

A General Method: Designing a Hypocrystalline Hydroxide Intermediate to Achieve Ultrasmall and Well-Dispersed Ternary Metal Oxide for Efficient Photovoltaic Devices

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Solution-process fine metal-oxide nanoparticles are promising carrier transport layer candidates for unlocking the full potential of solution process in solar cells, due to their low cost, good stability, and favorable electrical/optical properties. However, exotic organic ligands adopted for achieving small size and monodispersion can mostly cause poor conductivity, which thus impedes their electrical application. In this work, a concept of constructing a hypocrystalline intermediate is proposed to develop a general method for synthesizing various ternary metal oxide (TMO) nanoparticles with a sub-ten-nanometer size and good dispersibility without exotic ligands. Particularly, a guideline is summarized based on the understandings about the impact of metal ion intercalation as well as water and anion coordination on the hypocrystalline intermediate. A general method based on the proposed concept is developed to successfully synthesize various sub-ten-nanometer TMO nanoparticles with excellent ability for forming high-quality (smooth and well-coverage) films. As an application example, the high-quality films are used as hole transport layers for achieving high-performance (stability and efficiency) organic/perovskite solar cells. Consequently, this work will contribute to the development of TMO for large-scale and high-performance optoelectronic devices and the concept of tailoring intermediate can leverage the fundamental understandings of synthesis strategies for other metal oxides.

fabrication approaches, such as roll-to-roll printing,^[1] inject printing,^[2] and blade-coating.^[3] In these multilayered optoelectronic devices, carrier transport layer (CTL) plays an indispensable role in suppressing interface recombination and promoting carrier extraction and transport to corresponding electrode. Among various hole transport materials, inorganic metal oxides featuring with chemical stability and high transparency have been intensively studied to serve as promising alternatives to organic materials such as acidic and hygroscopic poly(3,4-ethylenedioxythio-phenylene):poly(styrenesulfonic acid) (PEDOT:PSS) and costly and less-conductive 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene (Spiro-OMeTAD). Various binary transition metal oxides,^[4] such as such as NiO_x ,^[4a,b] FeO_x ,^[4c] CuO_x ,^[4d] CrO_x ,^[4e,f] ReO_x ,^[4g,h] MoO_x , V_2O_x , and WO_x ,^[4i-m] have been developed as efficient hole transport layer (HTL) with different features to simplify fabrication processes and improve device performances. However, there is a concern of poor electron

blocking ability for those metal oxides based HTL with the deep conduction band.^[5] To develop a robust and efficient HTL, many efforts have been conducted to develop promising p-type metal oxide HTLs.^[4a,b,6] Recently, ternary metal oxides including spinel, delafossite, and perovskite ternary metal oxides have come into particular attention due to their unique advantages of tunable composition for desirable optical and electrical properties.^[7]

HTL between photoactive layer and anode is for forming an Ohmic contact that can effectively reduce interface recombination induced by energy barrier. It requires hole transport materials to have suitable band structure. However, matched energy level cannot ensure high performance devices since that the film quality also have significant impact on device performances. Serious recombination and current leakage will happen when HTL contains defects and holes (exposed area of transparent electrode). Besides, device performances can be drastically affected by film roughness that results from the size of nanomaterials.^[8] Generally, in optimizing HTL thickness, there is a tradeoff between conductivity and coverage, since

1. Introduction

Solution process for optoelectronic devices, such as solar cells (SCs), light emitting diodes, and photodetectors has been considered as the emerging technologies with the features of low cost, high throughput, and easily scale-up for various device

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achieving good coverage needs to increase HTL thickness to a certain value while the hole mobility limits the HTL thickness. Nanoparticles with size less than 10 nm are very important for achieving excellent dispersion and small critical thickness with good coverage. In order to maintain the dispersion and stabilization of metal oxide nanoparticle, exotic organic ligands, e.g., phosphonates, fatty acids, carboxylate, carboxylic acids, and amines,^[9] are often attached to nanoparticle surfaces. However, the poor conductivity of most ligands impedes carrier transport between metal oxide nanoparticles, and ligand removal inevitably requires separate post-treatments (e.g., high-temperature annealing and plasma) that may cause damage to sublayers. The challenge to achieve good electrical properties and post-treatment free is to simultaneously avoid ligand addition in synthesis and dispersion and favor the synthesis of well-dispersion TMO nanoparticles. On the other hand, ternary metal oxides with different crystal structures (spinel, delafossite, and perovskite) have been synthesized via various approaches, such as hydro/solvothermal, thermal decomposition, coprecipitation, and pulsed laser deposition.^[8b,10] Typically, materials with different nanostructures and sizes are prepared by different and specific methods. To better promote the development of metal oxide synthesis, it is highly desirable to develop a general/universal approach with the ability to synthesize a series of materials. Overall, it has attracted enormous research interest in developing a general method for synthesizing well-dispersed and ultrasmall metal oxide nanoparticles without using long-chain ligands or surfactants.

Herein, we demonstrate a general scheme to synthesize sub-10 nm and highly dispersed ternary metal oxides by proposing the concept of constructing a hypocrystalline hydroxide intermediate. In the intermediate, the coordination of small species (water molecules and nitrite ions) and intercalation of metal ions are strategically control to form a loose layered structure. The loose layered structure is hereafter named as hypocrystalline structure that contains two kinds of layers, namely less crystallized layered double metal hydroxide (LDMH) layer and disordered coordination layer (DCL). In the crystalline layer, hydroxide unit is formed from two kinds of metal ions in a certain ratio that allow them having interaction with each other and can finally form spinel ternary metal oxide at relatively low temperature. Interestingly, this hypocrystalline structure with controlled calcination can realize small dimension of sub-10 nm and well dispersed TMO nanoparticles. To demonstrate the universal ability of the concept to synthesize small-size nanoparticles, four spinel ternary metal oxides are prepared, namely ZnCo_2O_4 , NiCo_2O_4 , CuCo_2O_4 , and CuGa_2O_4 . Moreover, two typical spinel oxides (ZnCo_2O_4 and NiCo_2O_4) are also served as efficient HTL in photovoltaic devices with power conversion efficiency (PCE) of 9.5% and 15.78% for PTB7-Th:PC₇₁BM and PM6:Y6 based organic solar cells and PCE of 19.24% (forward scan) and 19.13% (reversed scan) for MAPbI_{3-x}Cl_x based perovskite solar cells. Consequently, this work contributes to developing the universal pathway for synthesizing various TMO based carrier transport materials which favors the development of scalable and flexible high performance solar cells and other optoelectronic devices.

