

Solution-Processed Metal Oxide Nanocrystals as Carrier Transport Layers in Organic and Perovskite Solar Cells

Dan Ouyang, Zhanfeng Huang, and Wallace C. H. Choy*

There has been rapid progress in solution-processed organic solar cells (OSCs) and perovskite solar cells (PVSCs) toward low-cost and high-throughput photovoltaic technology. Carrier (electron and hole) transport layers (CTLs) play a critical role in boosting their efficiency and long-time stability. Solution-processed metal oxide nanocrystals (SMONCs) as a promising CTL candidate, featuring robust process conditions, low-cost, tunable optoelectronic properties, and intrinsic stability, offer unique advantages for realizing cost-effective, high-performance, large-area, and mechanically flexible photovoltaic devices. In this review, the recent development of SMONC-based CTLs in OSCs and PVSCs is summarized. This paper starts with the discussion of synthesis approaches of SMONCs. Then, a broad range of SMONC-based CTLs, including hole transport layers and electron transport layers, are reviewed, in which an emphasis is placed on the improvement of the efficiency and device stability. Finally, for the better understanding of the challenges and opportunities on SMONC-based CTLs, several strategies and perspectives are outlined.

state-of-the-art fullerene-based OSCs^[6] and nonfullerene-based OSCs, respectively.^[7] PVSCs, a highly efficient newcomer to the solar cell family, possess the advantages of wideband light absorption (high extinction coefficient in the visible and near-infrared range), low exciton binding energy (≈ 2 meV), and long diffusion length and carrier lifetime.^[8] During the past few years, the overall PCE has quickly increased from 3.8% first reported in 2009^[9] up to record values 22.7%,^[10] which make it become a leading candidate for next-generation photovoltaic technology. Despite the difference in the photoactive layer, OSCs and PVSCs both show a typical multiple layered device architecture, shown in Figure 1.

Carrier (electron and hole) transport layers (CTLs) play an important role in achieving high-efficiency photovoltaic devices, which not only promote the

1. Introduction

As there is increase in global energy demand and the global environmental issue, it is urgent to explore efficient, renewable, and carbon-neutral energy. Solar energy is one of the most promising candidates featuring clean, renewable, abundant, and sustainable properties.^[1] To date, various photovoltaic technologies have been developed to harvest solar energy and generate electricity efficiently.^[2] Among them, solution-processed organic solar cells (OSCs) and perovskite solar cells (PVSCs) are of particular interest due to their potential for scale-up manufacture via roll-to-roll technique. OSCs based on photoactive polymer and small molecules have achieved significant breakthroughs and rapid evolution in the last several decades, thanks to the developments of novel donor/acceptor materials,^[3] the innovations of the device structure,^[4] the exploration of morphology, and interface engineering.^[5] So far, the power conversion efficiency (PCE) has reached 11.7% and 14% for the

efficient extraction and transport of carriers, but also suppress the recombination between the active layer and the electrode.^[11] Generally, an efficient CTL should meet several requirements: first, decent electrical properties of high electron/hole mobility, and the ability to form an ohmic contact with the adjacent active layer and electrode, and the blocking ability of the counter carrier; second, a high stability including the self-stability of CTLs and the compatibility with the active material and electrode; and finally, a relative transparency to make sure the active layer can absorb as much light as possible to achieve optimal performance.^[12] In addition, CTLs deposited atop the electrode are also expected to favor the morphology optimization of the active layer to reduce the device series resistance. To date, a great number of CTLs have been developed and incorporated in OSCs and PVSCs, including organic (e.g., small molecules, polymers, and organometallic complexes) and inorganic materials (e.g., metal oxides and metal salts)^[13] (Figure 2), which have been summarized in some reviews.^[11,13b,c,14] In the development of CTLs, inorganic metal oxides have drawn enormous attention and are believed to be one of the most promising candidates for CTLs because of the widely variable band energies and excellent electrical properties, coupled with potential transparency and chemical stability.^[11,14,15]

At present, many approaches have been utilized in fabricating different types of metal oxide CTLs, such as sputtering, thermal evaporation, sol-gel, and atom layer deposit. However, high-cost and high-energy consumption limit their further development in the low-cost production application. Employing metal oxide

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nanocrystal (MONC) solution to directly deposit CTLs (named nanocrystal (NC) approach) is particularly attractive for the fabrication of low-cost, high-performance, and large-area optoelectronic products and favorable for roll-to-roll industrial mass production. Moreover, the nanocrystal approach decouples the crystallization of oxide from the film-formation process, which not only provides more freedom on the synthesis of oxide materials (including reaction conditions, purification method, and dispersion) but also makes the room-temperature deposition of oxide-based CTLs becomes possible. This review aims to provide illustrative accounts of solution-processed metal oxide nanocrystal (SMONC) based CTLs, and their applications in OSCs and PVSCs. Since the synthesis approach will significantly affect the properties of metal oxides, and thus the performance of photovoltaic devices, in this review, we will first summary widely used synthesis approaches of metal oxide nanocrystals (Section 2). In the next section (Section 3), we will focus on the applications of metal oxide nanocrystals in CTLs, including hole transport layers (HTLs) and electron transport layers (ETLs), for both OSCs and PVSCs, in which we will emphasize device efficiency and stability. In the final section (Section 4), we outline some perspectives from synthesis to interface engineering for further improvements on metal oxide nanocrystal-based CTLs to enhance photovoltaic device performance.

2. Synthesis of Metal Oxide Nanocrystals

Inorganic MONCs possess interesting optical and electrical properties depending on their size and shape, which can be tuned via synthetic techniques (Table 1). Many of them can be prepared via solid-state chemistry, namely, simply mixing powder reactants and calcining to give the desired products. However, there are some challenging issues for this method, including the inhomogeneity of reaction, high temperature, and uncontrollable particle morphology. To obtain uniform and controllable properties, liquid phase synthetic methods are exploited, such as co-precipitation, hydrothermal/solvothermal methods, and others.^[16] In the following, we explicitly focus on low-temperature solution-processed methods for synthesis of MONCs: co-precipitation method, hydrothermal and solvothermal method, and other high energy (microwave, sonochemical) assisted methods. They are commonly used to synthesize MONCs for achieving high-quality CTLs via a low-temperature solution process. Other approaches, such as using high boiling, coordination solvents or through aerosol flame synthesis, employing high-temperature and gas-phase pathways, and pulsed laser deposition techniques, are discussed in some other reviews and will not be detailed here.^[17]

2.1. Co-Precipitation Method

2.1.1. Basic Principle of Co-Precipitation Method

The co-precipitation of sparingly soluble products from aqueous solutions (or other solvents) followed by thermal decomposition of those products to oxides, named co-precipitation method, has been one of the most common



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methods for the synthesis of MONCs. A typical co-precipitation reaction involves the simultaneous occurrence of nucleation, growth, Ostwald ripening, and/or agglomeration processes^[16] (Figure 3). Under the high-supersaturating condition, the sparingly soluble species are induced to form. When precipitation begins, numerous small crystallites initially form (nucleation process), but they tend to quickly aggregate together to form larger, more thermodynamically stable particles (growth process). Smaller particles are consumed by larger particles during the growth process, which is called Ostwald ripening. Due to the thermodynamics, the agglomeration phenomenon is inevitable because the particle favors the optimization of the surface/volume ratio in the absence of a stabilizer. Ostwald ripening and aggregation exist in the whole precipitation process, which will dramatically affect the size, morphology, and properties of the products.

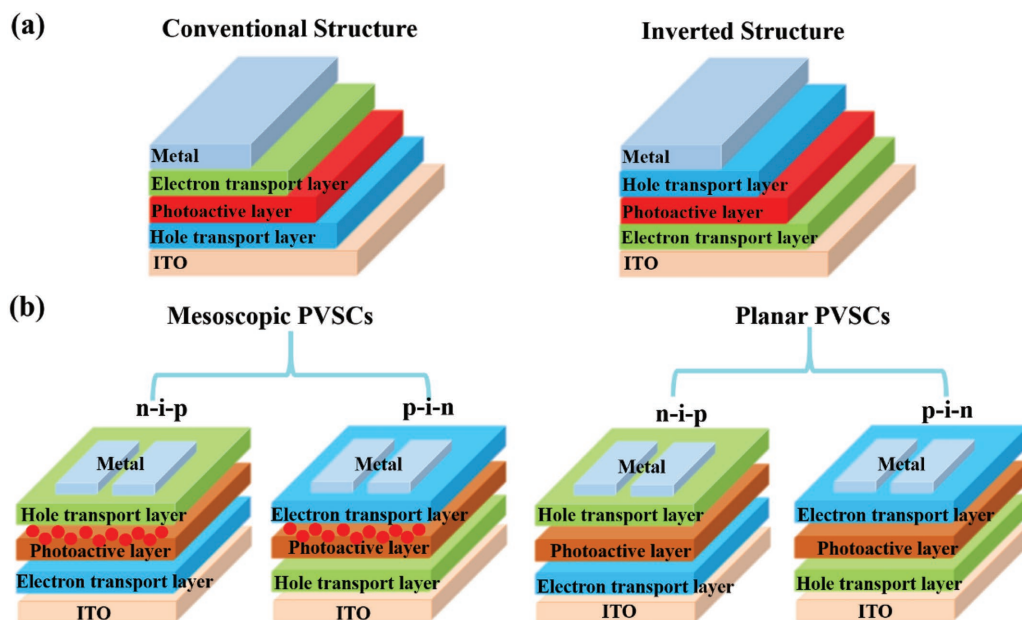


Figure 1. Multiple layered device structure of a) OSCs and b) PVSCs.

For the nucleation process, the key is the degree of supersaturation (S), which is given by

$$S = \frac{C}{C_{eq}} \quad (1)$$

where C and C_{eq} are the solute concentrations at saturation and at equilibrium, respectively. Notably, the difference in C and C_{eq} , $\Delta C = C - C_{eq}$, is the “driving force” for precipitation.

