

Strategic Synthesis of Ultrasmall NiCo_2O_4 NPs as Hole Transport Layer for Highly Efficient Perovskite Solar Cells

Dan Ouyang, Junyan Xiao, Fei Ye, Zhanfeng Huang, Hong Zhang, Lu Zhu, Jiaqi Cheng, and Wallace C. H. Choy*

This study proposes a novel strategy of controllable deamination of Co-NH_3 complexes in a system containing Ni(OH)_2 to synthesize ultrasmall ternary oxide nanoparticles (NPs), NiCo_2O_4 . Through this approach, ultrasmall (5 nm on average) and well-dispersed NiCo_2O_4 NPs without exotic ligands are obtained, which enables the formation of uniform and pin-hole free films. The tightly covered NiCo_2O_4 films also facilitate the formation of large perovskite grains and thus reduce film defects. The results show that with the NiCo_2O_4 NPs as the hole transport layer (HTL), the perovskite solar cells reach a high power conversion efficiency (PCE) of 18.23% and a promising stability (maintained $\approx 90\%$ PCE after 500 h light soaking). To the best of the author's knowledge, it is the first time that spinel NiCo_2O_4 NPs have been applied as hole transport layer in perovskite solar cells successfully. This work not only demonstrates the potential applications of ternary oxide NiCo_2O_4 as HTLs in hybrid perovskite solar cells but also provides an insight into the design and synthesis of ultrasmall and ligand-free NPs HTLs to enable cost-effective photovoltaic devices.

1. Introduction

Organic–inorganic hybrid perovskite solar cells (PVSCs) have emerged as a promising photovoltaic technology with power conversion efficiency (PCE) expeditiously improved over 22%.^[1] Carrier (electron and hole) transport layers connected with perovskite in PVSCs are fundamentally crucial for the improvement of device PCE and stability.^[2] For hole transport layers (HTLs), numerous materials have been used in PVSCs, but most of them are very expensive, such as 2,2',7,7'-tetrakis[N,N-di-(4-methoxyphenyl)amino]-9,9'-spirobifluorene,^[3] poly-3-hexylthiophene,^[4] and poly(triarylamine).^[5] Some relatively low-cost material such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has good electrical property and simple solution process conditions, while acidic nature and hygroscopic nature of PEDOT:PSS cause poor device performance and instability.^[6]

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The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aenm.201702722>.

DOI: 10.1002/aenm.201702722

Inorganic HTLs are low-cost materials with versatile optoelectronic properties, superior physical and chemical stabilities.^[2e,7] Generally, they can be classified into binary, ternary compounds, etc., according to their element composition, and ternary oxides are substantially attractive and promising in PVSCs application due to their good conductivity and tunable optical and electrical properties. Recently, sol-gel synthesized $\text{Cu}_x\text{Cr}_2\text{O}_3$ particles with size >100 nm as HTL in PVSCs have been reported, yielding a PCE of 17.19%.^[8] CuGaO_2 nanoplates with 50–75 nm in diameter and 10–15 nm in thickness were synthesized by the microwave-assisted method at 230 °C and the PVSCs based on 345 nm thickness CuGaO_2 HTL have been achieved with a PCE of 18.51%.^[9] $\text{Co}_{1-y}\text{Cu}_y\text{O}_x$ thin film was demonstrated as HTL into PVSCs via high-cost magnetron

cosputtering technique, displaying a relatively low PCE of 10%.^[10] Considering that small nanoparticles (NPs) favor the formation of a high-quality film including well-packed (i.e., elimination of the voids and gaps) and functional morphology (i.e., smooth and compact film), inorganic NPs with diameters in a few nanometers fabricated by facile methods to ensure low-cost and good-quality film for highly efficient HTLs in PVSCs still demand.

Spinel NiCo_2O_4 , with Ni occupying octahedral sites and Co occupying both octahedral and tetrahedral sites, is a p-type semiconductor with a conductivity of 500 S cm^{-1} , at least two orders of magnitudes higher than that of NiO and Co_2O_3 .^[11] It has been applied in photodetector, oxygen reduction, Li-ion batteries, and electrocatalysis due to its outstanding merits like electrochemical activity, environmental friendliness, low-cost, and abundance.^[12] Several synthesis methods of NiCo_2O_4 , such as thermal decomposition, combustion, electrospinning, spray pyrolysis, sol-gel, hydrothermal, and pulsed laser deposition, have been exploited.^[11a,12b–d,13] However, the synthesized NiCo_2O_4 featuring different microstructures or large particle size is unsuitable for forming films, let alone the complicated fabrication processes, high temperature, and even toxic chemical agents (such as NH_4F). Furthermore, surfactants such as ethylene glycol (EG) are typically added to decrease the particle size ($\approx 10\text{--}20$ nm) and maintain monodispersion,^[14] making the application of NiCo_2O_4 in PVSCs more difficult considering the degraded electrical properties resulting from surfactant ligands. The above issues

explain the situation that successful application of NiCo_2O_4 HTL in PVSCs has never been reported.

