARY MATERIALS

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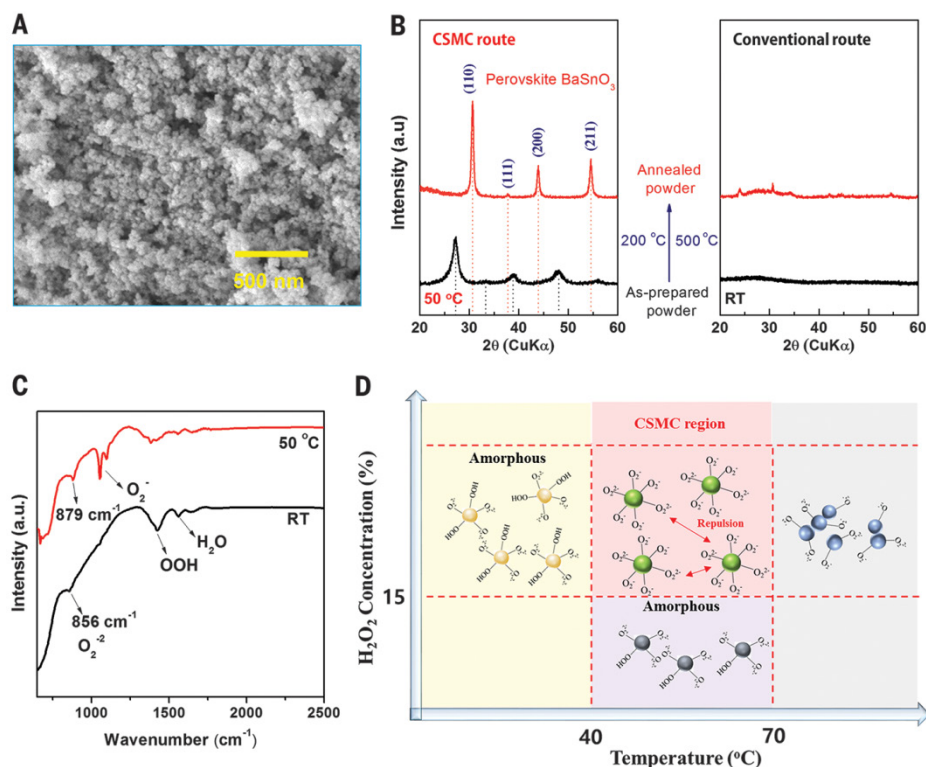


Fig. 1. Synthesis of CSMC and BSO. (A) SEM image of the as-prepared BSO powder synthesized at 50°C. (B) XRD spectra of the as-prepared powder synthesized at 50°C and annealed powder at 200°C for 30 min (left), and the as-prepared powder synthesized at room temperature and annealed at 500°C for 1 hour via the conventional route (right). (C) FT-IR spectra of the as-prepared BSO powder synthesized at room temperature and 50°C. (D) Schematic illustration of the formation map for the superoxide precursor colloidal solution.

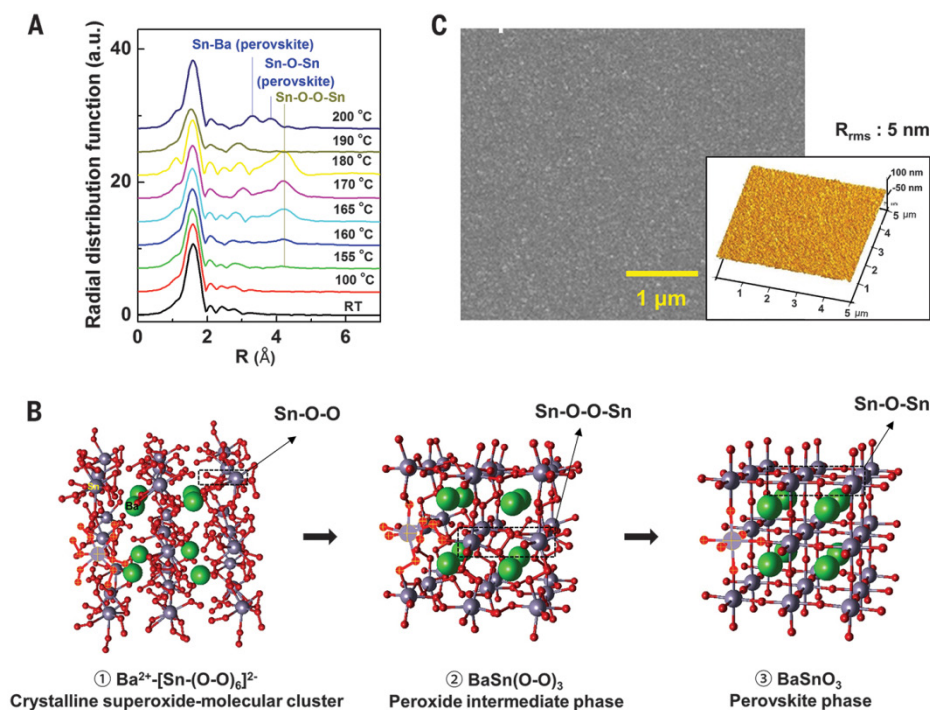


Fig. 2. Formation process and DFT simulation. (A) In situ EXAFS spectra (Sn K-edge) for the as-prepared powder (nonannealed powder) synthesized at 50°C with a heating rate of 0.5°C min⁻¹. (B) Proposed crystal structure of the phase evolution in the CSMC route: (1) crystalline superoxide-molecular cluster consisting of Ba, Sn, and O₂⁻; (2) peroxide intermediate phase, including the peroxo anion (O₂²⁻); and (3) BaSnO₃ perovskite phase (green, gray, and red spheres indicate Ba, Sn, and O ions, respectively). (C) SEM and 3D topographical AFM images of film deposited on FTO by spin-coating with the prepared LBSO colloidal solution.