As nucleation begins in a supersaturated solution, there exists an equilibrium critical radius (R^*) for formed particles

$$R^* = \frac{\alpha}{\Delta C} \quad (2)$$

The term α is given by

$$\alpha = \left(\frac{2\sigma_{SL}}{kT \ln S} \right) v C_{eq} \quad (3)$$

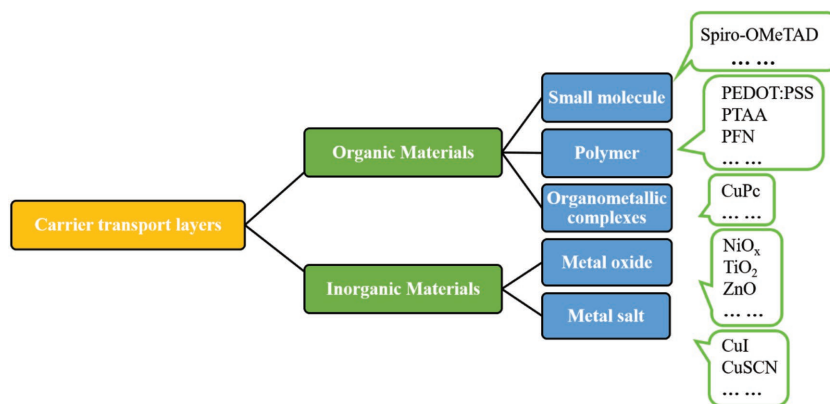


Figure 2. Different types of carrier transport layers.

where σ_{SL} is the surface tension at the solid–liquid interface, v is the atomic volume of solute, k is the Boltzmann constant, T is the temperature, and S is the supersaturation. Nucleated particles with $R > R^*$ will continue to grow; the growth rate is determined by concentration gradients and reaction temperatures, which is limited by the diffusion effect. Notably, when the particles become larger, they tend to quickly aggregate together to form larger and more thermodynamically stable particles.

While those particles with $R < R^*$ will dissolve (referred to as Ostwald ripening). For those delay growth particles (decay process) during the diffusion-controlled Ostwald ripening process, the number density N of nucleated particles decays as

$$N(t) = \frac{0.22Q_0}{R(t)^3} = \frac{0.22}{2D\alpha t} \quad (4)$$

where Q_0 is the total initial supersaturation and D is the diffusion current of solute across the grain boundary. The number of solute particles decreased as t^{-1} during diffusion-controlled Ostwald ripening.^[18] The size distribution of particles is given by

$$f(R, t) = \left[\frac{N(t)}{R(t)} \right] P_0(\rho(t)) \quad (5)$$

where $\rho(t) = \frac{R}{R(t)}$ and $P_0(\rho)$ is a time-independent function of the absolute dimension of the grains, ρ . Therefore, the formation of particles with a narrow size distribution requires that the nuclei of all species present form simultaneously and without subsequent nucleation of smaller particles. Normally, smaller size and narrow size distribution of MONCs is desired for

Table 1. Electrical property of metal oxides NCs via different synthesis methods.

Metal oxides NCs	Synthesis method	Conductivity [S cm ⁻¹]	Hole mobility [cm ² V ⁻¹ s ⁻¹]	Reference
NiO _x	Co-precipitation		3.75×10^{-3}	[19]
NiO _x	Hydro/solvothermal	–	–	[45]
NiO _x	Ultrasound-assisted method	10–12		[55]
ZnO	Co-precipitation		0.066	[75]
ZnO	Hydro/solvothermal	5×10^{-5}		[36]
TiO ₂	Co-precipitation		2×10^{-3}	[28]
TiO ₂	Hydro/solvothermal	–	–	[37]
TiO ₂	Ultrasound-assisted method	6×10^{-6}		[54]
SnO ₂	Hydro/solvothermal	–	–	[41]
MoO ₃	Microwave-assisted method		5.77×10^{-5}	[49]
CeO ₂	Hydro/solvothermal	10^{-4}		[44]
La-BaSnO ₃	Co-precipitation		5×10^{-2}	[23]
NiCo ₂ O ₄	Co-precipitation	500		[24]
CuGaO ₂	Hydro/solvothermal		10^{-2} – 10	[68]
Zn ₂ SnO ₄	Hydro/solvothermal		10–30	[80]

film formation, especially for the fabrication of CTL films featuring smooth, uniform, and compact morphology.

Mostly, the synthesis of oxides must be subjected to further processing (drying, calcination, etc.). Sometimes, the oxides also can be obtained directly from precipitation reaction. In either case, the agglomeration of nanocrystals is inevitable. Generally, two approaches (a) steric repulsion: capping ligands (surfactants, polymers, or other organic species) are bound to the nanocrystals' surfaces to isolate nanocrystals. (b) Electrostatic (van der Waals) repulsions: the chemisorption of charged species (H⁺, OH⁻, or other ions) at the surfaces of nanocrystals is used to well disperse and stabilize metal oxide nanocrystals. Steric stabilization is somewhat more common in the synthesis

of metal oxide nanocrystals. However, there are concerns about having insulating capping ligands in the MONCs for CTLs due to the unexpected energy barriers for charge transport.^[14]

2.1.2. Metal Oxide Nanocrystals Synthesis

Co-precipitation method can synthesize various metal oxide nanocrystals in both aqueous and nonaqueous media (Table 2). Thanks to the good understanding of the mechanism, metal oxides precipitated from aqueous solutions have been widely investigated. Recently, nickel oxide (NiO_x) NCs have been successfully demonstrated by co-precipitation method via nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) reacting with sodium hydroxide (NaOH) in aqueous solution. By adjusting the pH value to 10, the precipitated hydroxide was collected and then calcined under 270 °C in the air to obtain NiO_x NCs with 3–5 nm

size.^[19] By using this method, NiO_x HTL film can be formed through a room-temperature solution process without any post-treatment during device fabrication. This method featuring simplicity, low cost, low temperature, and solution process, which is beneficial for the future scale-up production, has also been adapted to synthesize doped NiO_x (such as Cu, Cs-doped NiO_x).^[20] Similarly, cobalt oxide (Co₃O₄) nanocrystals were also synthesized by the chemical precipitation methods.^[21] Since it does not involve the use of surfactants or templates in the whole process, this method is environmentally friendly and reduces impurities in the final products. Ammonium hydroxide (NH₃·H₂O), in some cases, is used to replace strong alkali (such as NaOH) to prepare small size and highly crystalline nanoparticle (NP). By precipitating with NH₃·H₂O, ultrasmall iron oxide/hydroxide nanocomposite (6–10 nm in size) was obtained from the iron (III) chloride (FeCl₃) and iron (II) chloride (FeCl₂) aqueous solution.^[22] The ultrasmall nanocomposites are surfactant-free, favoring the formation of high-quality HTL film. Highly crystallized and monodispersed La-BaSnO₃ (LBSO) nanocrystals were also prepared by precipitating with NH₃·H₂O in the mixing solution of lanthanum (III) nitrate hexahydrate [La(NO₃)₃·6H₂O], barium nitrate (Ba(NO₃)₂), and tin (IV) chloride pentahydrate (SnCl₄·5H₂O).^[23] The well-dispersed and high-quality LBSO NCs facilitate the fabrication of compact and uniform ETL layer via a low-temperature solution process. NH₃·H₂O could not only serve as a weak base to produce OH⁻ ions but also coordinate with some metals to form complex, which favors the control of the synthesis reaction. Recently, spinel-structured NiCo₂O₄ was synthesized by the precipitation reaction of nickel and cobalt nitrates with NH₃·H₂O^[24] (Figure 4a,b). With the assistance of the coordination of ammonium, ultrasmall nanoparticles (5 nm on average) and well-dispersed NiCo₂O₄ NCs without exotic ligands can be obtained, which enables the formation of uniform and pinhole-free films.

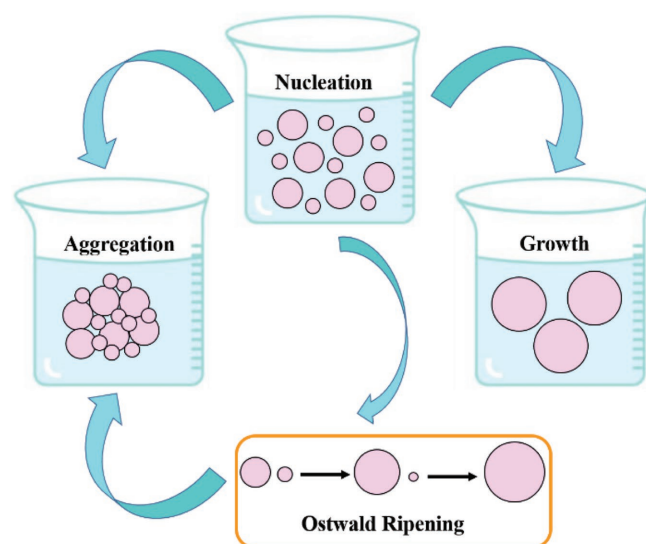


Figure 3. Four processes in co-precipitation approach: nucleation, growth, aggregation, and Ostwald ripening.

Table 2. Solution processed metal oxide nanocrystal synthesis. TMAH: tetramethylammonium hydroxide.