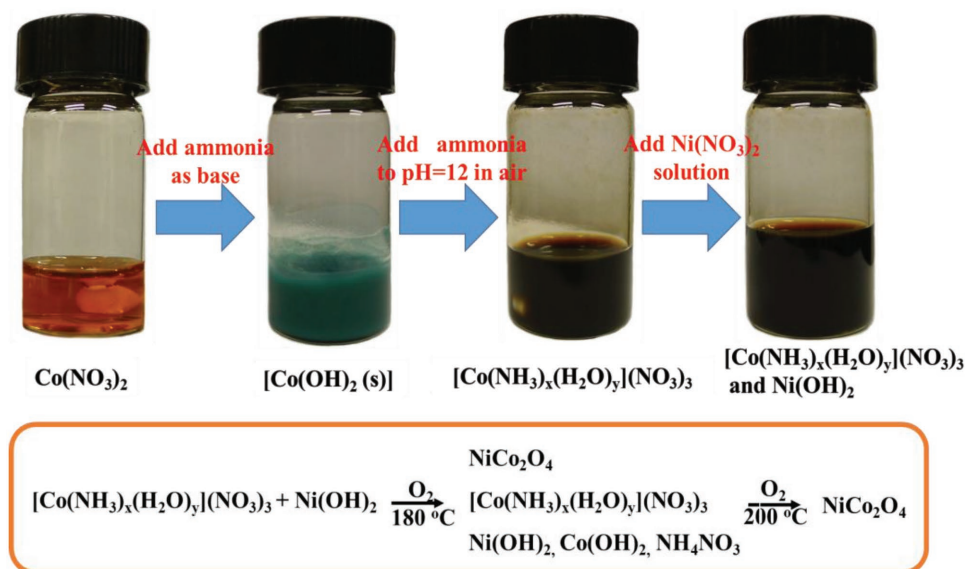
Here, we demonstrated a novel strategy of controllable deammoniation of Co-NH_3 Werner-type coordination compounds in a system containing Ni(OH)_2 to synthesize ultrasmall ternary oxide NPs, NiCo_2O_4 . Through this approach, ultrasmall (≈ 5 nm) and well-dispersed NiCo_2O_4 NPs are achieved, contributing to the formation of compact films with excellent coverage, interfacial contact, and hole extraction ability. Notably, NiCo_2O_4 HTL is first introduced in PVSCs with a decent PCE of 18.23% and a promising stability ($\approx 90\%$ PCE maintained after 500 h continuous light soaking). We attribute the promising performance to the desirable optoelectronic properties of the high-quality NiCo_2O_4 NPs, and the promoted perovskite crystallization due to the non-wettability of NiCo_2O_4 films. This work develops a new p-type inorganic layer for PVSCs, which will boost the device strategic design and development; and provides an insight into the design and synthesis of ultrasmall and ligand-free NPs HTLs to enable cost-effective photovoltaic devices.

2. Results and Discussion

The synthesis of NiCo_2O_4 NPs is shown in **Scheme 1**. The Co source, $\text{Co(NO}_3)_2$, was dissolved in water. Adding ammonia dropwise into $\text{Co(NO}_3)_2$ solution, the dark green precipitate was produced, and X-ray diffraction (XRD) pattern in Figure S1a (Supporting Information) confirmed the formation of Co(OH)_2 . When continuously adding ammonia to $\text{pH} = 12$, the dark green solid dissolved gradually and turned into red-brown solution due to the oxidation of Co^{2+} to Co^{3+} after stirring in air, yielding stable $[\text{Co}(\text{NH}_3)_x(\text{H}_2\text{O})_y](\text{NO}_3)_3$ complex, which was verified by Fourier transform infrared (FTIR) spectroscopy, as shown in Figure S1b (Supporting Information), and is consistent with the reference.^[15] Ni source for NiCo_2O_4 was provided by $\text{Ni(NO}_3)_2$, which was added into the as-prepared $[\text{Co}(\text{NH}_3)_x(\text{H}_2\text{O})_y](\text{NO}_3)_3$ complex

to form a mixture solution. The mixture solution was heated to release ammonia gradually (named as deammonia process) as well as to remove all water, and then NiCo_2O_4 crystals start to be detected in the obtained solid (as shown in Figures S2 and S4a, Supporting Information). We note that during the addition of $\text{Ni(NO}_3)_2$, a small amount of Ni(OH)_2 formed due to the strong base condition, identified from the (003) plane of Ni(OH)_2 (JCPDS card No: 00-038-0715) shown in Figure S3 (Supporting Information). Ni(OH)_2 decomposes into Ni^{2+} , serving as one of the components of NiCo_2O_4 in this system; and the gradually decomposed Co-NH_3 complex then combines with Ni to form NiCo_2O_4 . Further calcination of the above solid at 200°C obtains high crystalline and high-quality NiCo_2O_4 NPs. The sharp XRD peaks in **Figure 1a** and **Figure S2** (Supporting Information) show the disappearance of ammonium nitrate and the appearance of strong characteristic peaks of NiCo_2O_4 after calcination, suggesting the formation and good crystallinity of NiCo_2O_4 . The characteristic diffraction peaks in **Figure 1a** are indexed into a cubic spinel structure, which matches well with the standard JCPDF card (No. 20-0781)^[12d,14c,16] and no impurity phases were detected. Intercalating ammonia into the complex is crucial in achieving ultrasmall particles because the deammonia process can be thermally controlled to suppress the NPs growth. To prove this point, we investigated the NPs size evolution at 150 and 180°C . NiCo_2O_4 was formed at both 150 and 180°C , as shown by the XRD patterns in **Figure S4a** (Supporting Information). However, the NiCo_2O_4 NPs are larger than 14 nm at 150°C condition; while the particle size reduced to an average size of 4.60 nm at 180°C , as shown in **Figure S4b,c** (Supporting Information). The size reduction mainly attributes to the substantially shortened reaction time (from 24 h at 150°C to 2 h at 180°C), and therefore significantly suppressed NP growth after formation, indicating the size controllability in the deammonia process.

The excellent dispersity of NiCo_2O_4 NPs synthesized in our method is determined by the residual NH_3 ligands attached



Scheme 1. A schematic diagram for the synthesis of NiCo_2O_4 NPs.

