

Multifunctional Synthesis Approach of In:CuCrO₂ Nanoparticles for Hole Transport Layer in High-Performance Perovskite Solar Cells

Boping Yang, Dan Ouyang, Zhanfeng Huang, Xingang Ren, Hong Zhang, and Wallace C. H. Choy*

While there are very limited studies of doped ternary metal oxide based hole transport materials, a multifunctional synthesis approach of In doped CuCrO₂ nanoparticles (NPs) as efficient hole transport layers (HTLs) including simplifying the synthesis requirements is proposed, enabling doping and achievement of treatment-free HTLs. Remarkably, compared with conventional methods for synthesizing CuCrO₂ NPs, the newly proposed azeotropic promoted approach dramatically reduces the reaction time by 90% and the calcination temperature by one-third, which not only promotes high throughput production but also reduces power consumption and cost in synthesis. Equally important, indium is successfully doped into CuCrO₂, which is fundamentally difficult in low temperature processes. The In doping offers less d–d transition of Cr³⁺ and p-type doping characteristics for improving HTL transmittance and conductivity, respectively. Interestingly, In doped CuCrO₂ HTL with these improvements can be achieved by a simple ambient-condition process and exhibits thermal stability up to 200 °C, which allows perovskite solar cells (PSCs) to achieve a power conversion efficiency of 20.54%. Meanwhile, the devices show good repeatability and photostability. Consequently, the work contributes to establishing a simple approach to realize pristine and doped multinary oxides based HTL for the development of practical and high performing PSCs.

1. Introduction

Organic lead halide perovskite solar cells (PSCs) with planar structure have gained wide attention from their rocket-fast improvement of the power conversion efficiency (PCE) from less than 4% to above 23%.^[1,2] For achieving the high-performance PSCs, a lot of work has been done for understanding

and developing perovskite layers, electron transport layers (ETL), hole transport layers (HTL), and their relation.^[3–7] As an important component of planar PSCs with p–i–n structure, HTL located between the perovskite and anode serves for effectively extracting holes, blocking electron, and reducing nonradiative recombination due to any unexpected poor contact between the perovskite layers and the metal electrode. Additionally, HTLs can contribute to protecting perovskite active layer from its sensitive species such as oxygen, moisture, and even ultraviolet radiation. These all closely influence the realization of high performance and stability of PSCs.

With the consideration of the good energy level alignment, hole mobility, and stability, p-type metal oxides, such as binary metal oxide nanoparticles (NPs) of NiO_x,^[8–10] CuO_x,^[11] and CoO₃,^[12] have been used as HTL in PSCs. Meanwhile, there are different approaches to explore ways for further improving the electrical properties.

Recently, ternary metal oxide NPs such as CuCrO₂,^[13,14] CuGaO₂,^[15] and NiCo₂O₄,^[16,17] NPs have been studied for HTL in PSCs due to their advantage of bandgap tunability by changing the metal ratio and their decent conductivity. For p–i–n inverted PSC structures, there are concerns on the quality of the film formed from NPs such as the packing of NPs and the morphology of the film particularly for large size NPs such as CuGaO₂ NPs, which may influence the quality of perovskite film and increase dark current. CuCrO₂ NPs show a fine size of about 10 nm and can be well-dispersed for forming well-pack HTL film in PSCs.^[13,14] The common method for synthesizing CuCrO₂ NPs is the hydrothermal method and most reported process takes very long reaction time of 50–60 h at the temperature of 240 °C.^[13,14] Furthermore, doping delafossite metal oxide is very challenging. On the one hand, a high temperature which is needed for the preparation of a pure polycrystalline delafossite phase is not suitable for stabilizing of doping metal cation in delafossite due to the natural tendency of this cation to decompose before forming reaction starts.^[18] On the other hand, different decomposition of each metal precursor and the stepwise growth behavior will favor the formation of a mixture of the corresponding oxides of each metal

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DOI: 10.1002/adfm.201902600

precursor rather than forming the doped ternary metal oxide.^[19] In addition, all the reported CuCrO_2 NPs require annealing of 100–150 °C for 10 min for forming effective HTLs.^[13,14] It is highly desirable not only to reduce the synthesis time and temperature for high throughput and low-cost production but also to realize the treatment-free formation of high-quality HTL for practical PSC applications. Furthermore, doping in CuCrO_2 NPs for better HTL in PSCs has not been reported so far from the best of our knowledge.

In this work, we demonstrate a multifunctional synthesis approach of In doped CuCrO_2 nanoparticles as efficient hole transport layers including simplifying the synthesis requirements, enabling doping and achievement of treatment-free HTLs. We propose a strategic azeotropic promoted approach (APA) in solvothermal synthesis to form pristine and In doped CuCrO_2 nanoparticles. Particularly, an azeotropic solvent with a low boiling point (lower than that of water) is introduced in this method to provide high pressure at considerably low temperature and realize the remarkable reaction time reduction in synthesizing of the NPs. Our results show that the reaction time is dramatically shortened by 90% and the annealing temperature is reduced by one-third as compared to that of conventional solvothermal synthesis. The mechanism of the APA reaction is analyzed through different reaction conditions. Interestingly, the NPs obtained from APA approach can easily form efficient HTLs at simple room ambient condition without any treatment. We demonstrate the planar p–i–n PSCs based on this efficient HTL with PCE of 20.54%, which is higher than that (18.37%) of the control PSCs with pristine CuCrO_2 NPs. The high performance can be explained by In doping induced improvement of the optical transmittance and hole conductivity of the HTL. Additionally, the In doped CuCrO_2 based PSCs made from APR approach shows good photostability with nearly 90% PCE after 800 h illumination at AM1.5G (100 mW cm⁻²). Consequently, we demonstrate a simple and robust approach to realize doped ternary oxide based HTL which favors the development of scalable and flexible high performance PSCs.

2. Results and Discussion

Motivated by the excellent properties of indium doped tin oxide (ITO) and CuInO_2 , we choose indium as the dopant in CuCrO_2 , which has not been reported so far. Moreover, the relative high solubility of $\text{In}(\text{OH})_3$ (in the water at room temperature (RT)) is beneficial for the chemical reaction at low-temperature hydrothermal treatment.^[20] The main synthesis process of In doped CuCrO_2 NPs is shown in Figure S1 in the Supporting Information. For pristine CuCrO_2 NPs, the only difference in the synthesis was the absence of indium acetate. After all the precursor salts were mixed and stirred uniformly in ethanol, NaOH was dissolved in water and added into the former solution. By mixing ethanol and deionized water with the volume ratio of ethanol:water = 12:0.4, the azeotropic solvent with a low boiling point of 78 °C will form. Importantly, the small amount of water is critical for APA reaction system because NaOH can be dissolved more effectively and adequately in water than other solvents. This benefits enough contact of metal cations with OH^- , favoring the formation of hydroxides and good

uniformity of the turbid liquid for further reaction in the autoclave. Equally important, we strategically select ethanol to serve the nontoxic solvent for realizing a green process for realizing the APA synthesis. We find that although other solvents such as trichloromethane, carbon tetrachloride, benzol, nitrile, and ethyl acetate can be used to replace ethanol to form azeotropic solvent with water, they will make the synthesis become toxic and not being selected for further studies.