2. Results and Discussion

2.1. The Concept for Constructing Hypocrystalline Intermediate

As shown in Figure 1a, sub-10 nm and highly dispersed spinel TMOs are synthesized as described by the schematic diagram of the proposed concept in which constructing the LDMH intermediate is of particular importance on tuning the size and dispersibility of final oxides. Typically, a clear solution containing two metal ions was precipitated to form the LDMH under near-neutral solution with pH value in the range of 6–8 by adding less than stoichiometric amount of sodium hydroxide (NaOH). Meanwhile, under the condition of near-neutral reaction solution, the nitrate ion and water molecular are coordinated to the precipitated LDMH then form a so-called hypocrystalline intermediate which can partially degrade from LDMH to two kinds of dissociative hydroxides that are detrimental to dispersibility of final metal oxide nanoparticles. Basing on the concept of tailoring the hydroxide intermediate, a general method is proposed for synthesizing nanomaterial with small size and good dispersion. As demonstrated below, four ternary metal oxides have been successfully synthesized by the general approach. To have the insights and present the concept, different techniques are adopted to investigate the crystal structure and coordinated species. The disordered layer is the key for forming a loose structure in the proposed hypocrystalline intermediate, so the Fourier-transform infrared spectroscopy (FTIR) is used to study the possible species. As indicated in Figure 1b for an example of zinc cobalt hydroxide intermediate, the signal of water molecule and nitrate ion are detected, with the signal from O–H stretching vibration at around 3483 cm^{-1} and bending vibration around 1634 cm^{-1} ,^[11] while the signal from nitrate ion is found at around 1344 cm^{-1} that comes from the coordinated nitrate ions in the interlayer of the hydroxide intermediate.^[11a] Since the layered structure of crystalline hydroxide tends to be formed during the precipitation,^[12] it is proposed that the water molecules and nitrate ions intercalate in the LDMH to form a disordered interlayer that separates the less crystallized LDMH. With these intercalated coordinated species and controlled crystalline hydroxide (described below), hypocrystalline intermediate is constructed. During thermal treatment on the intermediate, the coordinated small species in disordered layer will gradually release. It allows the less crystallized double metal hydroxide to contact with adjacent layers which favors their nucleation and growth to become ternary metal oxide nanoparticles. As shown in Figure S1a in the Supporting Information for the TMO example of the zinc cobalt oxide, the intensity of absorption from O–H and N–O vibration significantly reduces as the decomposition of the hydroxide and release of water and nitrate ions. Two peaks at low wavenumber side (648 and 548 cm^{-1}) arising from metal oxide bond are assigned to the Zn–O or Co–O bond in tetrahedral sites and Co–O bond in the octahedral site of the spinel structure, respectively.^[11d] The appearance of the peak indicates the oxidation of Co^{2+} to Co^{3+} and the formation of the spinel nanocrystal during thermal annealing. Notably, the absorption from N–O bond vibration in spinel ternary metal oxide means there are still some nitrate ions in the nanoparticles, which probably plays an important role on achieving stable and highly dispersed nanoparticles in