Metal oxides	Method	Liquid system	Precursors	Reference
NiO _x	Co-precipitation	Aqueous	Ni(NO ₃) ₂ 6H ₂ O, NaOH	[19]
NiO _x	Co-precipitation	Ethanol	Ni(NO ₃) ₂ 6H ₂ O, C ₂ H ₂ O ₄	[25]
Co ₃ O ₄	Co-precipitation	Aqueous	Co(NO ₃) ₂ 6H ₂ O, NaOH	[21]
FeO _x	Co-precipitation	Aqueous	NH ₃ H ₂ O, FeCl ₃ , FeCl ₂	[22]
ZnO	Co-precipitation	Methanol	NH ₃ H ₂ O, Zn(CH ₃ COO) ₂	[26]
TiO ₂	Co-precipitation	Benzyl alcohol	TiCl ₄	[28]
SnO ₂	Co-precipitation	Ethyl glycol	SnCl ₄ 5H ₂ O, CH ₃ COOH, TMAH, NH ₃ H ₂ O	[27]
La-BaSnO ₃	Co-precipitation	Aqueous	NH ₃ H ₂ O, La(NO ₃) ₃ 6H ₂ O, Ba(NO ₃) ₂ , SnCl ₄ 5H ₂ O	[23]
NiCo ₂ O ₄	Co-precipitation	Aqueous	NH ₃ H ₂ O, Ni(NO ₃) ₂ 6H ₂ O, Co(NO ₃) ₂ 6H ₂ O	[24]
ZnO	Hydrothermal/solvothermal	Alcohol	Different precursors	[35]
TiO ₂	Hydrothermal/solvothermal	Alcohol	Different precursors	[37]
CeO ₂	Hydrothermal/solvothermal	Aqueous or Alcohol	Ce(NO ₃) ₃	[44]
SnO ₂	Hydrothermal/solvothermal	Ethanol	SnCl ₄ 5H ₂ O, TMAH	[41]
NiO _x	Hydrothermal/solvothermal	Tert-butanol	Ni(acac) ₂	[45]
CuGaO ₂	Hydrothermal/solvothermal	Aqueous	KOH, Cu(OH) ₂ , Ga(OH) ₃ , ethyl glycol	[46]
CuCrO ₂	Hydrothermal/solvothermal	Aqueous	NaOH, Cu(NO ₃) ₂ , Cr(NO ₃) ₃ , ethyl glycol	[46]
BaTiO ₃	Hydrothermal/solvothermal	Aqueous	TiOCl ₂ , Ba(OH) ₂	[47]
MoO ₃	Microwave-assisted method	n-butanol	Mo(acac) ₃ , H ₂ O ₂	[49]
CuCrO ₂	Microwave-assisted method	Aqueous	NaOH, Cu(NO ₃) ₂ , Cr(NO ₃) ₃	[50]
InZnO	Ultrasounds-assisted method	Benzyl alcohol	Zn(CH ₃ COO) ₂ , InCl ₃	[51]
TiO ₂	Ultrasound-assisted method	Benzyl alcohol	TiCl ₄	[54]
WO ₃	Ultrasound-assisted method	Benzyl alcohol	WCl ₆	[54]
V ₂ O ₅	Ultrasound-assisted method	Benzyl alcohol	VOCl ₃	[54]
NiO _x	Ultrasound-assisted method	Aqueous	NiCl ₂ , TMAH	[55]
CuO	Ultrasound-assisted method	Aqueous	CuCl ₂ , TMAH	[56]

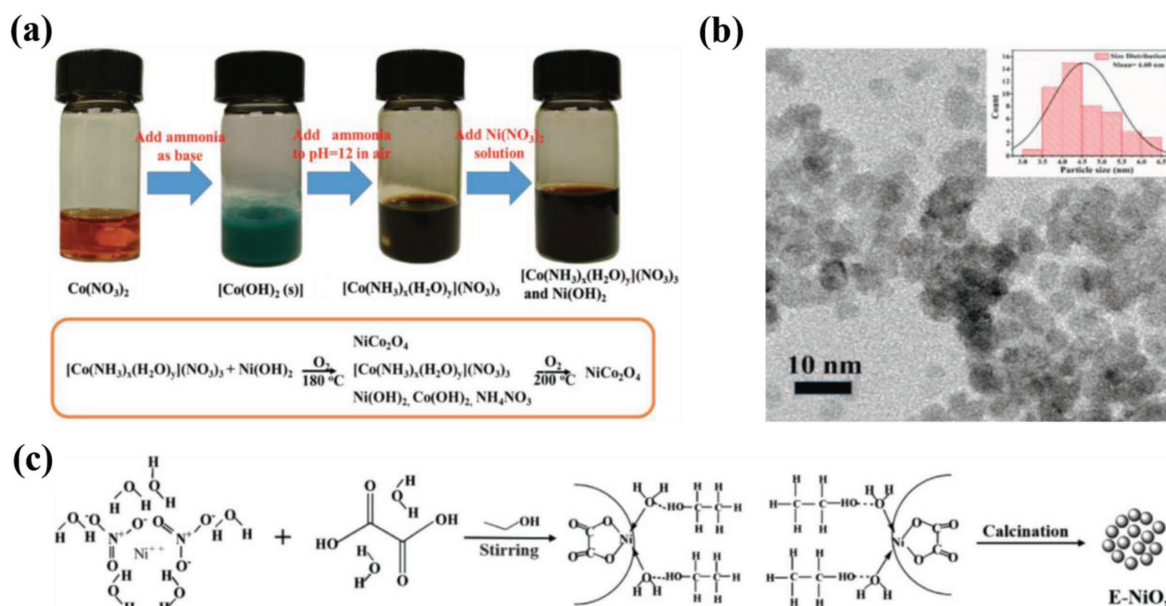


Figure 4. a) The synthesis schematic diagram of NiCo₂O₄ NCs. b) Transmission electron microscopy (TEM) image and size distribution histogram (inset) of NiCo₂O₄ NCs. a,b) Reproduced with permission.^[24] Copyright 2018, Wiley. c) The synthesis schematic diagram of ethanol dispersed NiO_x (E-NiO_x) nanocrystals. Reproduced with permission.^[25a] Copyright 2018, Wiley.

Co-precipitation reaction can also be carried out in non-aqueous solvents that offers more solvent choices for dispersing metal oxides, thus widens the application to water-sensitive devices. Recently, ethanol dispersed NiO_x (E- NiO_x) has been obtained via using oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) as the precipitation agent and ethanol as the solvent^[25] (Figure 4c). These high-quality, ligand-free nanocrystals could be spin-coated onto a substrate to form a smooth, compact E- NiO_x film with good hole extraction capability. Bodke and co-workers prepared zinc oxide (ZnO) nanocrystals in methanol via hydroxylation of zinc acetate $[\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}]$.^[26] The obtained ZnO NCs of ≈ 5 nm diameter could be well dispersed in methanol mixing with suitable amounts of less polar solvents (such as chloroform or chlorobenzene) without other additional surfactants or ligands, which could be used to fabricate electron-transporting and hole-blocking interlayer by annealing-free processing for top CTL of photovoltaic devices. By dissolving $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in ethylene glycol and precipitating with a mixture solution of acetic acid, tetramethylammonium hydroxide (TMAH), and $\text{NH}_3 \cdot \text{H}_2\text{O}$, 2–4 nm diameter tin oxide (SnO_2) was obtained.^[27] The resulting nanoparticles are easily dispersed in polar solvents and assemble into compact thin films upon deposition and drying. In other cases, the hydrolysis reaction of metal chloride or metal alkoxide precursors in nonaqueous solvents are adopted to synthesize small size MONCs. It can produce nanocrystal with less agglomeration and high purity due to the prevented premature precipitation phenomenon and the absent of exotic precipitating agent. For example, the anatase phase titanium oxide (TiO_2) NCs with 2.5 nm size were synthesized by heating a mixture of titanium tetrachloride, ethanol, and benzyl alcohol at 85°C .^[28] Using the obtained NCs to form TiO_2 film via a self-assembly and solution-processed method, it features good uniformity, as well as capable for large-area applications. Later, the corresponding Au or Ag NPs incorporated TiO_2 , and Cs-doped TiO_2 could also be prepared via the same approaches.^[28,29]

In some special cases, crystalline oxides can be precipitated from aqueous or nonaqueous solution directly, which could greatly reduce the risk of agglomeration and further growth

due to the elimination of calcination. Take copper oxide (CuO) NCs as an example, it can be directly prepared by heating the solution of copper (II) chloride (CuCl_2) in dimethyl sulfoxide.^[30] Importantly for printed electronic applications, this proposed synthetic route can be used to develop functional CuO HTLs at room temperature elimination, the requirement of the annealing step during the fabrication process.

In summary, the co-precipitation method is a potential method to synthesize ultrafine nanoparticles for large-scale application due to its low cost, low temperature, and solution process. However, achieving monodispersed of oxide nanoparticles usually requires the addition of capping ligands or other surface bound stabilizers to prevent agglomeration. These insulating capping ligands affect the charge transporting capacity and even cause long-term instability issues in photovoltaic devices. Therefore, a co-precipitation method with the ability to produce ultrafine ligand-free metal oxide nanocrystal is still needed to be developed in the future.

2.2. Hydrothermal and Solvothermal Methods

2.2.1. The Principle of Hydrothermal and Solvothermal Method

Hydrothermal and solvothermal techniques can be defined as a method of formation and growth of crystals by chemical reactions and solubility changes of substances in a sealed heated aqueous/nonaqueous solution above ambient temperature ($>100^\circ\text{C}$) and pressure (>1 atm), which is one well-established nanomaterial synthesis method in the laboratory and industry^[31] (Figure 5). Hydrothermal is carried out in water, while solvothermal is generally in the organic solvent. In a tightly closed system, a high reaction temperature implies pressure increase because of the vapor confinement. When increased to a certain pressure and temperature, the water (defined as supercritical fluids at 374°C and 218 atm) or other solvents will change their viscosity, surface tension, dielectric constant, and dissolving ability; thus it will promote the crystallization of nanomaterials and enable the possibility of some