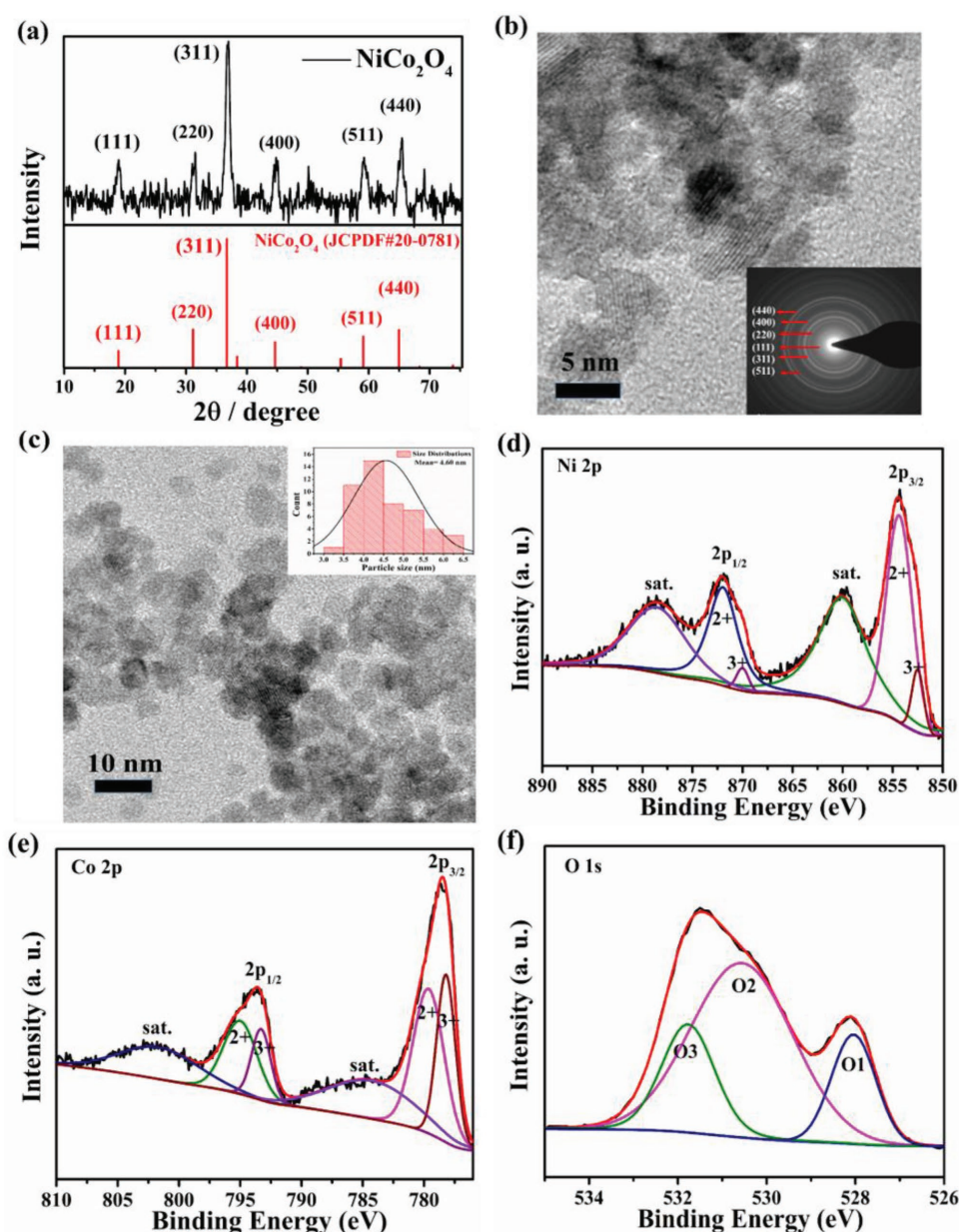


Figure 1. a) XRD pattern of the NiCo_2O_4 NPs. b) HRTEM image and the corresponding diffraction pattern (inset) of the NiCo_2O_4 NPs. c) TEM image and size distribution histogram (inset) of the NiCo_2O_4 NPs. d) Ni 2p, e) Co 2p, and f) O 1s XPS data for NiCo_2O_4 NPs.

to NPs, which prohibits NPs aggregation during annealing. It is supported by the poor dispersity of NPs after replacing ammonia with sodium hydroxide (NaOH), as shown in Figure S5b (Supporting Information). The residual NH_3 molecules were detected via FTIR technique, which displayed stretching bands of 3500–3000, 1766, 1390, and 845 cm^{-1} , as shown in Figure S5a (Supporting Information). They absorb on the surface of NPs and form H-bond with water to assist the dispersion of NiCo_2O_4 NPs.^[14c,17] NH_3 molecules can be easily removed during film fabrication and thus avoid electrical property deterioration as is the case for most organic ligands.

We further characterize the NiCo_2O_4 NPs by high-resolution transmission electron microscope (HRTEM) image, as shown

in Figure 1b. Diffraction rings were indexed to the (311), (400), (111), (220), (511), and (441) planes of NiCo_2O_4 , consistent with the XRD pattern. Transmission electron microscopy (TEM) image in Figure 1c showed NiCo_2O_4 with an average diameter of 4.6 nm (for ≈ 50 nanoparticles), which is the smallest NiCo_2O_4 NPs ever reported. The ultrasmall NiCo_2O_4 NPs are favorable for fabricating uniform and compact NiCo_2O_4 film, as shown in the scanning electron microscope (SEM) image in Figure S6 (Supporting Information).

To obtain more detailed information about the elemental composition and the oxidation state of our prepared NiCo_2O_4 NPs, X-ray photoelectron spectroscopy (XPS) measurements were performed and shown in Figure 1d–f. With Gaussian fitting,

the spectrum of Ni2p (Figure 1d) exhibits spin–orbit doublets (Ni^{2+} and Ni^{3+}) and shakes up satellite peaks. The peaks at 854.3 and 871.9 eV are indexed to Ni^{2+} , and the peaks at 852.5 and 870.0 eV are indexed to Ni^{3+} . There are a pair of spin–orbit peaks ($\text{Co } 2p_{1/2}$ and $\text{Co } 2p_{3/2}$) and two shakeup satellites peaks which are assigned to the characteristic of Co^{2+} and Co^{3+} (Figure 1e). The peaks at 779.6 and 795.0 eV are indexed to Co^{2+} , and the two at 778.2 and 793.3 eV are ascribed to Co^{3+} . As shown in Figure 1f, the fitting peak O1 at 528.0 eV represents a typical metal–oxygen bond, and O2 with a binding energy of 530.5 eV is attributed to defects, impurities, and surface species, like hydroxyls, chemisorbed oxygen, and undercoordinated lattice oxygen.^[12e] O3 (with a binding energy of 531.7 eV) is associated with the multiplicity of physical and chemisorbed water at/within the surface.^[14d] Consequently, XPS results are consistent with the literature^[18] and demonstrate the formation of cubic spinel NiCo_2O_4 . The Ni:Co atomic ratio is about 1.25:2 based on the XPS peak areas and the sensitivity factors, indicating a higher surface Ni concentration in comparison to that of designed (Ni:Co, 1:2).