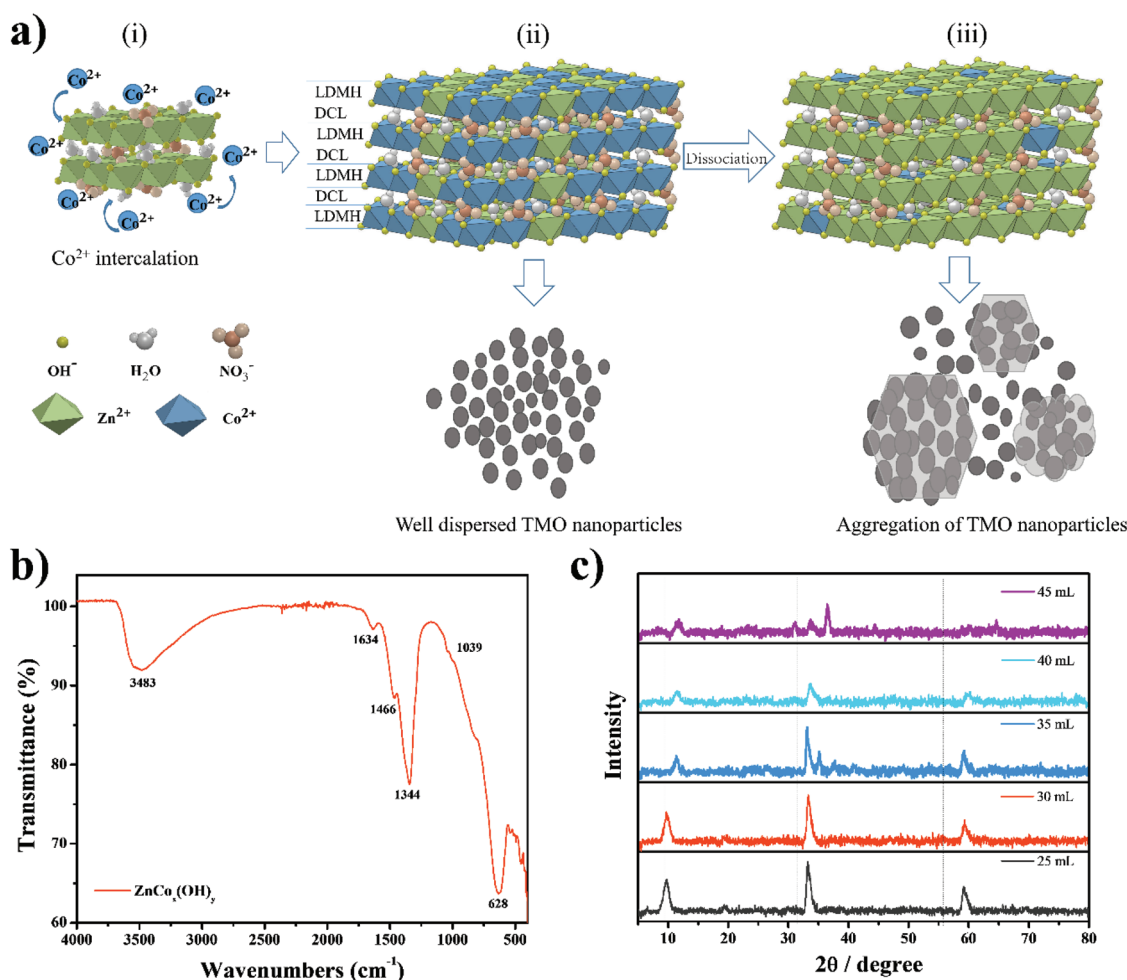


Figure 1. a) A schematic diagram of proposed concept for the synthesis of sub-10 nm nanoparticle, in inset a-(ii) the LDMH and DCL refer to layered double metal hydroxide and disordered coordination layer; b) FTIR spectrum of prepared zinc cobalt hydroxide intermediate; c) The XRD patterns of zinc cobalt hydroxide precipitated from different amount of NaOH, y-axis in the same scale for five layers.

water.^[13] Consequently, as the concept proposed, small molecules with ligating atom (like water molecule and ammonia molecule) and some anion (such as nitrate ion and carbonate ion) are coordinated in the double metal hydroxide intermediate to form a hypocrystalline intermediate that contribute to small size and good dispersibility.

2.2. The Realization from Concept to Hypocrystalline Intermediate

In the proposed hypocrystalline intermediate, the LDMH is a core component. To realize the concept on constructing hypocrystalline intermediate, different synthesis parameters have been controlled, such as solution acidity (amount of NaOH), reaction time and mole ratio between the precursors. To better understand the influences of control methods, it is necessary to observe the evolution of chemical composition and geometrical structure of the hypocrystalline intermediate via various techniques. To be more specifically, products of hydroxide precipitated from different amount of NaOH

were collected and characterized by X-ray diffraction (XRD) as shown in the Figure 1c. When a small amount (25 mL, pH around 5) of NaOH was added, only the zinc nitrate hydroxide ($\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2$) is identified from the XRD pattern. However, the results of energy-dispersive X-ray spectroscopy (EDX) (Figure S2, Supporting Information) prove the existence of cobalt ion in the sample prepared from 25 mL NaOH and the element ratio between Zn and Co is close to 1:1. Besides, the XRD pattern (Figure S1b, Supporting Information) of the final oxide obtained by calcining the hydroxide shows characteristic peaks of spinel structure while there are no peaks for zinc oxide, which further attests the existence of cobalt ion. From the results of XRD and EDX, it is clear that large amount of cobalt ions are in the hydroxide sample but there is no diffraction peaks in the XRD pattern of hydroxide. It is supposed that the cobalt ion is intercalated in the zinc hydroxide since the valence and ion diameter of Zn^{2+} and Co^{2+} are quite similar.^[14] Moreover, when the amount of the NaOH increases, the Zn/Co ratio gradually increase from initial 1:1 to 1:2 (same as the ratio of precursors) as shown in Table S1 in the Supporting Information. The continuously increased intercalated cobalt

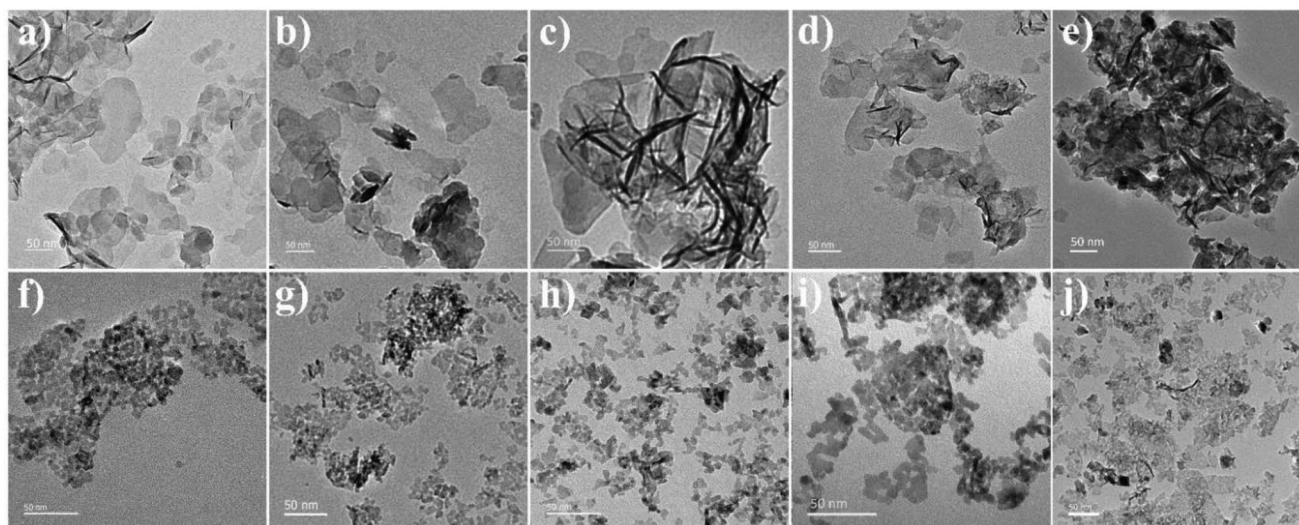


Figure 2. a–e) TEM image of zinc cobalt hydroxide precipitated from different amount of NaOH, 25, 30, 35, 40, 45 mL respectively; f–j) TEM image of the zinc cobalt oxide prepared from the hydroxide precipitated with different amount of NaOH, 25, 30, 35, 40, 45 mL, respectively. All scale bar is 50 nm.