Various methods for synthesizing oxides have been developed.^[21–30] Regarding the hydrothermal method, which is governed by two factors of thermodynamic and chemical,^[31] has been widely used. Typically, pressure and temperature dominate the thermodynamic process.^[31] To demonstrate the effects of pressure in our APA process, reactions under different conditions were carried out and the results are listed in Table S1 in the Supporting Information. As the cases of a, b, and c stated in Table S1 in the Supporting Information, when the solvent is pure water (i.e., the volume ratio of ethanol:water = 0:12.4 in Table S1, Supporting Information), no NPs are obtained at the temperature of 160 °C or less. When the amount of ethanol increases with the volume ratio reaching 6.2:6.2, reaction still did not occur at the temperature of 160 °C and NPs are obtained when temperature increases to 220 °C (cases d and e in Table S1, Supporting Information). Interestingly, when the volume ratio further changes to 12:0.4, reaction at 160 °C is more efficient than that at 220 °C (cases e and f in Table S1, Supporting Information). In this case, the adequately high pressure due to the low boiling point of the mixed solvent is beneficial to the three-step APA process shown in Figure S1 in the Supporting Information. In details, the volume ratio of ethanol:water at 12:0.4 can form an azeotropic solvent with a low boiling point of 78 °C, which makes it possible to realize high pressure at low temperature and promote the chemical reaction. However, when the solvent is pure ethanol, NaOH is not soluble. The solvent cannot synthesize NPs due to no hydroxide formation for oxides synthesis (case g in Table S1, Supporting Information). The products obtained from the reaction in water only under 160 °C are hydroxides and/or oxides containing one metal element of Cu, Cr, or In (Figure 1a), which are dissolved in hydrochloric acid (Figure 1b). Very differently, as shown in Figure 1c, the products synthesized in azeotropic solvent do not dissolve in hydrochloric acid. They are In doped CuCrO_2 NPs confirmed

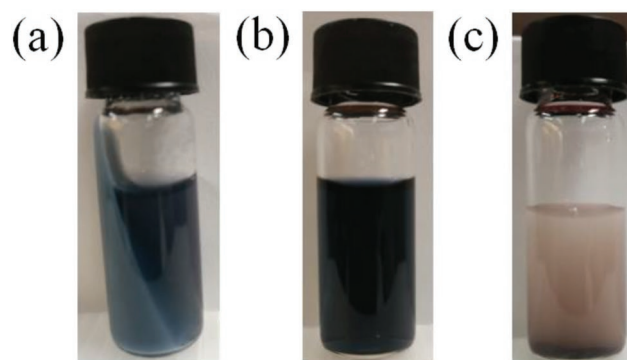


Figure 1. Digital images of the products gained from a) the water only reaction, b) the water only reaction with the addition of hydrochloric acid, and c) the ethanol and water reaction with addition of hydrochloric acid.

by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) as discussed later. Different products gained from different reaction conditions demonstrated the efficiency of our synthesis strategy.

It is important to point out that we successfully demonstrate In doping in CuCrO_2 NPs through the azeotropic promoted approach, while such doping is fundamentally difficult to realize by the solvothermal synthesis using pure water as a solvent due to the ultralow solubility of $\text{In}(\text{OH})_3$.^[20] In a closed system, the reaction mixture heating implies a pressure increase as a consequence of the vapor confinement, resulting in the change of solvent properties. In this work, the azeotropic solvent with a lower boiling point (78 °C) than water can decrease polar at low temperature, dissolving $\text{In}(\text{OH})_3$ to provide In source for the realization of doping in CuCrO_2 , which is not possible to occur at the pristine water system.

We summarize a mechanism of the whole process as shown in Figure S1 in the Supporting Information. First, by designing an azeotropic solvent with a lower boiling point compared to generally used water, a higher pressure could be produced at relatively low temperature and promote the dissolution of metal hydroxides (which can never occur in normal conditions). When the concentration of metal ions get the minimum value for nucleation, small particles nucleate. Moreover, high pressure could accelerate the movement of metal ions, which improves the particle growth. The results above demonstrate that the pressure produced (even at a lower temperature) is beneficial to the main reaction process of dissolve, nucleation, and growth. Consequently, substantial shortened reaction time and low temperature are demonstrated for synthesizing the pristine and In doped CuCrO_2 NPs. The APA approach is beneficial for the production of hole transport materials, which is promising for commercial-scale PSC fabrication at a lower cost.

The XRD patterns of pristine and In doped CuCrO_2 NPs show delafossite structures (as shown in Figure 2a). The patterns demonstrate that the synthesized NPs are free of other phases^[13,14] such as oxides and/or hydroxide of copper, chromium, or indium. Besides, In doping does not affect the phase of CuCrO_2 NPs. While it is challenging to obtain the pure 2H phase of CuCrO_2 as reported,^[13,32] the XRD patterns of In doped CuCrO_2 NPs show that no obvious 3R phase exists, implying that we have achieved dominantly pure 2H phase in the NPs, which corresponds to the peaks of 35.1°, 37.3°, 48.9°, 62.2°, and 66.1°.^[18] Transmission electron microscopy (TEM) image (Figure 2b and the inset) shows that the average size of In doped NPs is 12 nm, which is slightly larger than the previous reports with average size (10 nm) of CuCrO_2 NPs.^[13,14] This may have originated from accelerated growth in the synthesis due to the higher solubility of the metal hydroxides and the promoted moving speed resulting from the higher pressure. Compared to pristine CuCrO_2 NPs, there is no obvious change in the NP size after doping of In (Figure S2, Supporting Information). Meanwhile, as the XPS spectra shows in Figure 2c,d–g, Cu 2p, Cr 2p, and O1s peaks were clearly observed, which corresponds to Cu^{1+} , Cr^{3+} , and O^{2-} , respectively. The XPS spectrum of In doped NPs show In 3d peaks, demonstrating In^{3+} from the successful doping. The energy dispersive X-ray (EDX) spectra in Figure S3 in the Supporting Information also confirm the successful doping of In. The

ratios of Cu:Cr:O in CuCrO_2 NPs and In:Cu:Cr:O in In doped CuCrO_2 NPs are 0.98:1:2 and 0.023:0.98:0.96:2, and illustrate that they are both p-type semiconductors due to cation vacancies.^[18,33] The total valences of cations and anions in the NPs are 3.98:4 and 3.93:4, respectively. This means that In doping results in more cation vacancies, acting as p-type doping to improve the conductivity. Besides, the ratio of In:Cr in doped oxides is 0.95:40, which agrees well with the mole ratio of In and Cr salts for synthesis (1:40; shown in the Experimental Section). Consequently, the various characterizations confirm that high-quality pristine CuCrO_2 NPs have been successfully synthesized and In doping into the NPs has been realized.