According to the contact angles (CA) shown in Figure S7 (Supporting Information), NiCo_2O_4 is more hydrophobic, with its CA ($= 23^\circ$) larger than that of PEDOT:PSS (CA $= 10^\circ$). The less wettability of NiCo_2O_4 favors the formation of large perovskite grains due to the suppressed heterogeneous nucleation,^[19] as demonstrated by atomic force microscope (AFM) in Figure 2a–d that average crystal size enlargement of 157 nm was obtained for poor wetting NiCo_2O_4 . We obtained the same positive result for other perovskites (e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$) yielding an average crystal size enlargement of 70 nm for NiCo_2O_4 , as shown in Figure S8 (Supporting Information). Furthermore, the strengthened and sharpened XRD diffraction (Figure 2e) suggests the improved crystallinity of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ on NiCo_2O_4 , which is consistent with the large grains shown in AFM.

The energy band diagram of the NiCo_2O_4 film determined by ultraviolet photoelectron spectroscopy (UPS) (see Figure S9, Supporting Information) suggests a promising candidate as HTLs in PVSCs. We fabricated inverted PVSCs with the architecture of indium tin oxide (ITO)/ NiCo_2O_4 / $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM): C_{60} /zirconium(IV) acetylacetonate (ZrAcac)/Ag to demonstrate the effectiveness of NiCo_2O_4 as HTL. The energy levels of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, PC_{61}BM : C_{60} , ZrAcac , and Ag collected from literature^[7e,20] and the cross-sectional SEM image of the NiCo_2O_4 based device are shown in Figure 3a,b. The current density–voltage (J – V) characteristics of the best PVSCs under the illumination of AM 1.5 G, 100 mW cm^{-2} are shown in Figure 3c. The champion PVSCs with NiCo_2O_4 HTL offered an open-circuit voltage (V_{OC}) of 1.07 V, a short-circuit current density (J_{SC}) of 21.75 mA cm^{-2} , a fill factor (FF) of 77%, and a PCE of 18.10% under reverse scan direction; and a V_{OC} of 1.07 V, a J_{SC} of 21.83 mA cm^{-2} , a FF of 78%, and a PCE of 18.23% under forward scan direction. The stabilized photocurrent and PCE at the maximum power output point under AM1.5 sun illumination are shown in Figure 3d, which displayed a stabilized photocurrent of 20.57 mA cm^{-2} and PCE of 18.52% at 0.90 V, agreeing well with the value measured from J – V curves (Figure 3c). Notably, our spinel-type NiCo_2O_4 is first reported as HTL in PCSVs with the best PCE of 18.23%, which is comparable to other reported ternary oxides.^[8,9] This highly efficient PVSC based on NiCo_2O_4 is mainly attributed to the promoted perovskite grains growth and very good optical and electrical properties of the NiCo_2O_4 film.

The integrated J_{SC} of NiCo_2O_4 based PVSCs obtained from incident-photon-to-current conversion efficiency (IPCE) spectrum (Figure S10a, Supporting Information) is 20.79 mA cm^{-2} , which is consistent with the value determined by the J – V measurement (see Figure 3c). Meanwhile, the PCE histogram of

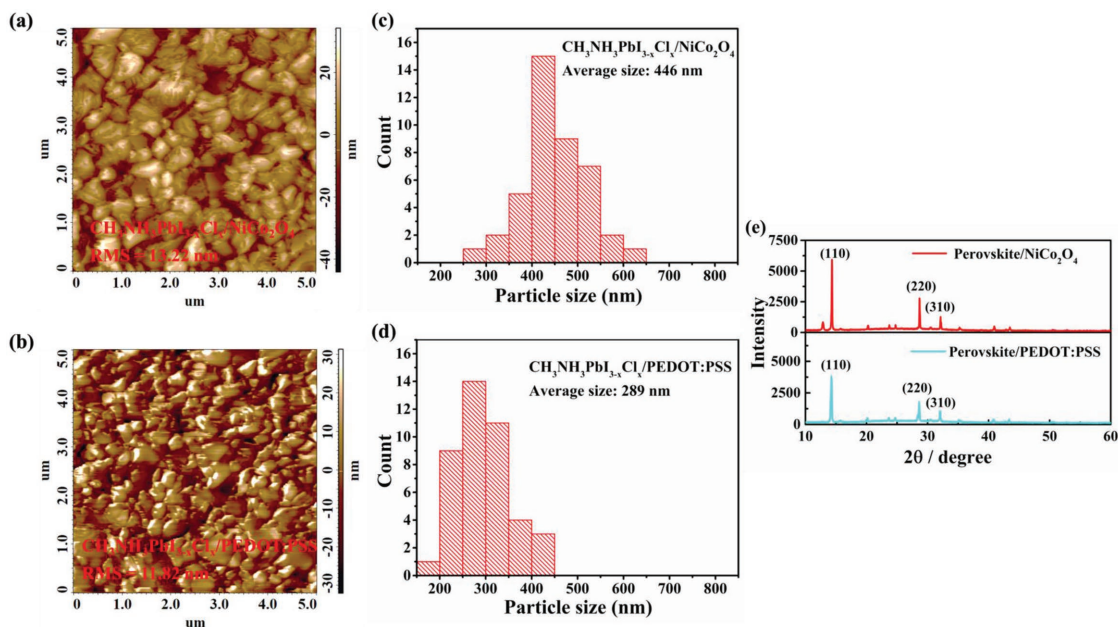


Figure 2. AFM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ a) on NiCo_2O_4 , b) on PEDOT:PSS and size distribution histogram of perovskites c) on NiCo_2O_4 , d) on PEDOT:PSS. e) XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ on NiCo_2O_4 and PEDOT:PSS, respectively.