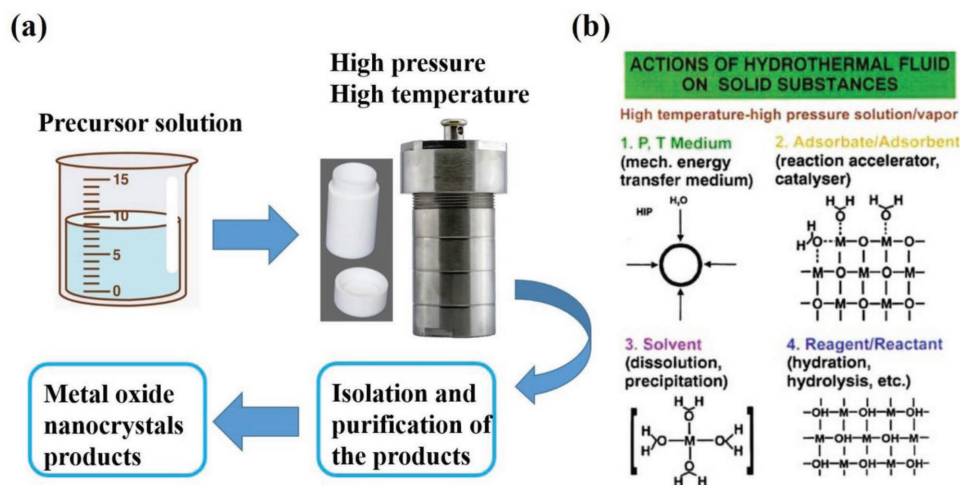


Figure 5. a) General reaction scheme of hydro/solvothermal approach. b) The action of hydrothermal fluids on solid substances. Reproduced with permission.^[31b] Copyright 2007, Springer Science.

chemical reactions (not occur in normal conditions). Precise control over hydro/solvothermal synthetic conditions, such as precursor concentration, pH value, reaction time, reaction temperature, solvent, and additives, is the key to the success of the preparation of metal oxide nanocrystals. Recently, the hydro/solvothermal method has been adopted as one of the attractive ways to realize low-temperature solution-processed MONCs with high purity and a narrow size distribution.^[31b,32] Especially some metal oxides synthesized by hydro/solvothermal method without the introduction of any organic additives or templates are suitable for CTL applications due to their advantages of convenient manipulation and the avoidance of extraneous impurities. However, there are many unclear issues on theoretical background, tailored phases, and nanoscale morphologies. Several previous reviews have devoted to the discussion of hydro/solvothermal synthetic techniques.^[33] Herein, we mainly focus on the effectiveness of using those MONCs synthesized by the hydro/solvothermal method as CTLs in the photovoltaic devices.

2.2.2. Metal Oxide Nanocrystals Synthesis

Due to the easy control on size and morphology of NCs by tuning the synthesis parameters, such as solvents, temperature, and reactant concentration, hydro/solvothermal method has been widely used to synthesize MONCs (Table 2).^[16,34] Highly-crystalline and homogeneous ZnO NCs featuring controlled size, well dispersion, and ultrauniformity without agglomeration were synthesized through a facile solvothermal method.^[35] The crystallite and particle size of ZnO could be tuned by employing different precursors, alcohols as the solvent, alkylammonium hydroxides as the base, and reaction temperatures. By using as-prepared ZnO NCs with different crystallite and particle size to form ETL films, it exhibited different devices performance.^[36] Some strategies, such as oxidation-hydrothermal combination method,^[37] the controllable thermal decomposition,^[38] and versatile wet-chemical process,^[39] have been proposed to synthesize highly crystal TiO₂ under low reaction temperature. Based on the similar one-step hydrothermal method, La, Er-doped TiO₂ have been synthesized simultaneously.^[40] The hydrothermal method was also adopted to prepare the SnO₂ NCs since it has been reported to facilitate the growth of crystalline SnO₂ NCs under high temperature (200 °C) and pressure in an autoclave. The homogeneous SnO₂ NC layer with a grain size of 5–10 nm showed higher crystallinity than sol–gel prepared SnO₂ NCs, which facilitate the electron transfer across the corresponding interface to mitigate charge recombination.^[41] Yttrium-doped SnO₂ NCs also have been synthesized via the low-temperature in situ hydrothermal method. The resultant Y-SnO₂ NCs could be used to form efficient thin films for photovoltaic devices without annealing.^[42] Walton has made a dedicated review for the solvothermal synthesis of cerium oxide (CeO₂).^[43] However, the long-chain ligands (typically adopted in solvothermal synthesis) absorbed on the surface of CeO₂ NCs may decrease the as-deposited film's electric behavior. Recently, Chen's group developed a facile surface modification method to exchange the surface capping agent. The as-prepared CeO_x NC films show

highly compact, pinhole-free morphology and relatively high conductivity of 10^{−4} S cm^{−1}, which contribute to achieving an efficient electron-transporting layer.^[44] Besides the ETLs, HTLs (NiO_x, CuGaO₂, etc.) could also be obtained via hydro/solvothermal treatment. NiO_x nanocrystals could be synthesized by adding nickel (II) acetylacetonate [Ni(acac)₂] into tert-butanol to form a turbid light green suspension and followed by 220 °C solvothermal treatment.^[45] The synthesized NiO_x could be dispersed in low-cost, low-toxicity ethanol, and form efficient hole transport layer via one-step room-temperature ethanol-based process without any pretreatment of indium tin oxide (ITO) and post-treatment. Recently, some ternary oxides, such as delafossite (CuGaO₂ and CuCrO₂),^[46] titanates (BaTiO₃ and SrTiO₃),^[47] and spinel (Zn₂SnO₄),^[48] have been synthesized through hydrothermal method.

In brief, the hydro/solvothermal method provides an alternative and mild synthetic method to prepare the materials (even the toughest or the most complex) with desired physic-chemical properties. Furthermore, the features of higher dispersion, low-temperature, and tunableness in hydro/solvothermal synthesis make it more popular for the synthesis of metal oxides for the application of low-temperature solution-processed photovoltaic devices. However, its disadvantages, such as the strict and costly equipment requirements (high temperature, high pressure, and corrosion resistant), poor safety, and not suitable for mass production, are concerned.

2.3. Other Methods

The microwave process provides high energy to heat the reaction mixtures, resulting in rapid nuclei and growth of nanocrystals (Figure 6a). This method attracts a lot of attention due to its short reaction time, small particle size, and narrow size distributions (Table 2). Lee et al. demonstrated a microwave-assisted method to synthesize stable molybdenum oxide (MoO₃) suspensions via reacting hydrogen peroxide (H₂O₂) with a brown intermedia suspension that is obtained from microwave treatment on the n-butanol solution of the molybdenum dioxide bis(acetylacetonate) at 200 °C.^[49] This approach yields MoO₃ nanoparticles with low size polydispersity, good stability, and short reaction time down to 3 min. Furthermore, the procedure does not require additional ligands for nanocrystal stabilization, resulting in the deposited film with good carrier transport properties even without post-treatment to remove electrical insulating ligands. Hsu's group synthesized sub-10 nm copper chromium oxide nanocrystals by using microwave-assisted techniques, which requires much shorter time than previous reports using conventional hydrothermal methods.^[50] Indium-doped zinc oxide (IZO) nanoparticles were synthesized by zinc acetate and indium chloride in benzyl alcohol and subjected to a two-step microwave heating process at 120 and 160 °C, respectively.^[51] These crystalline IZO NCs synthesized by microwave-assisted methods can be well dispersed and deposited on top of other layer using a low-temperature process. Ultrasounds, especially the low frequency (20 kHz to 1 MHz), are used in chemical synthesis. Its cavitation processes, i.e., the formation, growth, and implosion of bubbles within a liquid phase, play an important role in the synthesis process.^[52] The collapse of the bubble locally

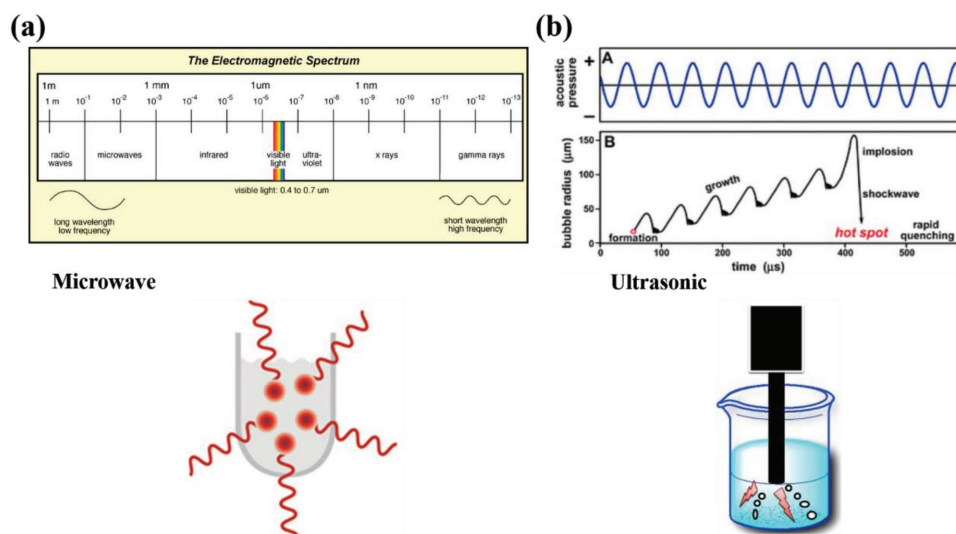


Figure 6. a) The electromagnetic spectrum and diagram of the microwave-assisted chemical method. b) Schematic illustration of the process of acoustic cavitation. Reproduced with permission.^[33f] Copyright 2015, American Chemical Society.

generates hot spots, characterized by transient high temperatures (≈ 5000 K) and high pressures (≈ 1800 atm) and very high cooling rates (10^{10} K s⁻¹), which favors the formation of amorphous materials via high energy liquid in short time^[16,53] (Figure 6b). Ohayon and Gedanken synthesized TiO₂, tungsten oxides (WO₃), and vanadium oxide (V₂O₅) in just a few minutes by reacting chloride precursors with benzyl alcohol using ultrasonic irradiation under argon atmosphere.^[54] Zhang et al. reported NiO_x nanocrystals with diameters of 4–8 nm, which were prepared from the metal salt nickel (II) chloride (NiCl₂) at low temperature via ultrasonic irradiation.^[55] This synthesis process can avoid completely the high-temperature postannealing that is required in the sol-gel route. Later, they used the same sonochemistry method to synthesize CuO nanocrystals at low temperatures.^[56]

3. Overview of Carrier Transport Layer Based on Metal Oxide Nanocrystals for Solution-Processed OSCs and PVSCs

Thanks to the salient features of ambient stability, good solution processability, and excellent optical and electrical properties, inorganic metal oxide CTLs have been extensively studied to improve both PCEs and long-term device stability. In this section, we review some recent progress on solution-processed metal oxide nanocrystal-based CTLs.