We have also studied HTL film quality (e.g., film coverage, morphology, and packing of NPs). Our results show that when the HTL thickens, the series resistance increases and the best performed PSCs is achieved when the HTL thickness is about 42 nm as discussed in details later. Meanwhile, the optimum doping level is 1:40 of In:Cr (Table S3, Supporting Information). It can be observed from Figure 3a that the In doped CuCrO_2 film is uniform, pinhole-free, and with high coverage on the indium tin oxide substrate. As compared to the reported method in forming CuCuO_2 NPs based HTL in which the film is formed from the mixed solvent of water and ethanol and air annealing at 150 °C for 10 min is required,^[14] the HTL in this work is formed from the NPs well-dispersed in methanol merely and thus can avoid the risk of any unexpected residual water damaging the perovskite layer. Moreover, it does not need to do any treatment such as thermal annealing in forming HTL from our approach. The simple process benefits the robust use in rigid and flexible PSCs. As shown in Figure 3b, the root means square roughness value of the In doped CuCrO_2 on ITO substrate is 6.2 nm. It is very little higher than that of reported CuCrO_2 HTL (5.2 nm) due to the slightly larger size of NPs in this work. Importantly, this difference does not affect film coverage and uniformity. Consequently, well-pack, pin-hole free, and smooth HTL is demonstrated from In doped CuCrO_2 NPs made from APA method.

Good optical transmittance is very important for efficient HTL. Figure 3c shows the transmittance of pristine and In doped CuCrO_2 HTLs with the optimized thickness of 42 nm on ITO. The transmittance of In doped CuCrO_2 on ITO is >84% in the wavelength range from 420 to 800 nm and >70% from 350 to 420 nm, which is higher than that of the pristine one in the whole wavelength range. The higher transmittance of In doped NP film can be explained by the lower absorption. Typically, Cr^{3+} cations at oxygen octahedrons of delafossite structure show d–d excitations, which cause the low transparency of CuCrO_2 . After In doping, more Cr^{3+} are replaced by In^{3+} , resulting in decreased absorption of d–d and higher transmittance in In doped CuCrO_2 .^[18] This high transmittance favors more light penetration and thus more carrier photogeneration in the perovskite layer. The bandgap of both CuCrO_2 and In doped CuCrO_2 NPs are 3.05 eV, which is wider than some reported hole transporting oxides such as 2.1–2.4 eV of NiCo_2O_4 ,^[17] 1.3 eV of CuO ,^[34] 2 eV of V_2O_5 ,^[35] and 2.15 eV of Ni:CoO_x ,^[36] which offer efficient UV radiation blocking capability for reducing the decomposition of perovskite. Meanwhile, the bandgap of 3.05 eV (as indicated by the absorption peak of 407 nm in Figures S4 and S6c, Supporting Information) is narrower than

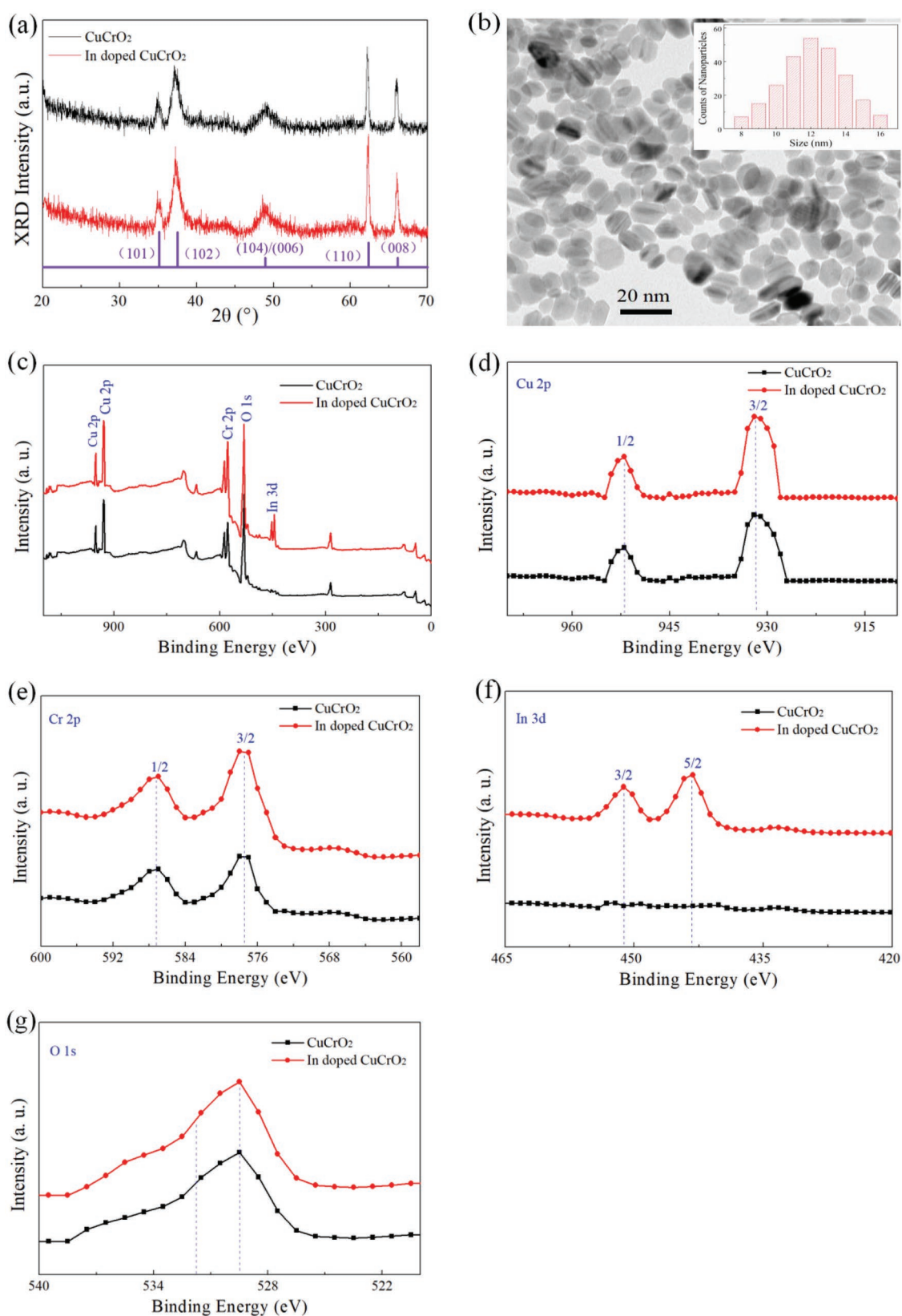


Figure 2. a) XRD patterns of CuCrO₂ and In doped CuCrO₂ NPs. The XRD pattern of bulk 2H-CuCrO₂ is shown in the bottom in purple color. b) TEM image and size distribution histogram (inset) of the In doped CuCrO₂ NPs. c) XPS spectra of the NPs. d–g) XPS spectra of Cu 2p, Cr 2p, In 3d, and O 1s, respectively.