ions gradually affect the crystal structure of the hydroxide intermediate and contributes to the crystalline changing from $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2$ to $\text{Zn}_2\text{Co}_3(\text{OH})_{10}$. When there are excess intercalated cobalt ions as the added NaOH over 40 mL (pH over 10), the hypocrySTALLINE structure tends to break down and forms the mixture of $\text{Zn}_2\text{Co}_3(\text{OH})_{10}$ and Co_3O_4 . Apart from the change of chemical composition, the nanostructure evolution of the hypocrySTALLINE intermediate and final spinel ternary metal oxide is also investigated by scanning electron microscope (SEM) as shown in **Figure 2**. Different shapes and nanostructures of intermediate and final oxides are observed in the samples from different solution acidity. Flat and thin LDMH is shown in the sample precipitated with less NaOH, which finally produces sub-10 nm nanoparticles in a connecting matrix that keeps the shape of the hydroxide intermediate. When the amount of alkaline increases, the hydroxide becomes larger and trends to be wrinkle that may due to unbalanced inner stress caused by ions intercalation. The spinel TMO nanoparticles prepared with more NaOH trends to be more monodispersed. After adding excess NaOH, the hydroxide is aggregative and large cobalt oxide particles occur as shown in **Figure 2e,j**. Consequently, our results show that the acidity of the reaction solution can either affect hydroxide crystal structure or promote the formation of some large-size cobalt oxides which influences the dispersibility of spinel oxide. To obtain better dispersibility, it is wise to construct the hypocrySTALLINE intermediate with the amount of NaOH at the range of 35–40 mL (solution pH varies from 6 to 8) to obtain suitable ion intercalation ratio and chemical composition in the hypocrySTALLINE intermediate.

Besides the solution acidity, the reaction time also has impact on the hypocrySTALLINE intermediate and thus the final oxide dispersibility. After adding NaOH solution, the reaction solution was continuously stirred for extending the reaction with different time. Samples with four different reaction times were collected for characterization. As shown in **Figure 3a,b**, a hypocrySTALLINE intermediate (both of nickel and zinc based) collected right after completely adding NaOH (without the extended reaction, 0 h) shows

low X-ray diffraction intensity, which indicates the hypocrySTALLINE intermediate has low crystallinity that is ascribed to the loose structure from intercalation of cobalt ions and coordination of nitrate ions and water molecules. However, the hypocrySTALLINE intermediate gradually shows high crystallinity after several hours' reaction. The identical peak of hydroxide in low diffraction angle has high intensity and small value of full width at half maximum, indexing well crystallization and large crystalline size of hydroxide. Notably, there is a characteristic peak of zinc hydroxide (PDF: 072–2032) appearing at around 32° in the zinc-based samples with the extended reaction. The intensity of this characteristic peak goes up gradually which indicates that the intercalated cobalt ions in zinc hydroxide matrix will gradually release to reduce the inner stress and form two independent hydroxide rather than the hypocrySTALLINE hydroxide. Overall, a loose structured hypocrySTALLINE intermediate readily form after addition of NaOH. Extended reaction time can cause relaxation of the hypocrySTALLINE intermediate and form well crystallized hydroxide.

To confirm the proposed concept on building hypocrySTALLINE intermediate, FTIR is also utilized to identify the trace of the hypocrySTALLINE intermediate evolution with different extended reaction time as shown in the **Figure 3c,d**. The characteristic peak at high wavenumber around 3650 cm^{-1} exists only in the cobalt hydroxide sample as shown in **Figure S3** in the Supporting Information, which is ascribed to the O–H bond vibration in cobalt hydroxide. Interestingly, this characteristic peak also shows up in the hypocrySTALLINE intermediate of more than 3 h of extended reaction but it is not in the zinc-based sample without any reaction extension as shown in **Figure 3c** (0 h). It indicates that dissociative cobalt hydroxide is produced during the extended reaction period which is consistent with the results of XRD data. However, the dissociation of the hypocrySTALLINE is unexpected due to the dissociative zinc hydroxide or cobalt hydroxide, which are hard to form spinel oxide in the temperature where hypocrySTALLINE decomposes as shown in **Figure S4** in the Supporting Information, will function as binder between the separated spinel TMO nanoparticles. As shown in **Figure S5** in the Supporting