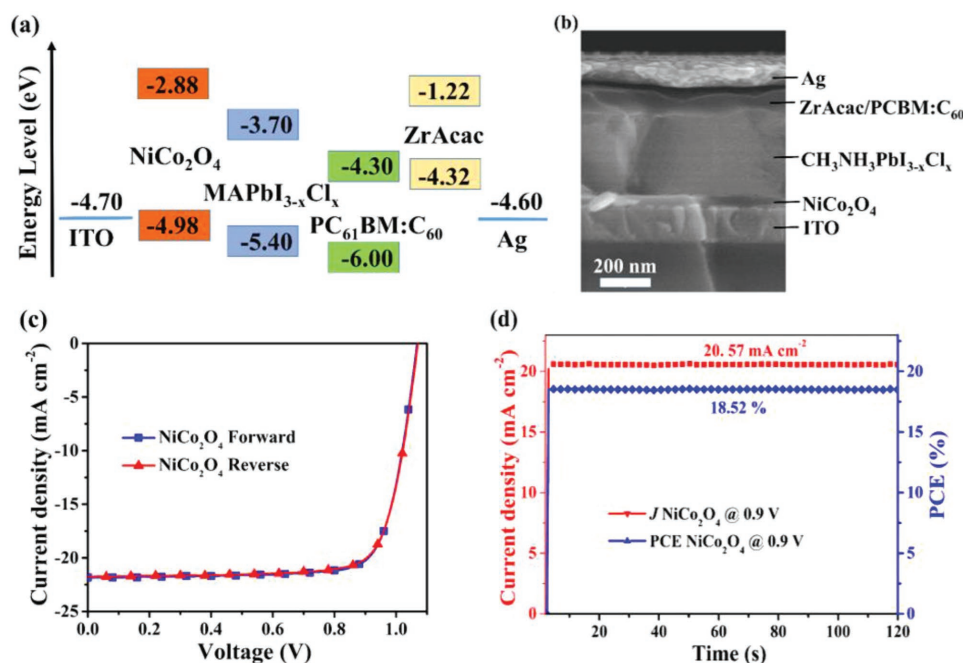


Figure 3. a) The energy diagram with respect to the vacuum level of the used materials. b) The cross-section SEM image of PVSC with the structure of ITO/NiCo₂O₄/CH₃NH₃PbI_{3-x}Cl_x/PC₆₁BM:C₆₀/ZrAcac/Ag. c) J–V characteristics of the best NiCo₂O₄ based PVSCs measured under AM 1.5 G 100 mW cm⁻² illumination. d) Steady photocurrent (red) and PCE (blue) under 1 sun illumination of the best NiCo₂O₄ based PVSCs.

20 NiCo₂O₄ based PVSCs presented in Figure S10b (Supporting Information) suggests good reproducibility with a narrow distribution in the range of 16–18%. Also, the device performances of NiCo₂O₄ based PVSCs are better than the PEDOT:PSS based PVSCs, as shown in Figure S11 (Supporting Information), which is comparable to our previously published results and is therefore used as a reference.^[7d]

The dark J–V characteristics of NiCo₂O₄ based PVSC (as shown in Figure S11c, Supporting Information) show a lower dark current density comparing with PEDOT:PSS based PVSC under the reverse bias, indicating the excellent blocking electron injection from ITO to NiCo₂O₄ HTL. The blocking electron injection originates from the large electron injection barrier (1.82 eV) between ITO and NiCo₂O₄ HTL (shown in Figure 3a). Furthermore, a large electron extraction barrier (0.82 eV) at NiCo₂O₄ HTL/perovskites interface reduces carrier recombination, and thus increases V_{OC} . Meanwhile, the Nyquist plot (dark) by the electrochemical impedance spectroscopy (EIS) measured at the open-circuit voltage in Figure S11d (Supporting Information) is also consistent with the dark current measurement. The arc at low frequencies has been assigned to the interfacial recombination process,^[21] and a large interfacial charge-recombination resistance ($R_{rec} = 383.3 \Omega$) of NiCo₂O₄ based PVSCs is obtained (for PEDOT:PSS, $R_{rec} = 48.03 \Omega$), suggesting a very low recombination rate at the interface of NiCo₂O₄ PVSCs.

The charge extraction ability of the HTLs is another significant factor governing PVSCs performances, which is characterized by photoluminescence (PL) and time-resolved PL measurements, as shown in Figure S11e,f (Supporting Information), respectively. Notably, the PL peak of CH₃NH₃PbI_{3-x}Cl_x on NiCo₂O₄ shows a blue-shifted 757 nm (CH₃NH₃PbI_{3-x}Cl_x on PEDOT:PSS

at 762 nm), indicating the reduced density of traps or subgap states for the perovskite on NiCo₂O₄ HTL.^[22] The average PL lifetime (τ_{ave}) of perovskite on NiCo₂O₄ is 32.83 ns (perovskite on PEDOT:PSS: 50.97 ns; perovskite on ITO: 291.35 ns) in a single exponential decay, which is sharply reduced and implies a more efficient carrier extraction from perovskite to NiCo₂O₄, contributing to the desirable PVSCs performance.

In addition to photovoltaic performance, we also checked the long-term stability of NiCo₂O₄ based PVSCs by the maximum power point (MPP) tracking.^[23] As shown in Figure 4,

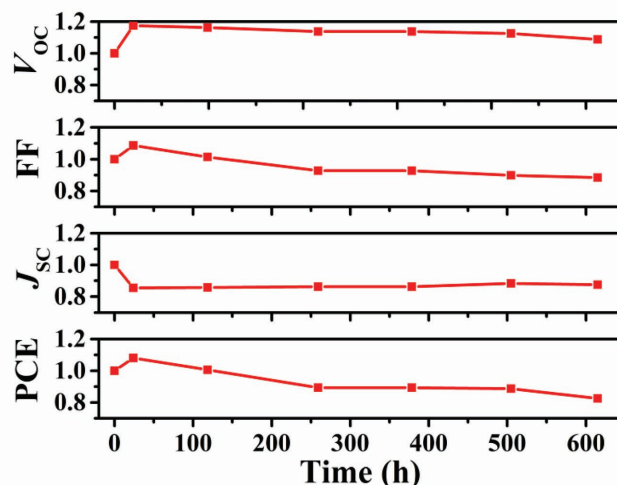


Figure 4. Time-course variation of the normalized V_{OC} , FF, J_{SC} , and PCE of NiCo₂O₄ based PVSCs under 1 sun continuous illumination with encapsulation.

the PCE of NiCo_2O_4 based PVSCs maintained $\approx 90\%$ of the initial PCE after 500 h illumination at AM 1.5G (100 mW cm^{-2}). This promising stability of NiCo_2O_4 based PVSCs is due to the formation of large perovskite grains (see Figure 2; Figure S8, Supporting Information) on NiCo_2O_4 as discussed above. The enlarged grain sizes of perovskite films lead to the reduction of grain boundaries density and thus the decrease of diffusion channel for the detrimental ions (e.g., I^-) and molecules (e.g., H_2O and O_2),^[24] which consequently enhances the long-term stability of NiCo_2O_4 based PVSCs.