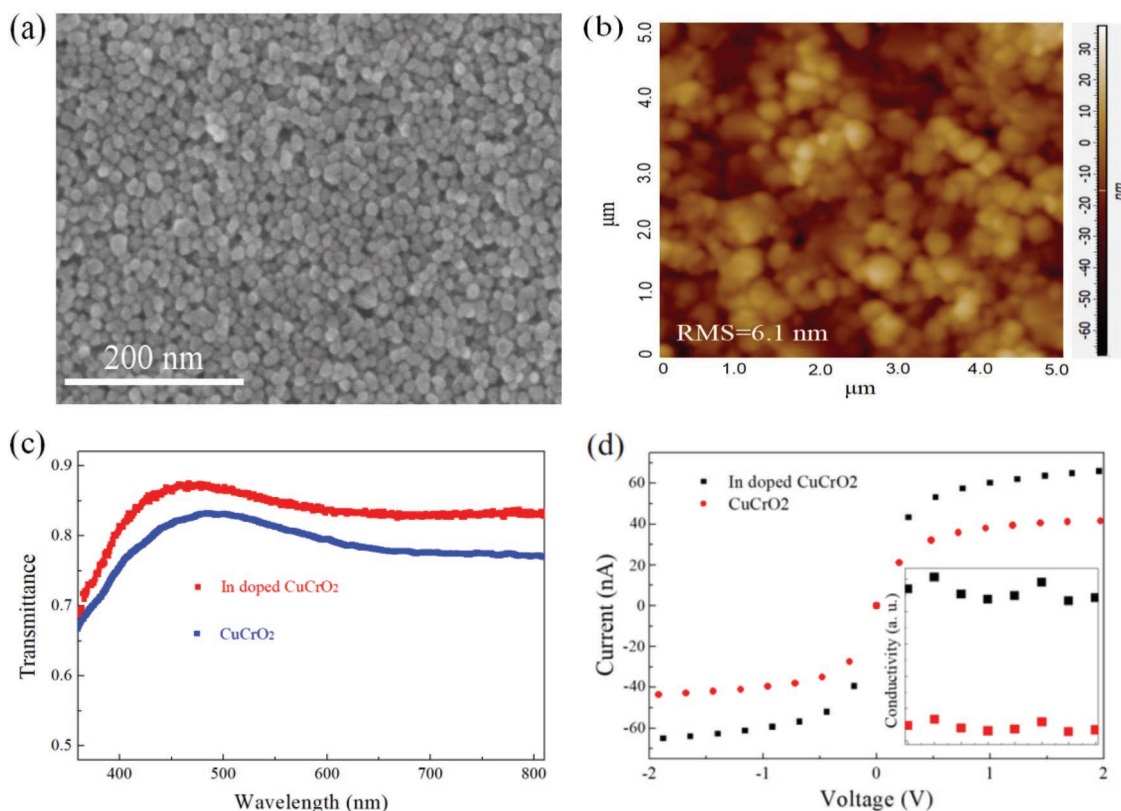


Figure 3. a) SEM image of In doped CuCrO_2 NPs on ITO glass. b) AFM image of In doped CuCrO_2 NPs on ITO glass. c) Visible light transmission of CuCrO_2 and In doped CuCrO_2 NP film with the optimized thickness. d) Example of I - V characteristics for CuCrO_2 and In doped CuCrO_2 NP film on ITO glass. The inset shows that the conductivity of In doped CuCrO_2 NP film is ≈ 2.5 times larger than that of CuCrO_2 NP film. All the above characterizations are based on the films formed in ambient conditions without any treatment.

the widely studied NiO_x of ≈ 3.7 eV.^[36] Consequently, the In doped CuCrO_2 NP based HTL offers higher transmittance in the whole visible region for better light-harvesting but also protects the perovskite layer from UV radiation.

The current (I)-voltage (V) curves of CuCrO_2 and In doped CuCrO_2 NP film on ITO as shown in Figure 3d show that the doped NP film is more conductive than its undoped counterpart. The HTL film also shows uniform conductivity in different regions of the film. The average conductivity values of CuCrO_2 is 0.029 S cm^{-1} which is comparative with the value of CuCrO_2 synthesized through hydrothermal method.^[33] After doping of In with the optimized level of 2.5 mol%, the conductivity increases by a factor of ≈ 2.5 – 0.069 S cm^{-1} which is resulted from the higher hole concentration and mobility (see Figure S5 in the Supporting Information). Overall, the In doped CuCrO_2 NP film with higher conductivity should be more efficient for hole transportation in PSCs.

The work function (WF) of In doped CuCrO_2 NPs is 5.12 eV (see Figure S6a in the Supporting Information), as same as the pristine NPs (not shown in the figure to void confusion). The corresponding energy band level is obtained by the ultraviolet photoemission spectroscopy (UPS) (see Figure S6b in the Supporting Information) and bandgap as shown in Figure 4a. It offers a good band alignment as shown in the energy band diagram of the PSCs with the structure of ITO/HTL/perovskite/phenyl-C61-butyric acid methyl ester (PCBM):C60/zirconium (IV)

acetylacetonate (ZrAcac)/Ag (see Figure 4a). As shown in Figure 4a, the conduction band of In doped CuCrO_2 NPs is 1.43 eV higher than that of perovskite, resulting in efficient electron blocking and less carrier recombination. The large electron injection barrier of 2.43 eV between ITO and In doped CuCrO_2 NPs indicates its efficient electron injection blocking.^[37–40]

Regarding the performance of PSCs with In doped CuCrO_2 NP as HTL (the typical cross-section scanning electron microscopy (SEM) image of PSCs is shown in Figure 4b), current density (J)- V curves with low hysteresis of the best PSCs based on pristine CuCrO_2 , and In doped CuCrO_2 NPs are plotted in Figure 4c. As compared to the undoped CuCrO_2 , there are improvements in J_{sc} (from 21.52 to 23.75 mA cm^{-2}) and fill factor (FF) (from 79.85% to 80.67%) after In doping in CuCrO_2 NPs. According to the records in Table S3 in the Supporting Information, the J_{sc} values based on different doping level NPs are larger than the undoped counterpart. The higher hole extraction capability is demonstrated by the shorter photoluminescence (PL) decay time (19.65 ns for doped vs 31.87 ns for pristine) and better PL quenching of perovskite/In doped CuCrO_2 shown in Figures S7 and S8 in the Supporting Information. This is also demonstrated by the electrochemical impedance spectroscopy (EIS) spectra of the devices in Figure S9 in the Supporting Information. The series resistances R_s are 33.5 (pristine) and 27.9Ω (doped), respectively. It suggests that the conductivity of In doped CuCrO_2 device