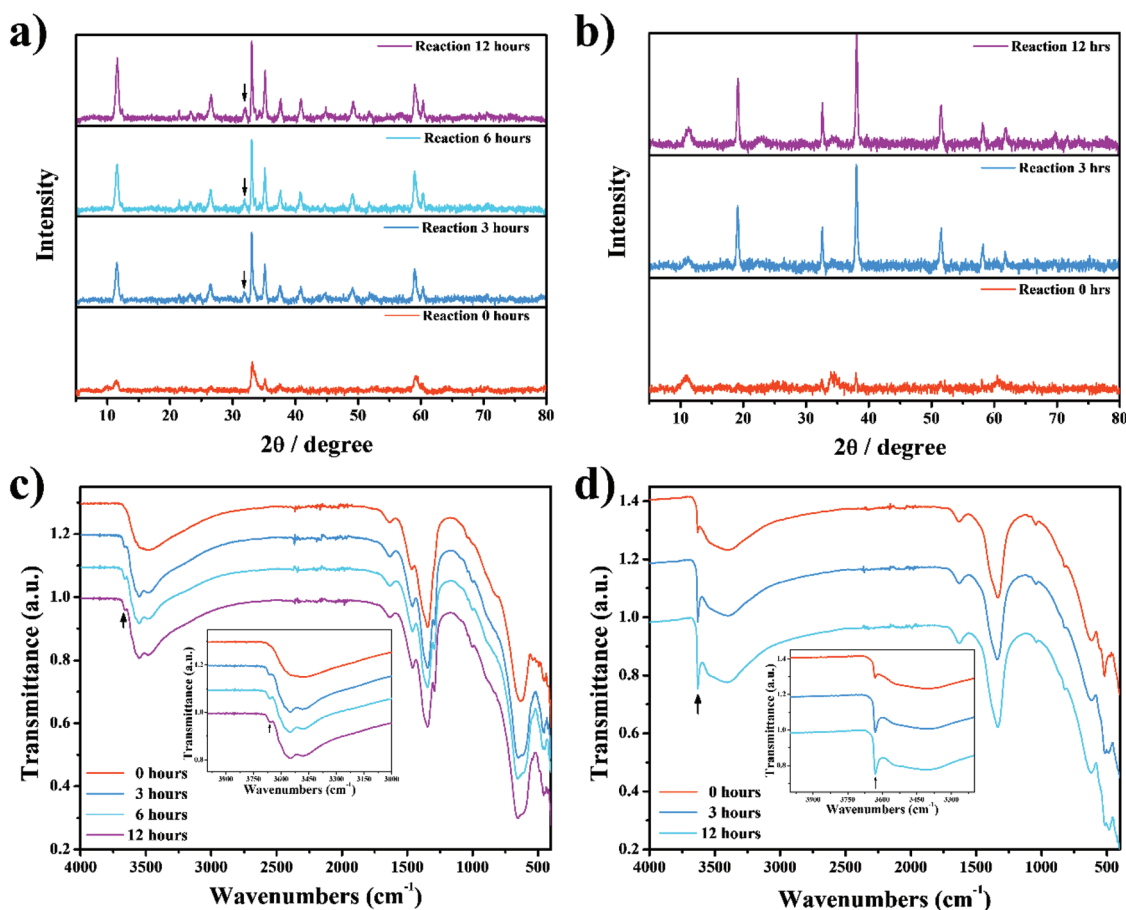


Figure 3. a) The XRD patterns of zinc cobalt hydroxide obtained from different reaction time, y-axis in the same scale, arrow pointing out the signal of zinc hydroxide; b) The XRD patterns of nickel cobalt hydroxide obtained from different reaction time, y-axis in the same scale; c) FTIR spectrum of zinc cobalt hydroxide obtained from different reaction time, arrow pointing out the change of the hydroxide, the inset is the magnified view of the change region; d) FTIR spectrum of nickel cobalt hydroxide obtained from different reaction time, arrow pointing out the change of the hydroxide, the inset is the magnified view of the change region.

Information, the spinel ternary oxide produced from hypocrytalline are all with an average size below ten nanometers, but the samples with 3 and 12 h of extended reaction after the addition of NaOH are all bound in a hexagonal nanoplate and shows very poor dispersibility. To sum up, a hypocrytalline intermediate, containing a cobalt ion intercalated LDMH layer and a DCS layer, is formed immediately (0 h extended reaction time) after adding sodium hydroxide under vigorous stirring. The extended reaction after completing the addition of alkaline solution can promote the dissociation of the cobalt ion intercalated hypocrytalline hydroxide and reduction of inner stress then lead to serious aggregation of sub-10 nm spinel TMO nanoparticles.

As discussed above, it is clear that the structure change and dissociation of hypocrytalline intermediate both have significant impact on nanoparticle size and dispersibility. Here, we summarize the synthesis guideline from the proposed concept of hypocrytalline intermediate as below:

1. Less than stoichiometric amount of NaOH shall be used to precipitate hydroxide intermediate and form near-neutral solution with pH in the range of 6–8 to keep the hypocrytalline structure with suitable intercalation and coordination;

2. After adding certain amount of alkaline solution, the precipitated hydroxide intermediate needs to be collected immediately without extended reaction time to avoid dissociation of hypocrytalline and obtain better dispersion; and
3. It is better to control the mole ratio between the precursors rather than the amount of NaOH for adjusting the element ratio in final spinel TMO nanoparticles. In the previous reports, the ratio between two metal salts is general set as 1:2 according to target spinel oxide.^[10d,15] For the case of zinc cobalt oxide, to prepare hypocrytalline intermediate with Zn/Co ratio close to 1:2 with NaOH amount less than 40 mL, the mole ratio of precursors is suggested to control at around 3:7 as the EDX results shown (Table S2, Supporting Information).

2.3. Demonstration of the General Method for Synthesizing Metal Oxide Nanoparticles and their Applications

Basing on the proposed concept, a general method is demonstrated to produce TMO nanoparticles with sub-10 nanometer size and good dispersibility. Typically, after adding NaOH, hypocrytalline hydroxide intermediate is collected immediately

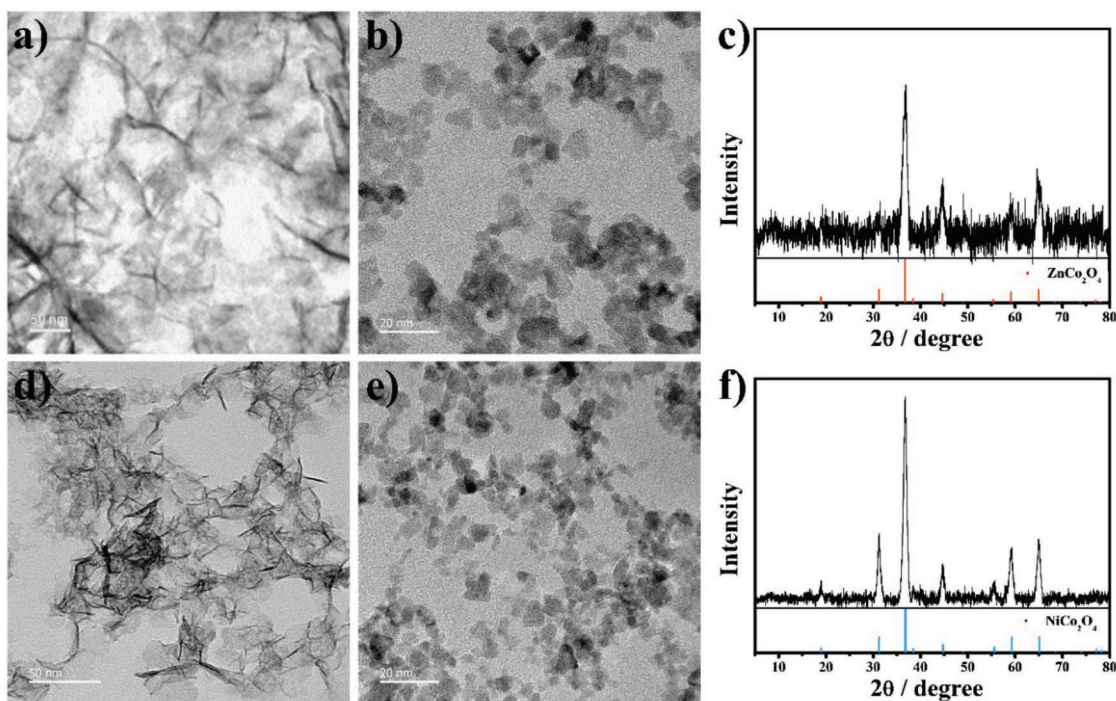


Figure 4. a,d) TEM image of the fresh zinc cobalt hydroxide and nickel cobalt hydroxide precipitated with 35 mL NaOH from solution with precursor ratio of 3:7, scale bar in 50 nm; b,e) TEM image of zinc cobalt oxide and nickel cobalt oxide prepared from the hydroxide in insets (a) and (d), scale bar in 20 nm; c,f) XRD pattern of the zinc cobalt oxide and nickel cobalt oxide.