3. Conclusion

We have demonstrated a novel strategy of controllable deamination of Co-NH_3 Werner-type coordination compounds in a system containing Ni(OH)_2 to synthesize ultrasmall NiCo_2O_4 NPs (5 nm in average), which favors the formation of a uniform thin film with a good surface coverage. The good dispersity in water of the ligand-free NiCo_2O_4 NPs counts on the residual coordinated- NH_3 in the synthesis, which is removable at low temperature and thus yields good film quality and gives very good electrical properties at the same time. Based on the above advantages, NiCo_2O_4 NPs are first applied as HTL in highly efficient PVSCs in this work, and a champion PCE of 18.23% is obtained, thanks to the promoted perovskite quality and very good electrical properties of NiCo_2O_4 . In addition, the enlarged perovskite grains on less wetting NiCo_2O_4 result in a promising long-time device stability (maintained $\approx 90\%$ PCE after 500 h light soaking). Therefore, the newly synthesized NiCo_2O_4 with the features of low-cost, low-temperature, simplicity, ligand-free, and solution processability exposes the opportunities of ternary oxides for the applications of emerging photovoltaic devices.

4. Experimental Section

Synthesis of NiCo_2O_4 Nanoparticles: All chemicals with analytical reagent grade were used as received unless otherwise noted. $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (97% in purity), lead (II) iodide (PbI_2 , 99%), lead (II) chloride (PbCl_2 , 99%), and zirconium (IV) acetylacetonate (ZrAcac , 98%) were purchased from Sigma-Aldrich. $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98% in purity) was purchased from J.K. Science. Ammonium hydroxide solution in water (28–30%), dimethylformamide (extra dry, 99%), 1,2-dichlorobenzene (extra dry, 98+%), chlorobenzene (extra dry, 99.8%), isopropanol (extra dry, 99.8%) were purchased from Acros Organics. PEDOT:PSS (PVP Al 4083) was purchased from Clevios. $\text{CH}_3\text{NH}_3\text{I}$ was purchased from Dyesol. PC_{61}BM and C_{60} were purchased from Solarmer Energy, Inc.

$\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8 mmol) was dissolved in 4 mL deionized water and followed by dropwise adding of 1.2 mL ammonium hydroxide solution. After sonicated 10 min, 2 mL $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (0.2 M in deionized water) was subsequently added and stirred for 30 min. Evaporating all solvent at 180°C in the air and then sintered at 200°C for 2 h. A black color solid was obtained without any treatment.

Preparation of NiCo_2O_4 Films and Fabrication of Devices: ITO-coated glass substrates were cleaned using sequential ultrasonication in deionized water, acetone, and ethanol for 15 min, respectively. A NiCo_2O_4 solution with a concentration of 20 mg mL^{-1} in deionized water was spin-coated on ultraviolet ozone-treated ITO substrates at 3500 rpm,

followed by drying at 200°C for 15 min. The thickness of the NiCo_2O_4 film is about 20 nm. For comparison, a thickness of 40 nm PEDOT:PSS (Clevios PVP Al 4083, Heraeus) film on ITO glass was also prepared at 4000 rpm and dried at 130°C for 15 min. After transferring samples into the nitrogen-filled glovebox, the film of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite was formed on top of PEDOT:PSS and NiCo_2O_4 layer, and annealed at 100°C for 10 min, respectively. A total concentration of 20 mg mL^{-1} mix solution of $\text{PC}_{61}\text{BM}/\text{C}_{60}$ (weight ratio, 2:3) in dichlorobenzene was spin-coated at 700 rpm for 60 s and then 4000 rpm for 60 s over the perovskite layer, followed by spin-coating ZrAcac (2 mg mL^{-1} in isopropanol) at 4000 rpm. Finally, Ag electrode with a thickness of 120 nm was thermally evaporated on top of the device under a base pressure of 10^{-4} Pa with a device area of 0.06 cm^2 . The device structure is ITO/PEDOT:PSS or $\text{NiCo}_2\text{O}_4/\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x/\text{PC}_{61}\text{BM}:\text{C}_{60}/\text{ZrAcac}/\text{Ag}$.

Characterization and Measurement: The NiCo_2O_4 crystal phase was identified by X-ray powder diffraction with $\text{Cu K}\alpha$ radiation under λ of $1.54056 \text{ \AA}$ (XRD, Bruker D2 PHASER). The nanoparticles morphology and lattice spacing were examined by tapping mode AFM (NT-MDT NTEGRA), TEM (Philips Tecnai G2 20 S-TWIN), and SEM (Hitachi S-4800, and LEO 1530 FEG), respectively. Chemical composition was verified by XPS of NiCo_2O_4 film on ITO, which was measured in the ultrahigh vacuum environment using Physical Electronics PHI 5802 with a monochromatic Al $\text{K}\alpha$ X-ray source. The thickness of the NiCo_2O_4 film was measured by a profilometer. The FTIR spectrum was recorded by using a Fourier transform infrared spectrometer (Bruker Tensor 27). UPS was characterized by using a He discharged lamp (He I 21.22 eV, Kratos Analytical).