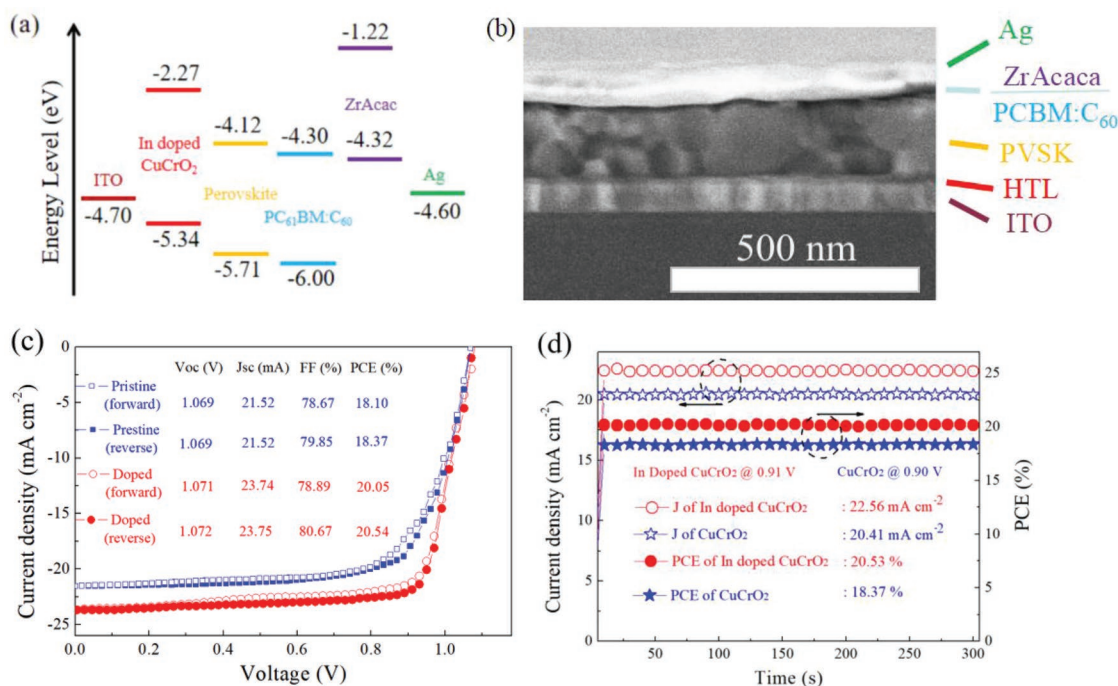


Figure 4. a) The energy band diagram of the PSC materials with respect to the vacuum level. b) The cross-section SEM of PSC. c) J - V curves, and d) stabilized photocurrent and efficiency of the best PSCs based on CuCrO₂ NPs (reference device) and In doped CuCrO₂ NPs.

is higher, which agrees with the above discussion of the conductivity of the HTL. Charge-transfer resistances (R_{ct}) of the charge recombination process are 1032 (pristine) and 1335 Ω (doped), illustrating less carrier recombination appears for the case of In doped CuCrO₂ HTL.^[10,17] The stabilized photocurrent and PCE at the maximum power point are shown in Figure 4d. The stabilized photocurrent and PCE corresponding to CuCrO₂ and In doped CuCrO₂ devices are 20.41 mA cm⁻², 18.37% and 22.56 mA cm⁻², 20.53%. This is well consistent with the measured J - V curves in Figure 4c. It should be noted that the PCE of p-i-n PSCs based on the pristine CuCrO₂ (in this study) is comparable with that of the previously reported.^[14] Interestingly, In doped CuCrO₂ PSCs showed improved performances as shown in Figure 4. The performances are among the best performed PSCs with oxide based HTL as shown in Table S5 in the Supporting Information.^[41–58] Additionally, the HTL using CuCrO₂ and In doped CuCrO₂ NPs offer ignorable hysteresis (Figure S10, Supporting Information) due to efficient hole extraction. The incident photo-to-electron conversion efficiency (IPCE) spectra and the integrated J_{sc} of the two devices are shown in Figure S11 in the Supporting Information. The integrated J_{sc} of the devices are 20.90 and 23.25 mA cm⁻², demonstrating that the values are consistent with the J - V curves (with the small mismatch of 2.87% and 2.11%). It should be noted that the values of PCE based on the HTL synthesized through our method have small fluctuations, suggesting good repeatability of the devices (detailed performances are shown in Tables S2 and S3 in the Supporting Information). Concerning the photostability of the devices, unsealed devices have been tracking in a N₂ filled glovebox under 1 sun continuous illumination and time-dependent variation of the normalized V_{oc} , J_{sc} , FF, and

PCE of the PSCs are shown in Figure 5. All the parameters are generally stable after 800 h of continuous radiation without encapsulation in the glovebox with a remaining PCE value of about 90%, illustrating an excellent photostability of the devices.

Furthermore, as shown in Table S4 in the Supporting Information, the PSCs maintain high PCE when the In doped CuCrO₂ HTL was annealed under room temperature to 200 °C for 10 min in air, suggesting excellent thermostability. When annealing temperature increased to 250 °C and higher, the PCE decreases obviously due to lower J_{sc} and FF. To understand the reasons, XPS spectra of the HTL under different annealing temperatures are obtained as shown in Figure 6. When annealing temperature is 200 °C or lower, the peaks of 932.1 and 952.1 eV with no satellite peaks indicated the only existence of Cu⁺ ions.^[19,59] When annealing temperature increased to 250 and 280 °C, some Cu⁺ ions were oxidized to Cu²⁺ ions, indicated by the peaks of 934.9 and 955.2 eV and obvious satellite peaks. If the annealing temperature reached 300 °C, Cu²⁺ ions dominated in the HTL and the PCE of PSC decreased by $\approx$ 25%. The change of Cu⁺ to Cu²⁺ means that the HTL is less p-type and thus the hole conductivity decreases, resulting in lower J_{sc} and FF. Consequently, the In doped CuCrO₂ HTL made from APA method shows good thermal stability up to 200 °C for practical application in PSCs.

3. Conclusions

In conclusion, we demonstrated the APA approach to synthesize pristine and In doped CuCrO₂ NPs. This strategy provides an efficient way to synthesize (doped) metal oxides in which the

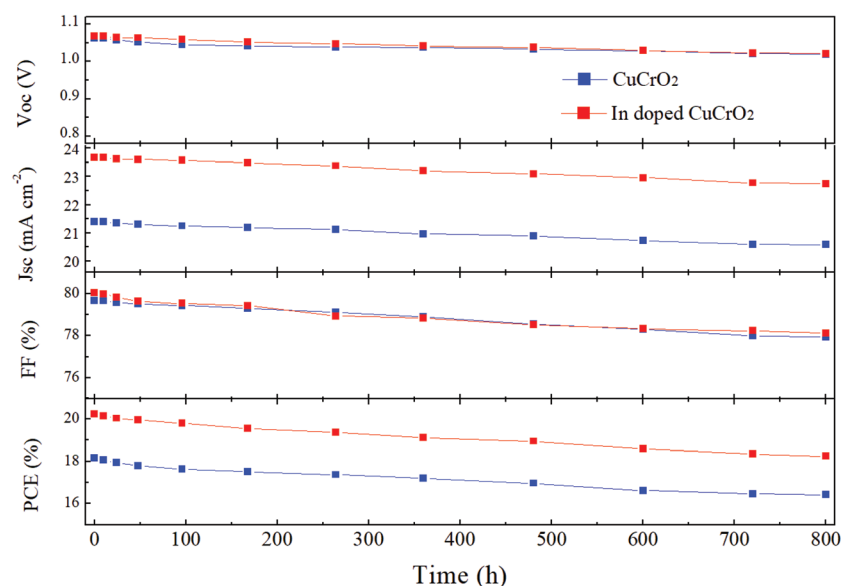


Figure 5. The time-dependent variation of the V_{oc} , J_{sc} , FF, and PCE of the best (unencapsulated) PSCs under 1 sun continuous illumination.