to obtain a thin and wrinkle hypocrystalline intermediate, as shown in the **Figure 4a,d**. Without an extended reaction to avoid dissociation and aggregation, highly dispersed spinel ternary metal oxide nanoparticle (ZnCo₂O₄ and NiCo₂O₄ as shown in **Figure 4b,e**, CuCo₂O₄ and CuGa₂O₄ as shown in **Figure S6** in the Supporting Information) are successfully prepared after calcination under the temperature derived from the thermogravimetric analysis curve (**Figure S7**, Supporting Information). XRD is employed to confirm the chemical phase of these two prepared oxides. As shown in **Figure 4c,f**, characteristic peaks of spinel structure are identified at around 31°, 36.8°, 44.5°, 59.3°, and 65° (PDF: 023–1390 and PDF: 073–1702 for ZnCo₂O₄ and NiCo₂O₄ respectively). Therefore, it is demonstrated that the general method is able to synthesize ternary metal oxides with average size less than 10 nm and highly dispersion (from TEM) via the decomposition of the hypocrystalline intermediate from the proposed concept.

In addition, to demonstrate the ability of spinel oxides' application as HTL, two cobalt based ternary metal oxides (ZnCo₂O₄ and NiCo₂O₄) are selected due to their suitable band structure as shown in **Figure S8** in the Supporting Information. As the ultrasmall size and good dispersibility of these spinel oxides, a uniform and fully-covered HTL film was formed with the well dispersed nanocrystal colloidal of spinel ternary oxide (**Figure S9**, Supporting Information). Two kinds of representative photovoltaic devices have been fabricated on the ternary metal oxide based HTLs, typically organic SCs based on PTB7-Th with PC₇₁BM and organic–inorganic hybrid perovskite solar cells (perovskite SCs) based on chlorine doped methylammonium lead iodide (MAPbI_{3-x}Cl_x). The characteristic current density to

voltage (*J*–*V*) curves are shown in the **Figure 5a,b** and the performance parameters are summarized and listed on Tables S3 and S4 in the Supporting Information. For PTB7-Th:PC₇₁BM based organic SCs, average PCE of 9.37% and 9.20% have been realized by spinel TMO ZnCo₂O₄ and NiCo₂O₄ respectively which is slightly higher than that of the commonly used PEDOT:PSS with average PCE of 9.17%. To further demonstrate the TMO in high-PCE organic SCs, nonfullerene based devices of PM6:Y6 have also been fabricated. As the *J*–*V* shown in **Figure 6a** and device parameter in Table S5 (Supporting Information), average PCE over 15.6% have been achieved on the ZnCo₂O₄ based HTL with a thin modification layer of F4TCNQ to form better contact with the active layer, while the average PCE of PEDOT:PSS is 15.07%. For MAPbI_{3-x}Cl_x based PVSK-SCs, average PCE in forward and reversed scan of 18.14% and 17.02% have been achieved on NiCo₂O₄ based devices which are substantially better than that of the PEDOT:PSS with only 12.84% and 12.80% in forward and reversed scan. Improved device performance has also been realized by deposited an electrical insulating polymer (polystyrene, PS) to suppressing recombination at the interface of cathode contact. As shown in **Figure 6b**, FFs of both PEDOT:PSS and TMO based devices have been significantly improved, which results in an average PCE over 19% realizing in TMO based devices in both forward and reversed scan as device parameters listed on Table S6 in the Supporting Information. Organic SCs and perovskite SCs based on TMO HTLs exhibit a higher fill factor (FF) which can be ascribed to better energy levels configuration as shown in **Figure S8** in the Supporting Information. Besides, the stability of two kinds of typical devices based on different