3.1. Hole Transport/Selective Layers for Solution-Processed OSCs and PVSCs

HTLs is one of the key components in OSC/PVSC device for high efficiency. In the last few years, significant progress has been made on developing low-temperature solution-processed metal oxide HTLs (Figures 7 and 8), including NiO_x, MoO₃, V₂O₅, and CuGaO₂.

Low-temperature solution-processed NiO_x is compatible with flexible devices and large-scale manufacturing of OSCs/PVSCs. However, in all the reported sol-gel synthesis of NiO_x film, the precursors have to be subject to high-temperature annealing at 250–400 °C to induce decomposition and crystallization.^[57] In 2014, Zhang et al. first prepared annealing-free solution-processible crystalline NiO_x nanoparticles at low temperature via ultrasonic irradiation. The synthesized NiO_x NCs via the sonochemical approach were directly used as the anode buffer layer in OSCs without high-temperature postannealing to induce decomposition and crystallization, which was compatible with flexible substrates and low-cost, high-throughput fabrication. Compared to poly[N-9''-heptadecanyle-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT):[6,6]-Phenyl C₇₀ butyric acid methyl ester (PC₇₀BM) OSCs with a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as HTL, the PCE of OSCs with an O₂-plasma-treated NiO_x HTL was increased from 5.84% to 6.30% and the device

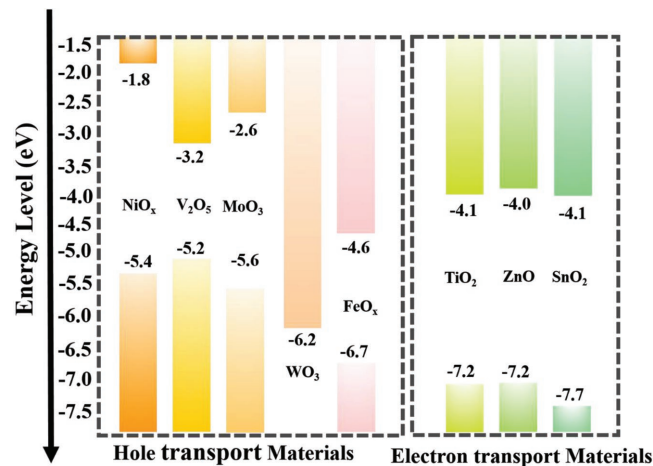


Figure 7. Schematic energy-level diagrams of several typical oxide carrier transport materials in OSCs.

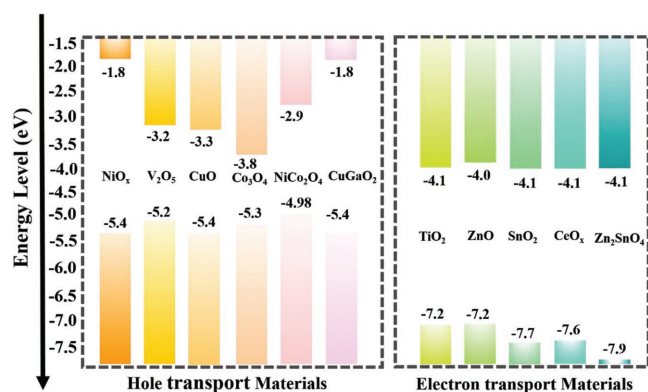


Figure 8. Schematic energy-level diagrams of several typical oxide carrier transport materials in PVSCs.

stability was also enhanced.^[55] Choy's group also demonstrated post-treatment-free and solution-processed NiO_x NCs by a facile chemical precipitation method.^[19a] Remarkably, these nonstoichiometric and ligand-free NiO_x NCs could well and stably be dispersed in deionized water over 120 d, which enables to form an efficient HTL film through a room-temperature solution process without any post-treatment during device fabrication. By using this efficient NiO_x HTL, an average PCE of 9.16% was achieved in PTB7-Th-based OSCs, which overwhelms the conventional PEDOT:PSS. Later, this group adopted these NiO_x NCs synthesized via chemical precipitation

process to form surface-nanostructured and flawless NiO_x film as HTL for high-performance flexible PVSCs. The surface-nanostructured NiO_x film can be readily formed on various substrates (ITO glass and polyethylene terephthalate (PET)) through simple and control room-temperature solution process without any post-treatment. The PCE reached a value of 14.53% and 17.6% for PVSCs on PET substrate and rigid ITO glass with no obvious hysteresis, respectively. Interestingly, the NiO_x -based PVSCs showed better photovoltaic performance and markedly improved air stability compared to those of the PEDOT:PSS-based devices^[19b] (Figure 9). Weber et al. compared the performance of planar p-i-n PVSCs based on this chemical precipitation synthesized NiO_x and sputtered NiO_x as HTL (Figure 10). In their study, they concluded that the solution processed NiO_x HTL performed better than sputtered NiO_x film due to the low film thickness of the sputtered NiO_x film of only 10 nm and thereby insufficient electron blocking properties.^[58] Cu and Cs-doped NiO_x could be synthesized through a similar chemical precipitation method. These doped films prepared by a simple solution-based method with uniformity and highly reproducible were applied in planar PVSCs with PCE of 19% and 20.26% for Cs: NiO_x ^[20a] and Cu-doped NiO_x -based PVSCs,^[59] respectively. The low-temperature processing condition is usually accompanied with defect formation, which deteriorates the film quality and device efficiency to a large extent. To suppress this setback, some materials, such as F6TCNNQ, benzoic acid self-assembled monolayers, and PEDOT:PSS, have been used to modify the surface of NiO_x film, resulting

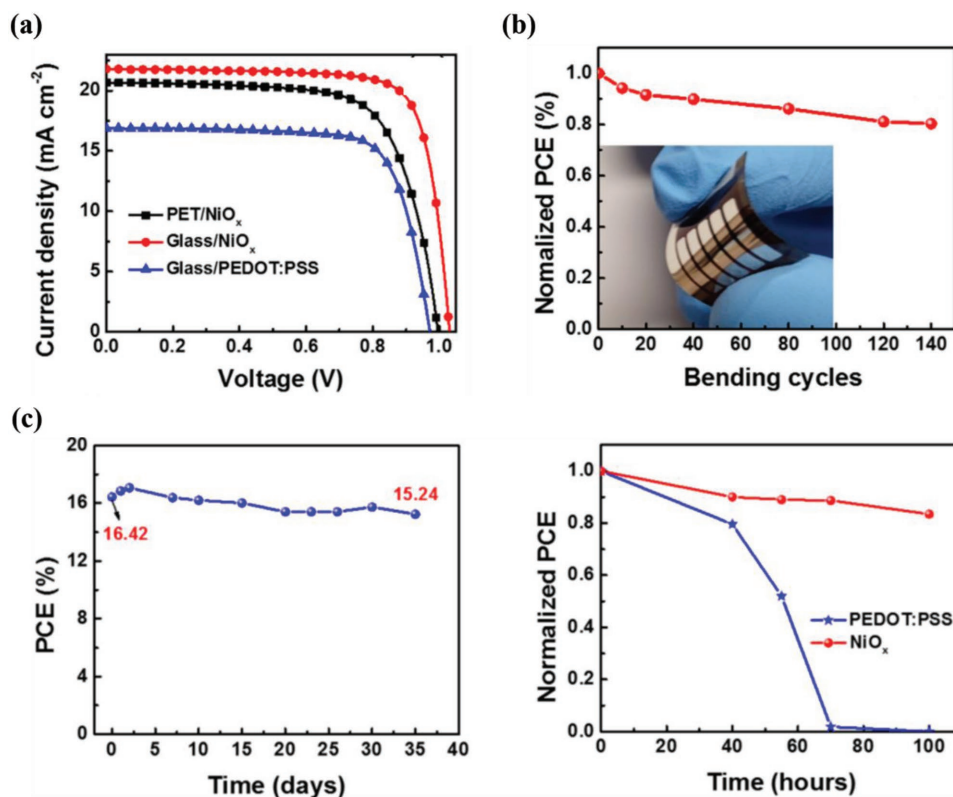


Figure 9. a) J-V curves. b) Normalized PCE of NiO_x -based flexible PVSC as a function of bending cycles and the photograph of NiO_x -based flexible PVSC (inset). c) The PCE evolution of an encapsulated NiO_x -based device and unencapsulated devices stored for different numbers of days, respectively. All panels reproduced with permission.^[19b] Copyright 2016, the American Chemical Society.