A Keithley 2635 sourcemeter was used to collect the current density–voltage (J – V) characteristics and the solar cells were tested by using a Newport AM 1.5 G solar simulator under a light intensity of 100 mW cm^{-2} , calibrated with a standard silicon reference cell. The steady-state PCE, PCE (t) was measured by setting the bias voltage to the V_{MPP} (obtained from the J – V curve) and then tracing the current density. The IPCE measurement was performed by a system combining xenon lamp monochromatic chopper, and a lock-in amplifier with a calibrated silicon photodetector (Hamamatsu mono-Si cell). Time-resolved PL spectra were measured on PicoQuant FluorTime 300 instrument. A picosecond 375 nm pulse laser (LDH-P-C-75) with a pulse width of $<40 \text{ ps}$ and repetition rate of 5 MHz was used to excite the samples. The EIS analysis was conducted on a CHI660C electrochemical workstation (CH Instrument, Inc.) at the open-circuit voltage 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

D.O. and J.X. contributed equally to this work. This research was supported by the University Grant Council of the University of Hong Kong (Grant nos. 201611159194 and 201511159225 and Platform Research Fund), the General Research Fund (Grant nos. 17211916 and 17204117), the Collaborative Research Fund (Grant C7045-14E) from the Research Grants Council of Hong Kong Special Administrative Region, China, and Grant CAS14601 from CAS-Croucher Funding Scheme for Joint Laboratories.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

hole transport layers, nanoparticles, perovskite solar cells, ternary oxides, ultrasmall

Received: September 28, 2017

Revised: January 12, 2018

Published online:

- [1] National Renewable Energy Laboratory, NREL Efficiency Chart, **2016**.
- [2] a) X. Ren, Z. Wang, W. E. I. Sha, W. C. H. Choy, *ACS Photonics* **2017**, *4*, 934; b) W. E. I. Sha, X. Ren, L. Chen, W. C. H. Choy, *Appl. Phys. Lett.* **2015**, *106*, 221104; c) R. Fan, Y. Huang, L. Wang, L. Li, G. Zheng, H. Zhou, *Adv. Energy Mater.* **2016**, *6*, 1600460; d) J. H. Heo, H. J. Han, D. Kim, T. K. Ahn, S. H. Im, *Energy Environ. Sci.* **2015**, *8*, 1602; e) W. Chen, Y. Wu, Y. Yue, J. Liu, W. Zhang, X. Yang, H. Chen, E. Bi, I. Ashraf, M. Gratzel, L. Han, *Science* **2015**, *350*, 944; f) D. Liu, T. L. Kelly, *Nat. Photonics* **2013**, *8*, 133; g) S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum, Y. M. Lam, *Energy Environ. Sci.* **2014**, *7*, 399; h) J. You, Z. Hong, Y. M. Yang, Q. Chen, M. Cai, T. B. Song, C. C. Chen, S. Lu, Y. Liu, H. Zhou, Y. Yang, *ACS Nano* **2014**, *8*, 1674; i) W. Nie, H. Tsai, R. Asadpour, J. C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H. L. Wang, A. D. Mohite, *Science* **2015**, *347*, 522; j) L. Peng, L. Hu, X. Fang, *Adv. Funct. Mater.* **2014**, *24*, 2591.
- [3] N. J. Jeon, H. G. Lee, Y. C. Kim, J. Seo, J. H. Noh, J. Lee, S. I. Seok, *J. Am. Chem. Soc.* **2014**, *136*, 7837.
- [4] J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-j. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel, S. I. Seok, *Nat. Photonics* **2013**, *7*, 486.
- [5] a) S. Ryu, J. H. Noh, N. J. Jeon, Y. Chan Kim, W. S. Yang, J. Seo, S. I. Seok, *Energy Environ. Sci.* **2014**, *7*, 2614; b) G. W. Kim, G. Kang, M. Malekshahi Byranvand, G. Y. Lee, T. Park, *ACS Appl. Mater. Interfaces* **2017**, *9*, 27720.
- [6] a) P. W. Liang, C. Y. Liao, C. C. Chueh, F. Zuo, S. T. Williams, X. K. Xin, J. Lin, A. K. Jen, *Adv. Mater.* **2014**, *26*, 3748; b) H. Azimi, T. Ameri, H. Zhang, Y. Hou, C. O. R. Quiroz, J. Min, M. Hu, Z.-G. Zhang, T. Przybilla, G. J. Matt, E. Spiecker, Y. Li, C. J. Brabec, *Adv. Energy Mater.* **2015**, *5*, 1401692; c) O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Graetzel, M. K. Nazeeruddin, H. J. Bolink, *Nat. Photonics* **2013**, *8*, 128; d) D. Wang, K. H. Chan, N. K. Elumalai, M. A. Mahmud, M. B. Upama, A. Uddin, S. Pillai, *Phys. Chem. Chem. Phys.* **2017**, *19*, 25016; e) Y. Hou, H. Zhang, W. Chen, S. Chen, C. O. R. Quiroz, H. Azimi, A. Osvet, G. J. Matt, E. Zeira, J. Seuring, N. Kausch-Busies, W. Lövenich, C. J. Brabec, *Adv. Energy Mater.* **2015**, *5*, 1500543; f) Q. Lin, D. M. Stoltzfus, A. Armin, P. L. Burn, P. Meredith, *Adv. Mater. Interface* **2016**, *3*, 1500420; g) A. M. Nardes, M. Kemerink, R. A. J. Janssen, J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, A. J. J. M. van Breemen, M. M. de Kok, *Adv. Mater.* **2007**, *19*, 1196.
- [7] a) J. W. Jung, C. C. Chueh, A. K. Jen, *Adv. Mater.* **2015**, *27*, 7874; b) 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; c) J. H. Park, J. Seo, S. Park, S. S. Shin, Y. C. Kim, N. J. Jeon, H. W. Shin, T. K. Ahn, J. H. Noh, S. C. Yoon, C. S. Hwang, S. I. Seok, *Adv. Mater.* **2015**, *27*, 4013; d) H. Zhang, J. Cheng, F. Lin, H. He, J. Mao, K. S. Wong, A. K. Jen, W. C. Choy, *ACS Nano* **2016**, *10*, 1503; e) H. L. Zhu, J. Y. Xiao, J. Mao, H. Zhang, Y. Zhao, W. C. H. Choy, *Adv. Funct. Mater.* **2017**, *27*, 1605469; f) Z. Liu, A. Zhu, F. Cai, L. Tao, Y. Zhou, Z. Zhao, Q. Chen, Y.-B. Cheng, H. Zhou, *J. Mater. Chem. A* **2017**, *5*, 6597.
- [8] P. L. Qin, Q. He, C. Chen, X. L. Zheng, G. Yang, H. Tao, L. B. Xiong, L. Xiong, G. Li, G. J. Fang, *Solar RRL* **2017**, *1*, 1700058.
- [9] H. Zhang, H. Wang, W. Chen, A. K. Jen, *Adv. Mater.* **2017**, *29*, 1604984.
- [10] A. Huang, L. Lei, J. Zhu, Y. Yu, Y. Liu, S. Yang, S. Bao, X. Cao, P. Jin, *Langmuir* **2017**, *33*, 3624.
- [11] a) R. Alcantara, *Chem. Mater.* **2002**, *14*, 2847; b) L. Hu, L. Wu, M. Liao, X. Hu, X. Fang, *Adv. Funct. Mater.* **2012**, *22*, 998.
- [12] a) S. Liu, L. Hu, X. Xu, A. A. Al-Ghamdi, X. Fang, *Small* **2015**, *11*, 4267; b) L. Hu, L. Wu, M. Liao, X. Fang, *Adv. Mater.* **2011**, *23*, 1988; c) P. F. Ndione, A. Garcia, N. E. Widjonarko, A. K. Sigdel, K. X. Steirer, D. C. Olson, P. A. Parilla, D. S. Ginley, N. R. Armstrong, R. E. Richards, E. L. Ratcliff, J. J. Berry, *Adv. Energy Mater.* **2013**, *3*, 524; d) L. Zhang, S. Zhang, K. Zhang, G. Xu, X. He, S. Dong, Z. Liu, C. Huang, L. Gu, G. Cui, *Chem. Commun.* **2013**, *49*, 3540; e) J. Cheng, Y. Lu, K. Qiu, H. Yan, J. Xu, L. Han, X. Liu, J. Luo, J. K. Kim, Y. Luo, *Sci. Rep.* **2015**, *5*, 12099.
- [13] a) Y. N. NuLi, P. Zhang, Z. P. Guo, H. K. Liu, J. Yang, *Electrochem. Solid-State Lett.* **2008**, *11*, A64; b) H. Jiang, J. Ma, C. Li, *Chem. Commun.* **2012**, *48*, 4465; c) Q. Wang, B. Liu, X. Wang, S. Ran, L. Wang, D. Chen, G. Shen, *J. Mater. Chem.* **2012**, *22*, 21647; d) G. Q. Zhang, H. B. Wu, H. E. Hoster, M. B. Chan-Park, X. W. Lou, *Energy Environ. Sci.* **2012**, *5*, 9453; e) L. Qian, L. Gu, L. Yang, H. Yuan, D. Xiao, *Nanoscale* **2013**, *5*, 7388.
- [14] a) E. M. Ibrahim, A. M. Abu-Dief, A. Elshafaie, A. M. Ahmed, *Mater. Chem. Phys.* **2017**, *192*, 41; b) C. Wang, X. Zhang, D. Zhang, C. Yao, Y. Ma, *Electrochim. Acta* **2012**, *63*, 220; c) M. Silambarasan, P. S. Ramesh, D. Geetha, *J. Mater. Sci.: Mater. Electron.* **2016**, *28*, 323; d) Y. Li, X. Wu, S. Wang, W. Wang, Y. Xiang, C. Dai, Z. Liu, Z. He, X. Wu, *RSC Adv.* **2017**, *7*, 36909.
- [15] a) S. Farhadi, Z. Roostaee-Zaniyani, *Polyhedron* **2011**, *30*, 1244; b) S. Farhadi, K. Pourzare, *Mater. Res. Bull.* **2012**, *47*, 1550.
- [16] C. Yuan, J. Li, L. Hou, L. Yang, L. Shen, X. Zhang, *J. Mater. Chem.* **2012**, *22*, 16084.
- [17] a) S. Farhadi, K. Pourzare, S. Sadeghinejad, *J. Nanostruct. Chem.* **2013**, *3*, 1; b) Y. Zhu, H. Li, Y. Kolytyn, A. Gedanken, *J. Mater. Chem.* **2002**, *12*, 729.
- [18] a) J. F. Marco, J. R. Gancedo, M. Gracia, J. L. Gautier, E. I. Ríos, H. M. Palmer, C. Greaves, F. J. Berry, *J. Mater. Chem.* **2001**, *11*, 3087; b) B. Cui, H. Lin, Y. Z. Li, J. B. Li, P. Sun, X. C. Zhao, C. J. Liu, *J. Phys. Chem. C* **2009**, *113*, 14083.
- [19] C. Bi, Q. Wang, Y. Shao, Y. Yuan, Z. Xiao, J. Huang, *Nat. Commun.* **2015**, *6*, 7747.
- [20] P. W. Liang, C. C. Chueh, S. T. Williams, A. K. Y. Jen, *Adv. Energy Mater.* **2015**, *5*, 1402321.
- [21] M. Bag, L. A. Renna, R. Y. Adhikari, S. Karak, F. Liu, P. M. Lahti, T. P. Russell, M. T. Tuominen, D. Venkataraman, *J. Am. Chem. Soc.* **2015**, *137*, 13130.
- [22] a) Y. Shao, Z. Xiao, C. Bi, Y. Yuan, J. Huang, *Nat. Commun.* **2014**, *5*, 5784; b) X. Li, X. Liu, X. Wang, L. Zhao, T. Jiu, J. Fang, *J. Mater. Chem. A* **2015**, *3*, 15024.
- [23] J. P. Correa-Baena, M. Saliba, T. Buonassisi, M. Gratzel, A. Abate, W. Tress, A. Hagfeldt, *Science* **2017**, *358*, 739.
- [24] Y. Yuan, J. Huang, *Acc. Chem. Res.* **2016**, *49*, 286.