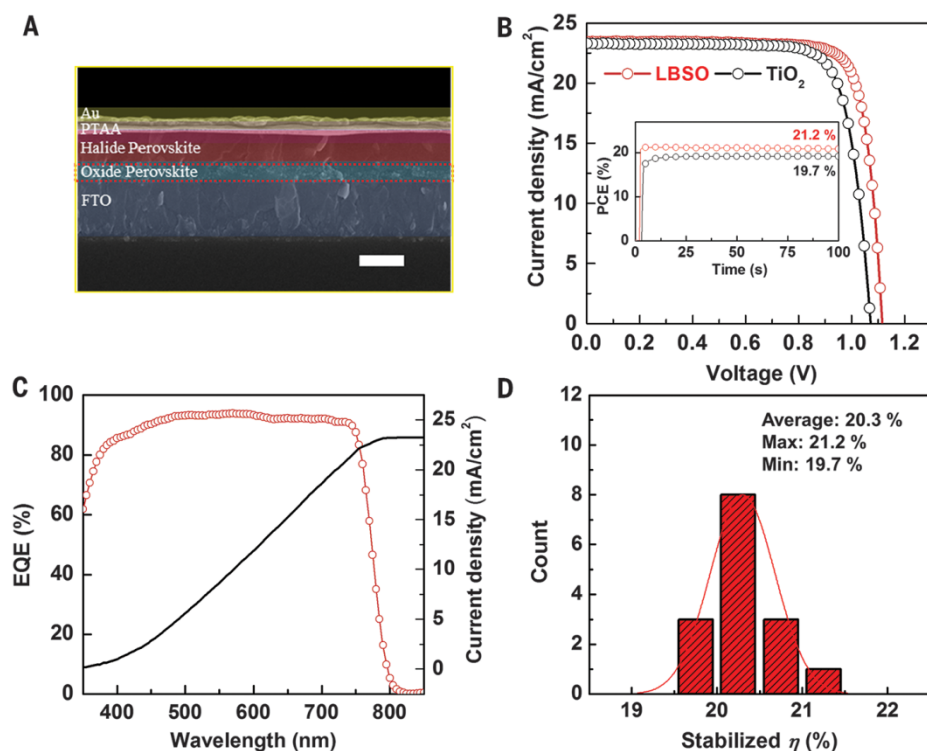


Fig. 3. Photovoltaic performance of PSCs (A) Cross-sectional SEM image of LBSO-based PSCs (scale bar, 500 nm). (B) J - V curves, and (inset) stabilized PCEs at a maximum power point (LBSO: 0.96 V; TiO_2 : 0.91V) for the best-performing LBSO- and TiO_2 -based PSC. (C) EQE spectrum and J_{sc} integrated from the EQE spectrum of the best-performing LBSO-based PSC. (D) Histograms of PCEs extracted from a photocurrent density stabilized at the maximum power point during 100 s for the LBSO-based PSCs.

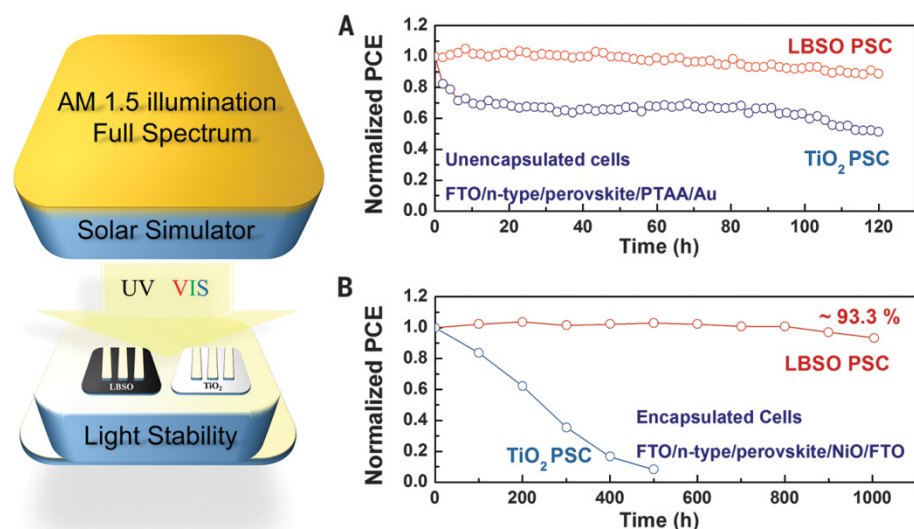


Fig. 4. Photostability test of PSCs. (A) Photostability tests under constant AM 1.5G illumination with a xenon lamp, including UV radiation for two unencapsulated devices of FTO/LBSO/MAPbI₃/PTAA/Au and FTO/ TiO_2 /MAPbI₃/PTAA/Au. (B) Long-term photostability test under constant AM 1.5G illumination with a metal-halide lamp, including UV radiation for two encapsulated devices of FTO/LBSO/MAPbI₃/NiO/FTO and FTO/ TiO_2 /MAPbI₃/NiO/FTO.



Colloidally prepared La-doped BaSnO₃ electrodes for efficient, photostable perovskite solar cells

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