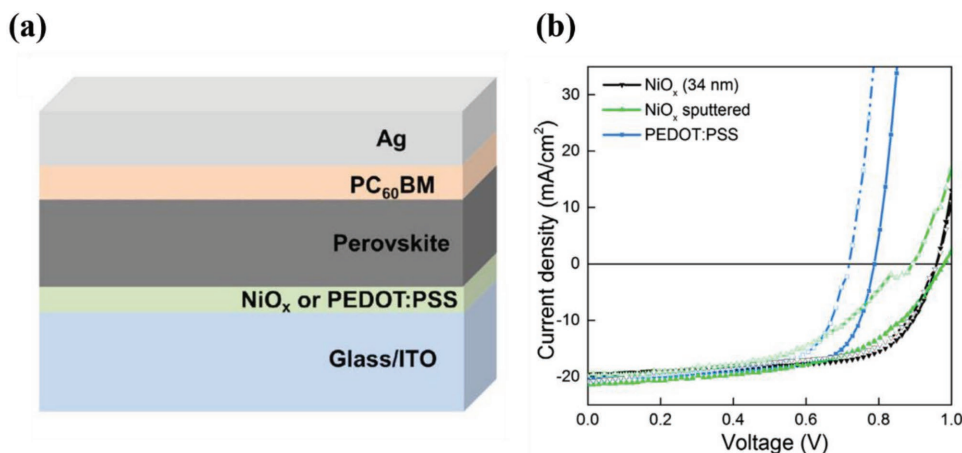


Figure 10. a) Schematic representation of the device structure. b) J - V curves of devices with solution processed NiO_x , sputtered NiO_x , and PEDOT:PSS as HTLs, respectively. Reproduced with permission.^[58] Copyright 2018, Springer Nature.

in more stable PVSCs with enhanced power conversion efficiency.^[59,60] These NiO_x and doped NiO_x NCs discussed above are all dispersed in water, which may face the same wetting and compatibility issue on different substrates as the water-based PEDOT:PSS, then nonaqueous disperse NiO_x was exploited. Choy's group synthesized ethanol dispersible ultrasmall NiO_x NCs through a hydrothermal method and fabricated NiO_x :F4-TCNQ nanocomposite film as HTL in OSCs without any pretreatment (ultraviolet-ozone (UVO) or oxygen-plasma treatment on the substrate) and post-treatment.^[45a] By

using one-step pre and posttreatment-free NiO_x :F4-TCNQ as HTL, the average PCE of 3.59% and 9.54% has been realized in P3HT:PC₆₁BM-based OSCs and PTB7-Th-based OSCs, respectively. Later, the same group demonstrated a self-assembled quasi-3D nanocomposite of NiO_x nanocrystals and graphene oxide (GO) nanosheets in ethanol, which enable it to successfully deposit atop polymer active layer. By applying this novel p-type HTL in inverted nonfullerene OSCs, the device exhibited a champion PCE of 12.31% due to the enhanced conductivity and electron blocking ability^[45b] (Figure 11). Ligands

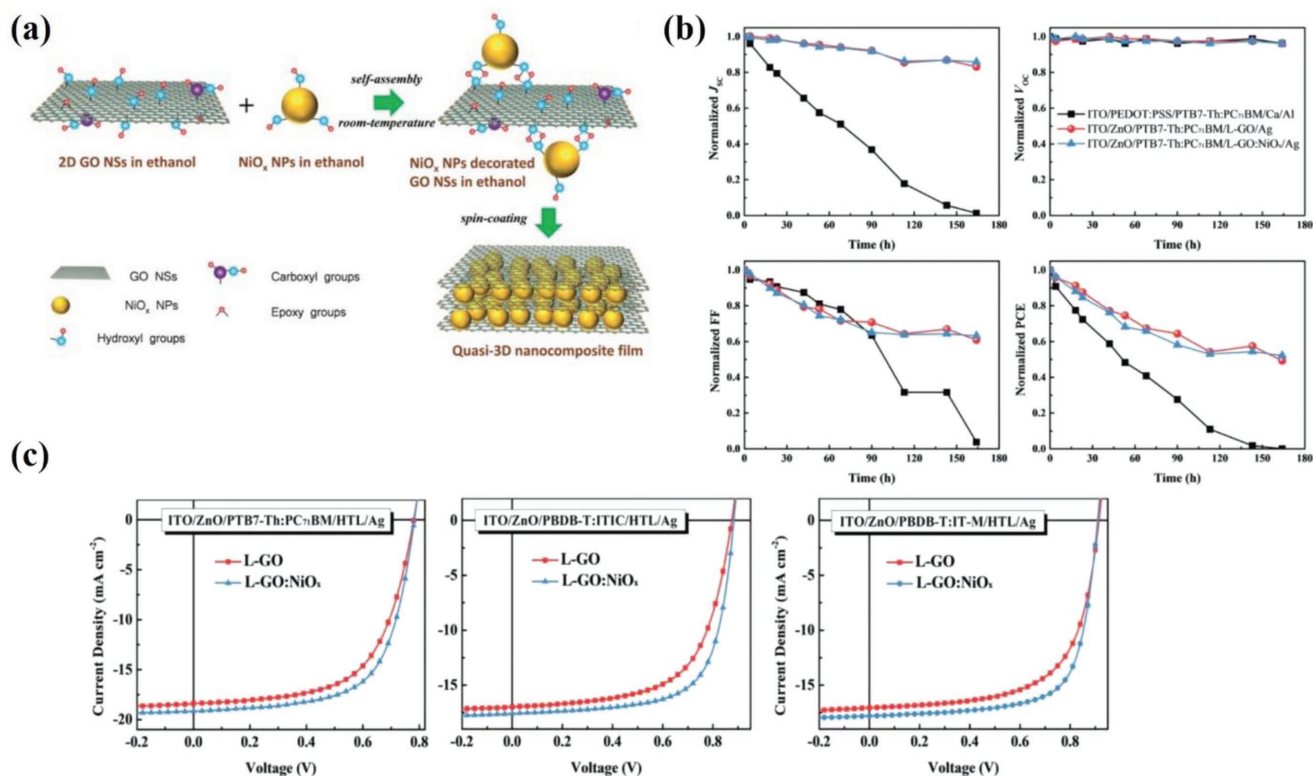


Figure 11. a) Schematic illustration of preparing room-temperature ethanol processed self-assembled quasi-3D GO: NiO_x nanocomposite. b) Normalized device characteristics as a function of air exposure time. c) J - V characteristics of inverted OSCs with GO and L-GO: NiO_x as HTL. Reproduced with permission.^[45b] Copyright 2018, Wiley.

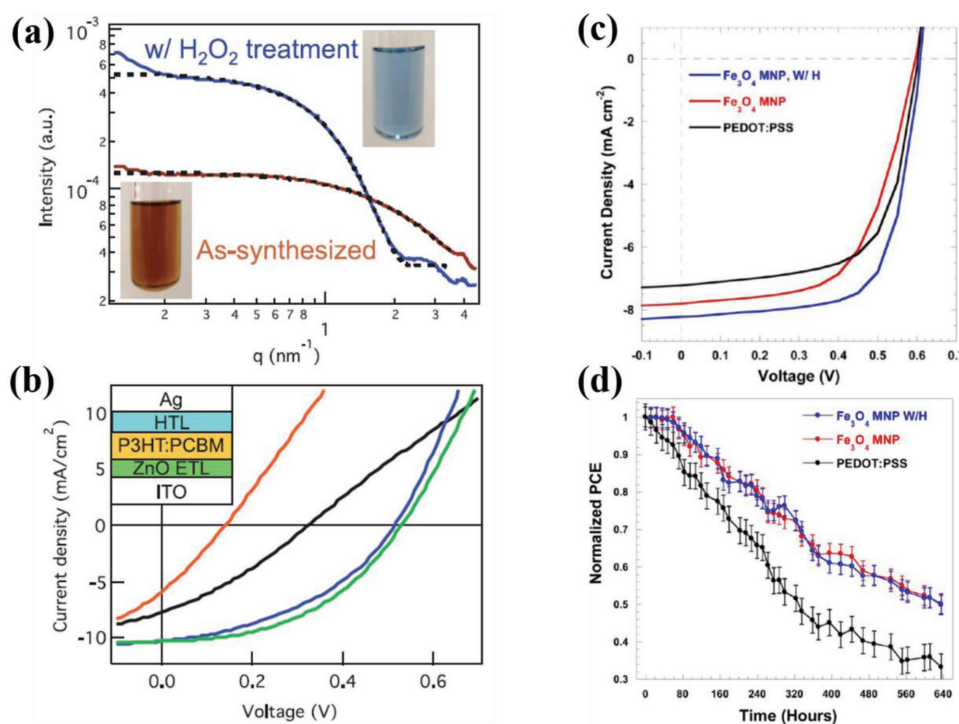


Figure 12. a) SAXS patterns of as synthesized (brown solid) and 0.11 M H_2O_2 treat (blue solid) np MoO_3 suspensions in b-butanol along with model fits (black dashed), inside: photographs of np MoO_3 suspensions after 100 times dilution. b) J - V curves for OSC devices with no HTL (orange), 20 nm np MoO_3 (black), 20 nm e MoO_3 (blue), and 20 nm PEDOT:PSS (green). a,b) Reproduced with permission.^[49] Copyright 2012, Wiley. c) J - V characteristics of OSCs measure under 100 mW cm^{-2} AM1.5G illumination. d) Shelf-stability of OSCs. c,d) Reproduced with permission.^[66] Copyright 2013, the American Chemical Society.

are typically subject to be added to disperse and stabilize metal oxide NCs. For example, Liang et al. reported lithium stearate stabilized NiO_x nanocrystals in hexane as HTL in OSCs, which achieves an average PCE of 6.1% (TQ1:PC₇₁BM as photoactive material) by using UVO treatment to remove the insulating surface ligands and increase the work function of NiO_x film.^[61] A low-temperature solution-processed NiO_x thin film composed of ligand-protected NiO_x NCs (dispersed in chlorobenzene) was also employed as HTL in p-i-n PVSCs with a promising PCE of 15.9%. When employed in n-i-p mesoscopic PVSCs, this non-aqueous solvent dispersed ligand-protected NiO_x can be directly deposited on the perovskite film as a top hole transport layer with a PCE of 9.11%.^[62] The used long chain ligands are typically insulating, which may influence the electrical property and some other absorbed ligands (e.g., water molecules and hydroxides) can reduce the stability of the devices. Therefore, Han's group recently demonstrated ligand-free E- NiO_x NCs to form a smooth, compact film with good hole extraction capability. The inverted PVSCs with E- NiO_x as the HTL (active area, 1.02 cm^2) exhibited a PCE of 18.49% and 15.89% on a rigid and flexible substrate, respectively. In addition, these devices retained 90% of their initial performance at 500 h under 85% relative humidity at 85 °C that is ascribed to less hydroxyl functional groups and H_2O molecules on the NiO_x surface.^[25a]