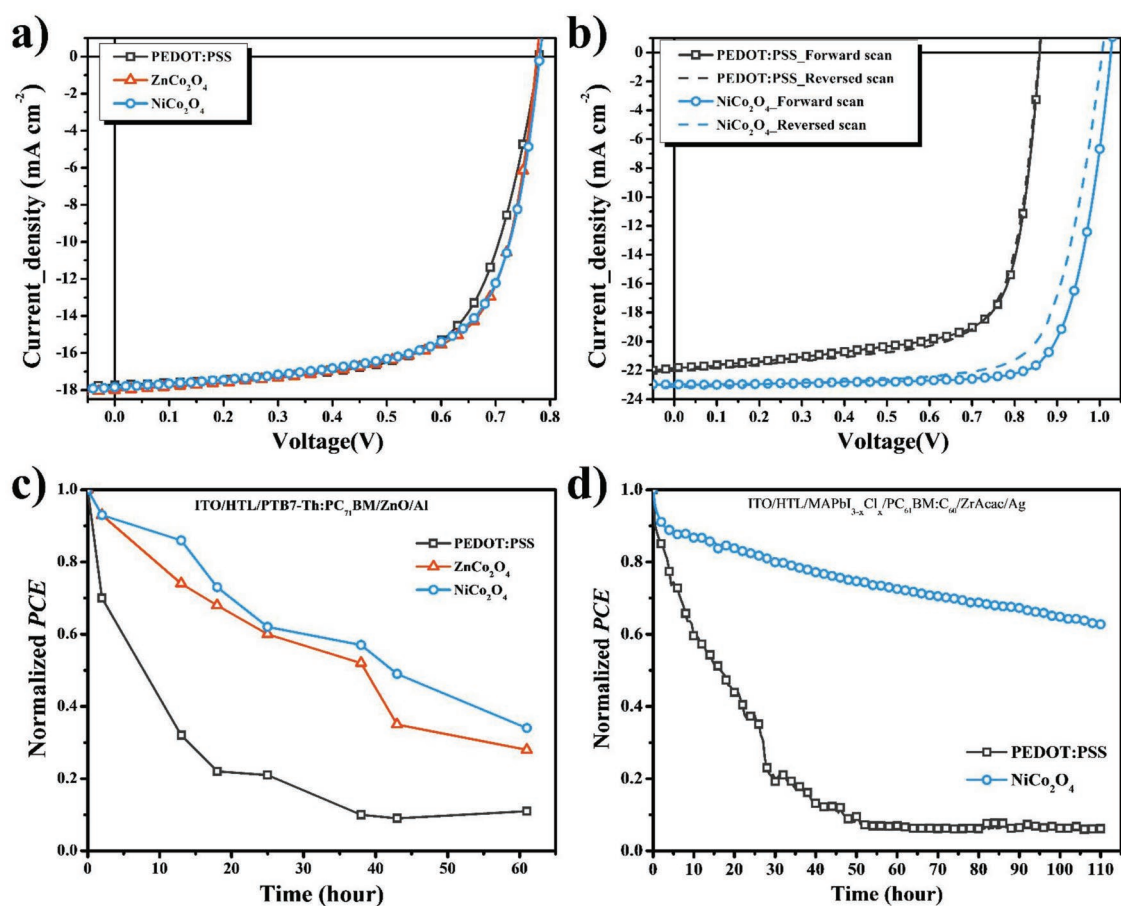


Figure 5. The representative characteristic J - V curve of a) the organic SCs with different HTL, in a device structure of ITO/HTL/ PTB7-Th:PC₇₁BM/ ZnO/Al; b) the perovskite SCs, in a device structure of ITO/HTL/MAPbI_{3-x}Cl_x/PC₆₁BM:C₆₀/ZrAcac/Ag; the change of normalized PCE of c) organic SCs and d) perovskite SCs based on different HTL.

HTLs is also studied as shown in the Figure 5c,d. For organic SCs measured in ambient environment with 50% relative humidity without capsulation, the performance of PEDOT:PSS based device drops rapidly to 20% of its initial value within 20 h while the devices with oxide based HTLs maintain over 60%

of its initial performance, which can be ascribed to its hygroscopic nature. For perovskite based SCs, the stability tracking is undertaken in ambient environment with capsulation and under continuous 1 sun illumination soaking (by a white LED lamp source), ternary oxide based devices show remarkable

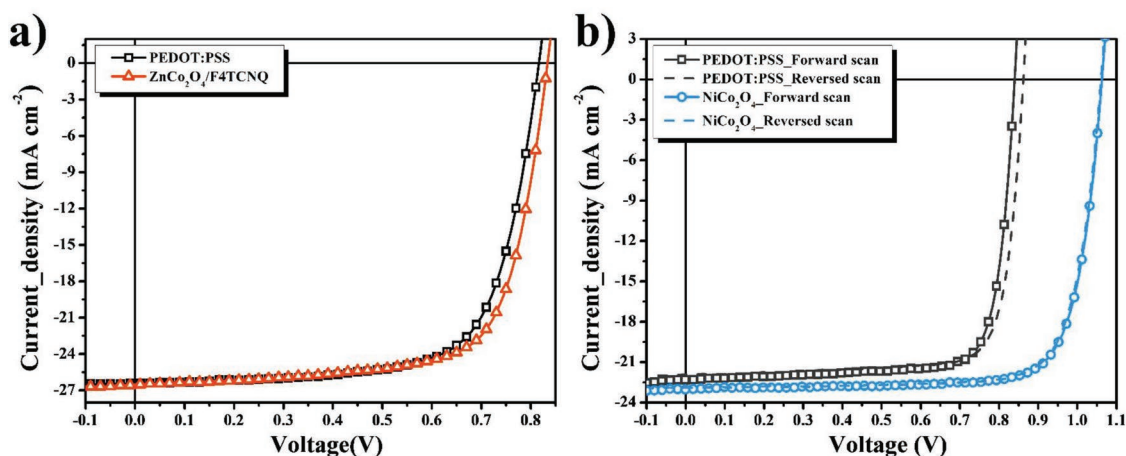


Figure 6. The representative characteristic J - V curve of a) the nonfullerene based organic SCs with different HTL, in a device structure of ITO/HTL/ PM6:Y6/ZnO/Al; b) the perovskite SCs, in a device structure of ITO/HTL/MAPbI_{3-x}Cl_x/PS/C₆₀/BCP/Ag.

improvement of photostability retaining over 60% initial performance after 110 h. However, the PEDOT:PSS based devices degraded dramatically to below 10% of initial PCE only within 50 h, which may due to interface damage by its acidic nature. Consequently, various ternary metal oxides can be simply synthesized by the general method, which show qualified ability on photovoltaic device for improving both device efficiency and stability.

3. Conclusion

In conclusion, a general method has been successfully demonstrated to synthesize sub-ten-nanometer spinel ternary metal oxides with excellent dispersibility. In this method, the concept of constructing the hypocrySTALLINE intermediate is realized through the intercalation of metal ions as well as the coordination of anions and small molecules with ligating atoms. Our results show that the acidity of reaction solution can significantly affect the structure of the hypocrySTALLINE intermediate and the process of intercalation and coordination. Meanwhile, the extended reaction time can promote the dissociation process of the LDMH in the hypocrySTALLINE intermediate that results in aggregation and bad dispersion of final ternary metal oxides. Overall, we offer the guideline to construct the hypocrySTALLINE intermediate with suitable intercalation and coordination for realizing the spinel TMO nanoparticle with ultrasmall size and quasi-monodispersing. Additionally, by using the high-quality (smooth and well-coverage) ternary metal oxide films as HTLs in organic SCs and perovskite SCs, improved stability and performances have been demonstrated. Consequently, our work, as a starting point for future research on the universal method for synthesizing ultrasmall, ligand-free, and well-dispersed metal oxide nanoparticles in a simple and cost-effective approach, will contribute to the development of large-scale and high performance optoelectronic devices. In addition, the concept of constructing intermediate can leverage the fundamental understanding of the synthesis strategies for other kinds of metal oxides for the long-term-uniform and quasi-monodispersed nanoparticle ink for emerging printing technologies.