reaction time is dramatically shortened by 90% and the calcination temperature is lowered by one-third as compared to previous reported hydrothermal method. While the NPs can form effective HTL, the HTL exhibits thermal stability up to 200 °C. The optical transmission and carrier mobility of the HTL are improved by doping In into CuCrO₂ NPs, which is beneficial for the harvest of solar light and hole transport. Using the NPs as HTL, PSCs with high PCE and photostability were fabricated. This work demonstrates a decent approach to synthesize pristine and doped multinary oxides for HTL of high-performance PSCs. Furthermore, the strategy facilitates the development of large-scale and flexible high performance PSCs.

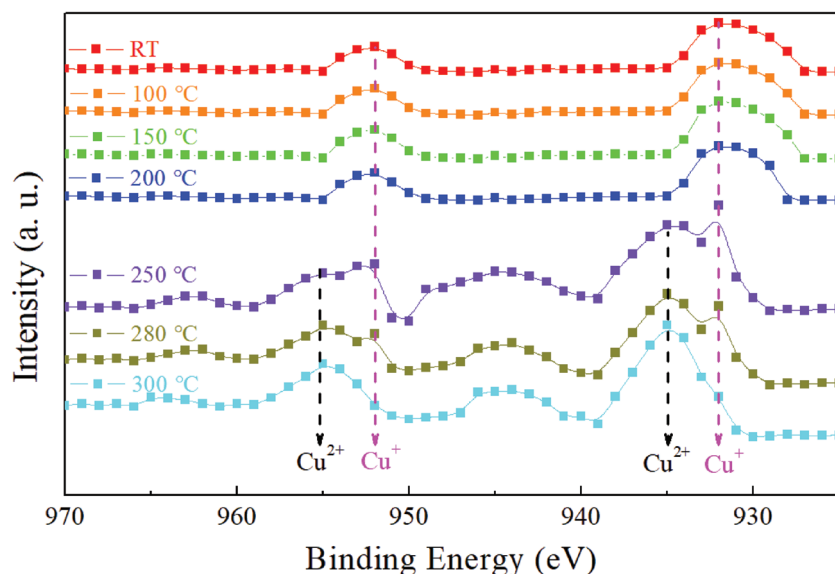


Figure 6. High-resolution XPS spectra of Cu 2p of the In doped CuCrO₂ films annealed under different temperatures for 10 min in air.

4. Experimental Section

Materials: Cu(NO₃)₂·3H₂O (99% in purity), Cr(NO₃)₃·9H₂O (98.5% in purity), In(C₂H₃O₂)₃·H₂O (99.99% in purity), and ZrAcac (98%) were purchased from Sigma-Aldrich. Ethanol absolute, methanol, chlorobenzene (CB, extra dry, 99.8%), hydrochloric acid (37%), dimethylformamide (DMF, extra dry, 99%), dimethyl sulfoxide (DMSO, extra dry, 99%), 1,2-dichlorobenzene (DCB, extra dry, 98+%), isopropanol (extra dry, 99.8%), and ammonium hydroxide solution in water (28%) were purchased from Acros Organics. Methylammonium iodide and formamidine iodide were purchased from Dyesol. PC₆₁BM and C₆₀ were purchased from Solarmer Energy, Inc. All chemicals were used without further treatments.

Synthesis of NPs: CuCrO₂ and In doped CuCrO₂ NPs were synthesized in azeotropic solvent of absolute ethanol and deionized water. The same stoichiometric cupric nitrate and chromium nitrate were mixed in 12 mL absolute ethanol for CuCrO₂ NPs and a certain amount of indium acetate was added for In doped NPs. After stirring for 10 min, 0.09 g NaOH in 0.4 mL deionized water was added in the above solution. After another 10 min stirring, the solution was placed into an 18 mL Teflon-lined autoclave, which was sealed and kept at 160 °C for 6 h. Then, the products were washed with diluted hydrochloric acid and absolute alcohol in sequence for several times, and were dried in vacuum under room temperature for further use.

Preparation of HTL Films and Fabrication of Devices: HTL films were spin-coated on clean ultraviolet ozone-treated ITO glasses and the thickness was controlled by spin speed and spin times. The suspension for spin coating was prepared by resolving the NPs powder in methanol and the concentration was 4 mg mL⁻¹. The optimal thickness of 42 nm was spin-coated at 2000 rpm twice. The samples were transferred into the nitrogen-filled glovebox without any treatments. As same as the previous work, the film of Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(I_{0.85}Br_{0.15})₃ perovskite was formed on top of the NP film and annealed.^[60] Then, PC₆₁BM/C₆₀ and ZrAcac were spin-coated on the perovskite layer successively. Finally, Ag electrode with a thickness of 120 nm was thermally evaporated on the top. The details of devices fabrication after NP film coating were as same as the report.^[17]

Characterization of NPs, Films, and Devices: The phase of NPs was detected by X-ray powder diffraction with Cu α radiation under λ of 1.54056 Å (XRD, Bruker D2 PHASER). The morphology of NPs and film was measured by TEM (Philips Tecnai G2 20 S-TWIN), SEM (Hitachi S-4800), and atomic force microscopy (AFM, NT-MDT NTEGRA), respectively. UPS spectra were gained from a He discharged lamp (He I 21.22 eV, Kratos Analytical). EDX spectrum was obtained by SEM (Hitachi S-4800). XPS and UPS measurements were performed with a Kratos Ultra Spectrometer (He I 21.22 eV). Work function of HTL was measured using a Kelvin probe (KP020, KP Technology). Ecopia HMS 5500 Hall system was used to gain the hole concentration and mobility. J - V curves were measured by a Newport AM1.5G solar simulator with the light intensity of 100 mW cm⁻². The steady-state J - V curves were recorded by setting the bias voltage at the value of the maximum power point. A system containing xenon lamp monochromatic shoper and a lock-in amplifier with a calibrated silicon photodetector was used to measure the IPCE. The electrochemical impedance spectroscopy

analysis was conducted on a CHI660C electrochemical workstation (CH Instrument, Inc.) at $V = 0.9$ V under a black condition with the frequency ranging from 100 000 to 1 Hz.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