Lee et. al demonstrated stable ultrasmall MoO_3 nanocrystals (np MoO_3) made by microwave-assisted synthesis can be directly spin-coated on top of P3HT:PC₆₁BM active layer to form HTLs without postsynthesis purification or thermal

processing. The np MoO_3 HTL inverted OSCs achieved a comparable PCE to those of PEDOT:PSS-based devices by being treated with air exposure and H_2O_2 solution^[49] (Figure 12a,b). Choy's group proposed a more easy way to one-step synthesize low-temperature solution-processed MoO_3 and V_2O_5 for HTLs. The as-prepared NCs could be dispersed uniformly and stably into water-free solvents, which are particularly beneficial to the device stability and processing. Furthermore, oxygen vacancies and the work function of MoO_3 and V_2O_5 could be controlled by manipulating the time of vacuum treatment and the amount of cesium intercalation, which could further improve the performance of OSCs.^[63] A similar solution-processed V_2O_5 nanocrystal was deposited on PEDOT:PSS to form bilayer structure as the HTL in the inverted PVSCs by Huang's group, which exhibited improved film surface properties as well as optical and electrical properties. A remarkable hysteresis-free PCE 17.5% and V_{oc} of 1.05 V were achieved, which is significantly higher than pristine PEDOT:PSS (PCE of 14.2% and V_{oc} of 0.85 V) and pristine V_2O_5 (PCE of 14.8% and V_{oc} of 0.98 V).^[64] Recently, Cs-doped V_2O_5 NCs were obtained by a similar synthesis method, which could form high electrical conductivity thin films as HTL in PVSCs via low-temperature solution-processed.^[65]

Gong's group reported solution-processed FeO_x magnetic nanocrystal thin film featuring a smooth surface, good transparency, and high electrical, which could serve as an efficient HTL in OSCs. It exhibited an enhanced efficiency and stability than those of PEDOT:PSS-based devices^[66] (Figure 12c,d).

Recently, Choy and co-workers proposed new room-temperature solution-processed nanocrystals composite of maghemite and iron hydroxide as efficient HTL. The PCE of devices was remarkably enhanced with the introduction of nanocomposite comparing with the optimized devices without HTL. In addition, the nanocomposite-based devices showed better stability than those of PEDOT:PSS-based devices.^[22b]

Recently, Achilleas Savva et al. produced monodisperse CuO nanocrystals via the solvothermal synthetic route, which can be used to develop functional CuO HTLs at room temperature eliminating the requirement of the annealing step during the fabrication process. The room-temperature solution-processed CuO HTL exhibit a high work function, transparency, and good surface properties to facilitate high-quality perovskite photoactive layers on top of them with significantly increased grain size compared with PEDOT:PSS, leading to a PCE of 15.3% and over 50% increase in PCE compared with the corresponding PEDOT:PSS-based p-i-n PVSCs.^[30]

Ternary metal oxides, featuring tunable optical and electrical properties, are adopted both in OSCs and PVSCs. Recently, Choy and co-workers synthesized ultrasmall NiCo_2O_4 NCs as HTL in PVSCs. These ultrasmall (5 nm on average) and well-dispersed NiCo_2O_4 NCs without exotic ligand enable the formation of uniform and pin-hole free film, which contributes to the perovskite crystal growth. The NiCo_2O_4 -based perovskite solar cells realized a high PCE of 18.23% and a promising stability (maintained $\approx 90\%$ initial PCE after 500 h light soaking).^[24] Hsu's group reported a microwave-assisted hydrothermal synthesis of p-type CuGaO_2 crystalline nanoplates as HTL in OSC devices.^[67] A thick CuGaO_2 HTL (≈ 280 nm) in P3HT:PC₆₁BM devices achieved 3.2% PCE. Jen's group adopted this solution-processed nanoplate CuGaO_2 as HTL in the n-i-p PVSCs, which exhibited an encouraging PCE of 18.51% in the reverse scan

mode and improved ambient stability, which is significantly better than that of spiro-OMeTAD-based devices.^[68]

3.2. Electron Transport/Selective Layers for Solution-Processed OSCs and PVSCs

ETL is in an equal position with HTL in the photovoltaic devices while it serves to extract electrons from the active layer to the electrode. Among n-type metal oxides, TiO_2 , ZnO, and SnO_2 are popular choices for solution-processed ETLs for high-performance and stable OSCs and PVSCs (Figures 7 and 8). Choy and co-workers proposed a self-assembled method to prepare solution-processed titanium oxide ETL in high quality for large-area OSCs.^[28b] They found that self-assembled TiO_2 ETL shows enhanced PCE than the spin-coated ETL with a small variation on PCE from different locations of the large-area film (cut into smaller pieces). Apart from the basic function of electrical conducting, optically enhanced effects from ETL by incorporating metal nanoparticles have also been investigated to further improve the performance of optoelectronic devices. They further introduced Au or Ag NPs into the above TiO_2 NCs to form a composite ETL for high-performance OSCs.^[28a,c,d] The redistribution of charges in the UV-irradiated metal NPs- TiO_2 system can assist the charge extraction in OSCs, which results in enhanced device performance (Figure 13). The optically induced electrical effect (termed the plasmonic-electrical effect) was later confirmed and further studied by Riedl and co-workers.^[69] As shown in Figure 8, there are some MONC-based ETLs applied in PVSCs. Wang et al. reported hydrothermal synthesized TiO_2 NCs combined with graphene as ETL in meso-superstructured PVSCs. By exploiting the graphene/ TiO_2 nanocomposite film in PVSCs via low-temperature solution

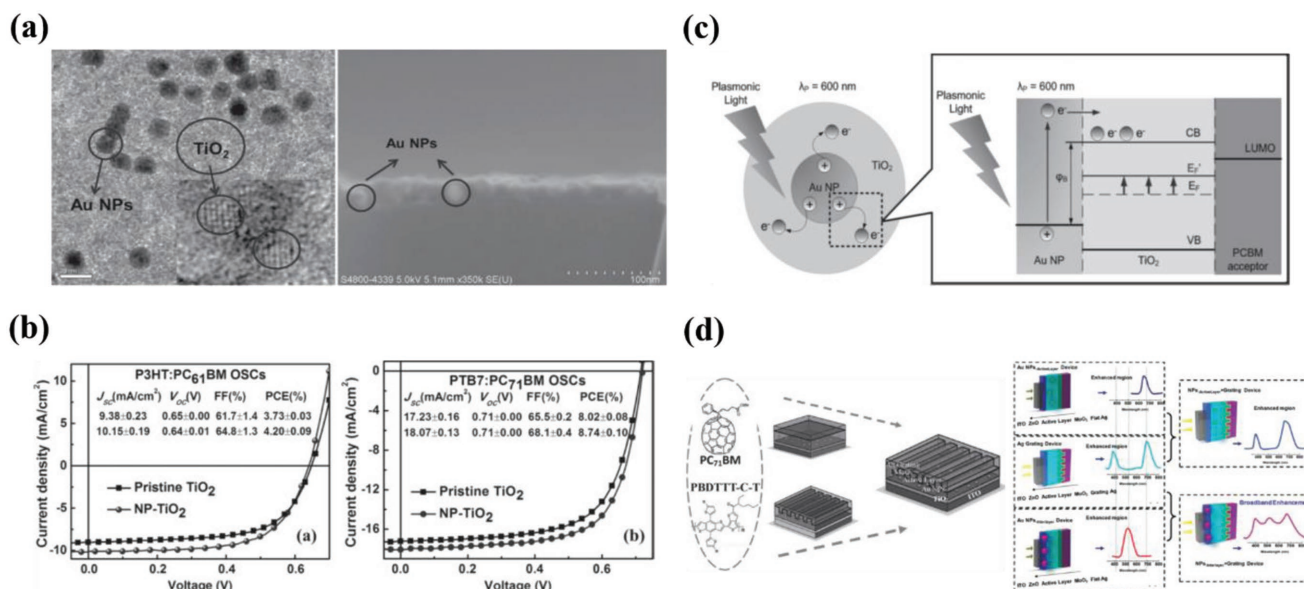


Figure 13. a) TEM image and cross-sectional scanning electron microscope (SEM) image of the Au NP- TiO_2 composite. b) $J-V$ characteristics of inverted OSCs with TiO_2 and NP- TiO_2 composite. c) Schematic plasmonic-induced charge injection process. a-c) Reproduced with permission.^[28d] Copyright 2013, Wiley. d) Chemical structures of PBDTTT-C-T and PC₇₁BM (left). Schematic of the device structure: NP device (top), the grating device (bottom), and dual metallic structural device (right). Reproduced with permission.^[28a] Copyright 2012, Wiley.