4. Experimental Section

Chemicals: Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), gallium(III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), sodium hydroxide (NaOH) were purchased from J&K Scientific Ltd. Chlorobenzene (CB, extra dry, 99.8%) was purchased from Acros. PEDOT:PSS (Baytron AL4083) was purchased from H.C. Starck GmbH, Germany. [6,6]-Phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM), poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluoro-thieno[3,4-b]thiophene-2-carboxylate-2,6-diyl)] (PTB7-Th), [6,6]-phenyl- C_{71} -butyric acid methyl ester (PC_{71}BM), poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-3-fluoro-thiophen-2-yl)-benzo[1,2-5:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PM6), and (2,2'-(2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanlylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y6),

C_{60} , were purchased from Solarmer Co., Ltd. F4TCNQ, BCP were purchased from Kintec Co., Ltd. 1,8-diiodooctane (DIO, >95.0%) was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). 1,2-Dichlorobenzene (DCB) and chlorobenzene (CB), dimethylformamide (DMF), and isopropanol were in extra dry grade and purchased from Acros Organics. Lead (II) iodide (PbI_2 , 99%), lead (II) chloride (PbCl_2 , 99%), and zirconium (IV) acetylacetonate (ZrAcac , 98%) were purchased from Sigma-Aldrich. $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was purchased from Dyesol. All chemicals were used as received.

Ternary Metal Oxide Synthesis: Typically for ZnCo_2O_4 , 3.33 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (while $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ for other two oxides) and 6.66 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved into 60 mL deionized water (DI water) by magnetic stirring. Certain amount of NaOH solution (0.5 mol L^{-1}) was used to adjust to acidity of reaction under vigorously stir. After adding NaOH solution, the precipitated hypocrySTALLINE hydroxide intermediate was collected by centrifugation and then washed with DI water and ethanol in sequence. For the CuGa_2O_4 , the hypocrySTALLINE hydroxide was prepared as the same method by precipitating the precursor solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$. Then, taking ZnCo_2O_4 as an example, the obtained hydroxide intermediate was transfer to muffle oven for calcination at 200 °C for 2 h. The color of the hydroxide changes from dark green to black. While the calcination temperature need slightly change to obtain good dispersion for other ternary metal oxides. As for the hydroxide mixture of zinc hydroxide and cobalt hydroxide, 10 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 10 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved into 60 mL DI water separately. Around 35 mL NaOH (0.5 mol L^{-1}) solution were added to precipitate the corresponding hydroxides. Then, the solution of zinc hydroxide and cobalt hydroxide were mixed in 1:2 vol (same ratio in mole amount) under vigorously stir. After completely mix, the hydroxide mixture was centrifuged out of the reaction solution and following with water and ethanol washing. The hydroxide powder was used for measurement and further process after drying and gridding.

Device Fabrication of Organic SCs and Perovskite SCs: ITO-coated glass substrate with resistance about 15 $\Omega \text{ sq}^{-1}$ was cleaned with DI water, acetone, and ethanol in sequence for 15 min respectively. Then, the cleaned substrates were treated by ultraviolet-ozone (UVO) for 15 min. PEDOT:PSS was spin-coated on substrate with a thickness around 30–40 nm. For the spinel ternary metal oxide HTL, the ternary metal oxide powder (ZnCo_2O_4 and NiCo_2O_4) was dispersed in DI water with a concentration around 20 mg and spin-coated on the substrate with a thickness about 20–30 nm. A thin layer of F4TCNQ (0.6 mg mL^{-1}) was spin-coated on ZnCo_2O_4 when it is used for fabricating non-fullerene based organic SCs. For PTB7-Th: PC_{71}BM devices, the active layer was optimized with a thickness around 100 nm by spin-coated its solution (1:1.5, 25 mg mL^{-1} in CB, with addition of 3% DIO), while the PM6:Y6 devices were fabricated as reported.^[6] Zinc oxide (ZnO) was prepared with the method introduced in the reference,^[17] and it was used as electron transport layer (about 30 nm) on top of active layer. Finally, aluminum electrode (100 nm) was thermally evaporated with a shadow mask with device area of 6 mm^2 . For $\text{MAPbI}_{3-x}\text{Cl}_x$ based PVSK-SCs, the perovskite films are deposited on HTLs with antisolvent approach by processing the precursor solution containing 500 mg PbI_2 , 190 mg MAI and 30 mg PbCl_2 in 1 mL DMF. After this antisolvent process, the perovskite films were annealed at 100 °C for 10 min. Then, a total concentration of 20 mg mL^{-1} solution of $\text{PC}_{61}\text{BM}/\text{C}_{60}$ (weight ratio, 2:3) in dichlorobenzene was spin-coated atop the perovskite layer and followed with a thin layer of spin-coated ZrAcac (2 mg mL^{-1} in isopropanol). Finally, 120-nm silver electrode was thermally evaporated to complete the devices. For perovskite device using $\text{PS}/\text{C}_{60}/\text{BCP}/\text{Ag}$ cathode, a thin PS layer was deposited on perovskite layer with a concentration of 0.2 mg mL^{-1} , then thermally evaporating C_{60} (20 nm), BCP (7 nm), and Ag (100 nm) in sequence.

Characterization: The crystal structure was characterized by X-ray diffraction in a powder analysis mode with Cu K α radiation (λ of 1.54056 Å). The nanoparticle size and structure were characterized by scanning transmission electron microscopy (TEM, FEI Tecnai G2 20 S-TWIN). The EDX was measured by an EDX detector on Hitachi S-3400N variable pressure scanning electron microscope while the film morphology was

characterized by tapping mode AFM (NT-MDT NTEGRA) and FEG SEM (Hitachi S-4800). The FTIR spectra were obtained by FTIR spectrometer of JASCO FT/IR-6600. For device characterization, the current density–voltage (*J*–*V*) characteristics were measured by a Keithley 2635 source-meter. Newport AM 1.5G solar simulator was used to provide white light with intensity of 100 mW cm^{−2} calibrated by a certified standard silicon solar cell.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

general method, hypocrystalline intermediate, organic solar cells, perovskite solar cells, ternary metal oxide nanoparticles

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