B.Y. and D.O. contributed equally to this work. This research was supported by the University Grant Council of the University of Hong Kong (Grant# 201611159194, 201511159225, and the Platform Research Fund) and the General Research Fund (Grant# 17211916, 17204117, and 17200518) from the Research Grants Council of Hong Kong Special Administrative Region, China. B.Y. acknowledges the financial support from the Special Foundation for Excellent Young Teachers and Principals Program of Jiangsu Province, China and the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (17KJB140027). The authors acknowledge the help of Lu Zhu and Fei Ye in the work.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

hole transport layers, In doped CuCrO_2 , perovskite solar cells, solvothermal synthesis

Received: March 30, 2019
Revised: May 21, 2019
Published online: June 26, 2019

- [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- [2] National Renewable Energy Laboratory (NREL) efficiency chart, <https://www.nrel.gov/pv/cell-efficiency.html> (accessed: June 2019).
- [3] Q. Hou, J. Ren, H. Chen, P. Yang, Q. Shao, M. Zhao, X. Zhao, H. He, N. Wang, Q. Luo, Z. Guo, *ChemElectroChem* **2018**, *5*, 726.
- [4] Q. Jiang, L. Wang, C. Yan, C. Liu, Z. Guo, N. Wang, *Eng. Sci.* **2018**, *1*, 64.
- [5] Q. Luo, H. Ma, Q. Hou, Y. Li, J. Ren, X. Dai, Z. Yao, Y. Zhou, L. Xiang, H. Du, H. He, N. Wang, K. Jiang, H. Lin, H. Zhang, Z. Guo, *Adv. Funct. Mater.* **2018**, *28*, 1706777.
- [6] M. M. Tavakoli, D. Prochowicz, P. Yadav, R. Tavakoli, M. Saliba, *Eng. Sci.* **2018**, *3*, 48.
- [7] L. Yang, X. Wang, X. Mai, T. Wang, C. Wang, X. Li, V. Murugadoss, Q. Shao, S. Angaiah, Z. Guo, *J. Colloid Interface Sci.* **2019**, *534*, 459.
- [8] H. Zhang, J. Cheng, F. Lin, H. He, J. Mao, K. S. Wong, A. K. Jen, W. C. Choy, *ACS Nano* **2016**, *10*, 1503.
- [9] H. L. Zhu, J. Cheng, D. Zhang, C. Liang, C. J. Reckmeier, H. Huang, A. L. Rogach, W. C. Choy, *ACS Nano* **2016**, *10*, 6808.
- [10] H. Zhang, X. Ren, X. Chen, J. Mao, J. Cheng, Y. Zhao, Y. Liu, J. Milic, W.-J. Yin, M. Grätzel, W. C. H. Choy, *Energy Environ. Sci.* **2018**, *11*, 2253.
- [11] W. Sun, Y. Li, S. Ye, H. Rao, W. Yan, H. Peng, Y. Li, Z. Liu, S. Wang, Z. Chen, L. Xiao, Z. Bian, C. Huang, *Nanoscale* **2016**, *8*, 10806.
- [12] A. E. Shalan, T. Oshikiri, S. Narra, M. M. Elshaniwany, K. Ueno, H. P. Wu, K. Nakamura, X. Shi, E. W. Diau, H. Misawa, *ACS Appl. Mater. Interfaces* **2016**, *8*, 33592.
- [13] W. A. Dunlap-Shohl, T. B. Daunis, X. Wang, J. Wang, B. Zhang, D. Barrera, Y. Yan, J. W. P. Hsu, D. B. Mitzi, *J. Mater. Chem. A* **2018**, *6*, 469.
- [14] H. Zhang, H. Wang, H. Zhu, C.-C. Chueh, W. Chen, S. Yang, A. K. Y. Jen, *Adv. Energy Mater.* **2018**, *8*, 1702762.
- [15] H. Zhang, H. Wang, W. Chen, A. K. Jen, *Adv. Mater.* **2017**, *29*, 1604984.
- [16] I. T. Papadas, A. Ioakeimidis, G. S. Armatas, S. A. Choulis, *Adv. Sci.* **2018**, *5*, 1701029.
- [17] D. Ouyang, J. Xiao, F. Ye, Z. Huang, H. Zhang, L. Zhu, J. Cheng, W. C. H. Choy, *Adv. Energy Mater.* **2018**, *8*, 1702722.
- [18] A. Barnabé, Y. Thimont, M. Lalanne, L. Presmanes, P. Tailhades, *J. Mater. Chem. C* **2015**, *3*, 6012.
- [19] J. Yang, F. Muckel, W. Baek, R. Fainblat, H. Chang, G. Bacher, T. Hyeon, *J. Am. Chem. Soc.* **2017**, *139*, 6761.
- [20] W. C. Sheets, E. Mugnier, A. Barnabé, T. J. Marks, K. R. Poeppelmeier, *Chem. Mater.* **2006**, *18*, 7.
- [21] C. Hou, Z. Tai, L. Zhao, Y. Zhai, Y. Hou, Y. Fan, F. Dang, J. Wang, H. Liu, *J. Mater. Chem. A* **2018**, *6*, 9723.
- [22] D. Pan, S. Ge, X. Zhang, X. Mai, S. Li, Z. Guo, *Dalton Trans.* **2018**, *47*, 708.
- [23] D. Pan, S. Ge, J. Zhao, Q. Shao, L. Guo, X. Zhang, J. Lin, G. Xu, Z. Guo, *Dalton Trans.* **2018**, *47*, 9765.
- [24] D. Pan, S. Ge, J. Zhao, J. Tian, Q. Shao, L. Guo, X. Mai, T. Wu, V. Murugadoss, H. Liu, T. Ding, S. Angaiah, Z. Guo, *Ind. Eng. Chem. Res.* **2019**, *58*, 836.
- [25] B. Zhao, Q. Shao, L. Hao, L. Zhang, Z. Liu, B. Zhang, S. Ge, Z. Guo, *J. Colloid Interface Sci.* **2018**, *511*, 39.
- [26] K. Le, Z. Wang, F. Wang, Q. Wang, Q. Shao, V. Murugadoss, S. Wu, W. Liu, J. Liu, Q. Gao, Z. Guo, *Dalton Trans.* **2019**, *48*, 5193.
- [27] Z. Lin, B. Lin, Z. Wang, S. Chen, C. Wang, M. Dong, Q. Gao, Q. Shao, T. Ding, H. Liu, S. Wu, Z. Guo, *ChemCatChem* **2019**, *11*, 2217.
- [28] J. Tian, Q. Shao, J. Zhao, D. Pan, M. Dong, C. Jia, T. Ding, T. Wu, Z. Guo, *J. Colloid Interface Sci.* **2019**, *541*, 18.
- [29] J. Zhang, Z. Zhang, Y. Jiao, H. Yang, Y. Li, J. Zhang, P. Gao, *J. Power Sources* **2019**, *419*, 99.
- [30] J. K. Zhao, S. S. Ge, D. Pan, Y. L. Pan, V. Murugadoss, R. J. Li, W. Xie, Y. Lu, T. T. Wu, E. K. Wujcik, Q. Shao, X. M. Mai, Z. H. Guo, *J. Electrochem. Soc.* **2019**, *166*, H3074.
- [31] P. Naumov, S. Chizhik, M. K. Panda, N. K. Nath, E. Boldyreva, *Chem. Rev.* **2015**, *115*, 12440.
- [32] M. Miclau, D. Ursu, S. Kumar, I. Grozescu, *J. Nanopart. Res.* **2012**, *14*, 1110.
- [33] I. Sullivan, B. Zoellner, P. A. Maggard, *Chem. Mater.* **2016**, *28*, 5999.
- [34] Q. Sun, S. Zhou, X. Shi, X. Wang, L. Gao, Z. Li, Y. Hao, *ACS Appl. Mater. Interfaces* **2018**, *10*, 11289.
- [35] W. Yan, S. Ye, Y. Li, W. Sun, H. Rao, Z. Liu, Z. Bian, C. Huang, *Adv. Energy Mater.* **2016**, *6*, 1600474.
- [36] A. Huang, L. Lei, Y. Yu, Y. Liu, S. Yang, S. Bao, X. Cao, P. Jin, *Nanotechnology* **2017**, *28*, 20LT02.
- [37] L. Calió, S. Kazim, M. Grätzel, S. Ahmad, *Angew. Chem., Int. Ed.* **2016**, *55*, 14522.
- [38] A. Dubey, N. Adhikari, S. Mabrouk, F. Wu, K. Chen, S. Yang, Q. Qiao, *J. Mater. Chem. A* **2018**, *6*, 2406.
- [39] R. Sandoval-Torrientes, I. Zimmermann, J. Calbo, J. Aragón, J. Santos, E. Ortí, N. Martín, M. K. Nazeeruddin, *J. Mater. Chem. A* **2018**, *6*, 5944.
- [40] S. Sajid, A. M. Elseman, H. Huang, J. Ji, S. Dou, H. Jiang, X. Liu, D. Wei, P. Cui, M. Li, *Nano Energy* **2018**, *51*, 408.
- [41] S. Yang, J. Dai, Z. Yu, Y. Shao, Y. Zhou, X. Xiao, X. C. Zeng, J. Huang, *J. Am. Chem. Soc.* **2019**, *141*, 5781.

- [42] W. Xu, L. Zheng, X. Zhang, Y. Cao, T. Meng, D. Wu, L. Liu, W. Hu, X. Gong, *Adv. Energy Mater.* **2018**, 8, 1703178.
- [43] X. Zheng, Y. Deng, B. Chen, H. Wei, X. Xiao, Y. Fang, Y. Lin, Z. Yu, Y. Liu, Q. Wang, J. Huang, *Adv. Mater.* **2018**, 30, 1803428.
- [44] Z.-K. Yu, W.-F. Fu, W.-Q. Liu, Z.-Q. Zhang, Y.-J. Liu, J.-L. Yan, T. Ye, W.-T. Yang, H.-Y. Li, H.-Z. Chen, *Chin. Chem. Lett.* **2017**, 28, 13.
- [45] B.-S. Kim, T.-M. Kim, M.-S. Choi, H.-S. Shim, J.-J. Kim, *Org. Electron.* **2015**, 17, 102.
- [46] H. Sun, X. Hou, Q. Wei, H. Liu, K. Yang, W. Wang, Q. An, Y. Rong, *Chem. Commun.* **2016**, 52, 8099.
- [47] F. Xie, C.-C. Chen, Y. Wu, X. Li, M. Cai, X. Liu, X. Yang, L. Han, *Energy Environ. Sci.* **2017**, 10, 1942.
- [48] P. L. Qin, Q. He, C. Chen, X. L. Zheng, G. Yang, H. Tao, L. B. Xiong, L. Xiong, G. Li, G. J. Fang, *Sol. RRL* **2017**, 1, 1700058.
- [49] W. Chen, Y. Zhou, G. Chen, Y. Wu, B. Tu, F. Z. Liu, L. Huang, A. M. C. Ng, A. B. Djurišić, Z. He, *Adv. Energy Mater.* **2019**, 9, 1803872.
- [50] J. H. Kim, P. W. Liang, S. T. Williams, N. Cho, C. C. Chueh, M. S. Glaz, D. S. Ginger, A. K. Jen, *Adv. Mater.* **2015**, 27, 695.
- [51] W. Nie, H. Tsai, J. C. Blancon, F. Liu, C. C. Stoumpos, B. Traore, M. Kepenekian, O. Durand, C. Katan, S. Tretiak, J. Crochet, P. M. Ajayan, M. Kanatzidis, J. Even, A. D. Mohite, *Adv. Mater.* **2018**, 30, 1703879.
- [52] W. Chen, F. Z. Liu, X. Y. Feng, A. B. Djurisic, W. K. Chan, Z. B. He, *Adv. Energy Mater.* **2017**, 7, 1700722.
- [53] Y. Wu, F. Xie, H. Chen, X. Yang, H. Su, M. Cai, Z. Zhou, T. Noda, L. Han, *Adv. Mater.* **2017**, 29, 1701073.
- [54] A. Huang, L. Lei, J. Zhu, Y. Yu, Y. Liu, S. Yang, S. Bao, X. Cao, P. Jin, *Langmuir* **2017**, 33, 3624.
- [55] P.-L. Qin, H.-W. Lei, X.-L. Zheng, Q. Liu, H. Tao, G. Yang, W.-J. Ke, L.-B. Xiong, M.-C. Qin, X.-Z. Zhao, G.-J. Fang, *Adv. Mater. Interfaces* **2016**, 3, 1500799.
- [56] N. Wijeyasinghe, A. Regoutz, F. Eisner, T. Du, L. Tsetseris, Y.-H. Lin, H. Faber, P. Pattanasattayavong, J. Li, F. Yan, M. A. McLachlan, D. J. Payne, M. Heeney, T. D. Anthopoulos, *Adv. Funct. Mater.* **2017**, 27, 1701818.
- [57] W.-Y. Chen, L.-L. Deng, S.-M. Dai, X. Wang, C.-B. Tian, X.-X. Zhan, S.-Y. Xie, R.-B. Huang, L.-S. Zheng, *J. Mater. Chem. A* **2015**, 3, 19353.
- [58] H. Rao, W. Sun, S. Ye, W. Yan, Y. Li, H. Peng, Z. Liu, Z. Bian, C. Huang, *ACS Appl. Mater. Interfaces* **2016**, 8, 7800.
- [59] W. Ou, Y. Zou, K. Wang, W. Gong, R. Pei, L. Chen, Z. Pan, D. Fu, X. Huang, Y. Zhao, W. Lu, J. Jiang, *J. Phys. Chem. Lett.* **2018**, 9, 274.
- [60] Y. Zhao, H. Zhang, X. Ren, H. L. Zhu, Z. Huang, F. Ye, D. Ouyang, K. W. Cheah, A. K. Y. Jen, W. C. H. Choy, *ACS Energy Lett.* **2018**, 3, 2891.