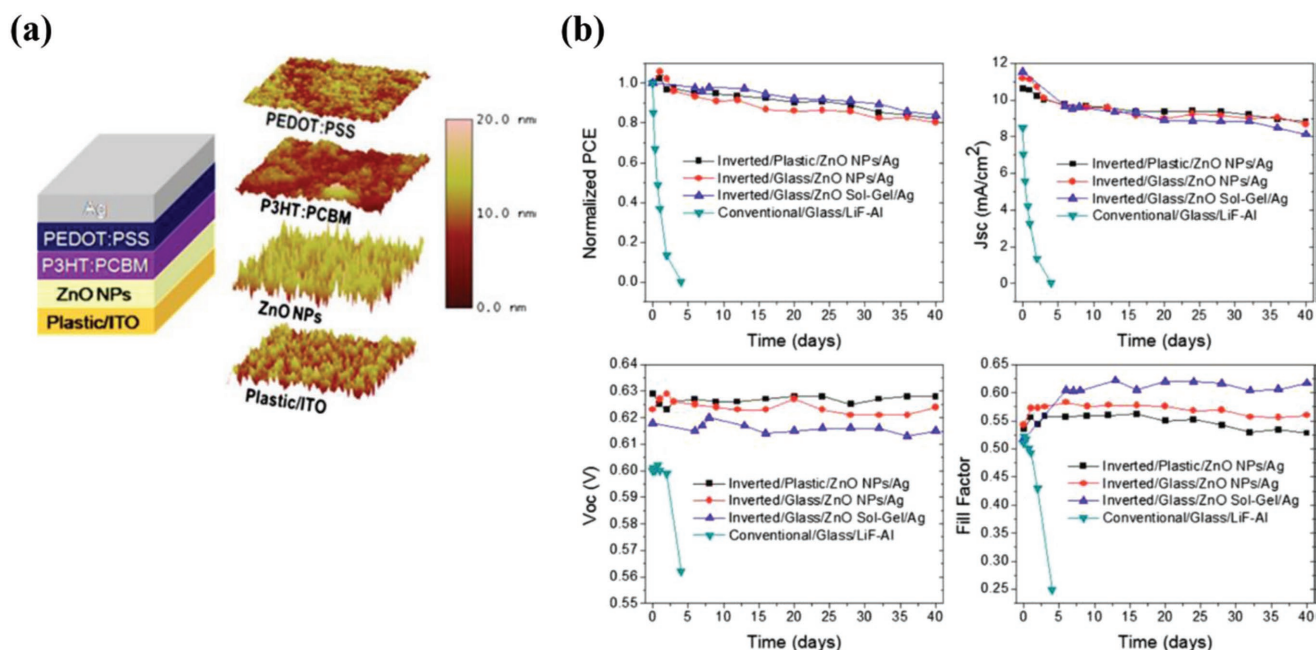


Figure 14. a) Left: Device configuration of the flexible inverted plastic solar cell. Right: atomic force microscope (AFM) images of the different layers in the flexible inverted plastic solar cell. b) Device performance of unencapsulated conventional and inverted solar cells stored 40 d in air under ambient conditions. Reproduced with permission.^[74] Copyright 2008, the American Institute of Physics.

procedure without sintering, a PCE of 15.6% was achieved, which is compatible with large-scale industrial manufacture on a range of substrates and multilayer architectures.^[70] Mg, La, and Er-doped TiO₂ were also synthesized via the hydrothermal process and applied in PVSCs with improved devices performance compared with undoped TiO₂.^[40,71] The capping agent used in the synthesis process, such as oleic acid, is good for the dispersion of NCs, which enables the formation of a compact and uniform film. Yet, such insulating ligands ultimately limit the functionality achievable, restricting electronic coupling and confining interparticle interaction. Recently, Zhang et al. demonstrated high-quality TiO₂ ETL fabricated with ligand-exchange induced OA-free TiO₂ NCs at low temperature. Owing to the advantages of OA-free TiO₂ ETLs including higher conductivity, faster electron extraction and transport property, and lower series resistance and higher shunt resistance in the assembled PVSCs, the devices exhibited a steady-state PCE of 18.82% with slight hysteresis and good reproducibility.^[72]

Tao and co-workers developed a solution-processed annealing-free ZnO NC as high-quality ETL for inverted OSCs. The ZnO NCs (average size $\approx$ 11 nm) were dispersed in chloroform and stabilized by propylamine, which can be used in the air directly and stable for one month. With the help of this ETL, the PCE of the nonencapsulated devices remains unchanged even after stored in air for 50 d.^[73] Comparing with ligand-stabilized ZnO NCs, ligand-free and stable ZnO NCs are more attractive due to their excellent electrical properties. Beek et al. obtained stable ZnO NCs without additional surfactants by a low-temperature solution process, and applied in conjugated polymer bulk heterojunction solar cells.^[29b] Jen and co-workers then fabricated and compared inverted OSCs with these low-temperature solution-processed ZnO NCs and sol-gel

processed ZnO layer as ETL, respectively. Similar device performance and stability are achieved in both the high-temperature sol-gel processed ZnO and the room temperature processed ZnO NCs, while the low-temperature solution-processed ZnO NCs have an inherent advantage of being implemented onto flexible plastic ITO substrates to develop low-cost, large-scale, and roll-to-roll printable solar cells^[74] (Figure 14). By using these ZnO NCs ETL for PVSCs with the structure of ITO/ZnO/MAPbI₃/spiro-OMeTAD/Ag via room-temperature solution processing techniques, Kelly and co-worker achieved PCEs of 15.7% on the rigid substrate (in excess of 10% for flexible devices).^[75] You et al. lately deposited this type of ZnO NCs on the top of the perovskite film, and fabricated p-i-n structure PVSCs with inorganic NiO_x as the HTL simultaneously, which produced a PCE of 16.1% and significantly improved device stability compared with solar cells using organic HTL and ETL.^[76] Aluminum-doped zinc oxide (AZO) as ETL was applied in inverted PVSCs by Savva et al, which exhibited a PCE of 13% and maintained 100% of the initial PCE after over 1000 h of exposure when AZO/Au was used as the top electrode.^[77] Choy and co-workers designed metal NP doped ZnO as ETL to fabricate the plasmonic-enhanced OSCs. The device showed broadband absorption enhancements in the range of 350–800 nm due to multiple plasmonic effects, which resulted in 9.26% PCE.^[29e] Different from the case in OSCs emphasizing on optical and electrical properties, people pay more attention to the stability issue in perovskite solar cells. Since the chemical interaction between the metal oxides and perovskite at the interface, the surface functional groups of metal oxides and the hygroscopic nature of metal oxides, both could influence the stability of perovskite solar cells, people propose different ways to solve the corresponding problems. For example,

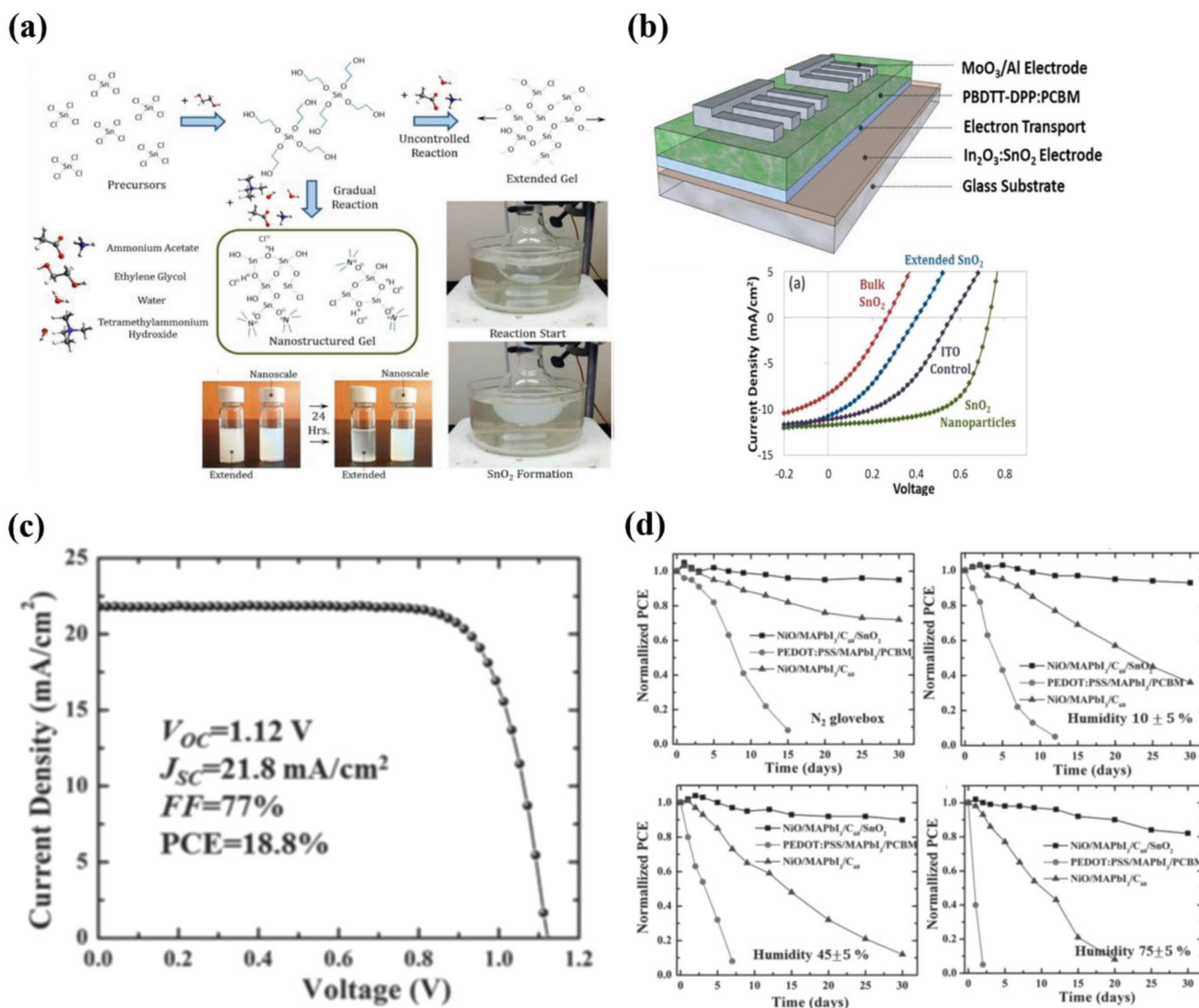


Figure 15. a) Schematic diagram of the proposed reaction mechanism and the synthesis process. b) The device structure and the corresponding J - V characteristics of PBDTT-DPP:PCBM solar cells using nanoscale SnO₂ as an electron transport layer. a,b) Reproduced with permission.^[27] Copyright 2013, the American Chemical Society. c) J - V curve of the studied PVSCs. d) Stability test of PVSC devices as a function of storage time in different environments. c,d) Reproduced with permission.^[41] Copyright 2016, Wiley.

in order to reduce the photocurrent loss and degradation of charge selectivity in the cathode interface caused by the surface defects of ZnO-nanocrystals, fullerene-based molecules, polymers, and metal oxides have been used to passivate the defect states of ZnO nanocrystals, which contributes to improve the long-term photostability of OSCs and PVSCs.^[78]

Bob et al. demonstrated a solvothermal route to stabilize gelled dispersions of SnO₂ NCs with diameters in the range of 2–4 nm. The as-prepared SnO₂ with desirable morphological properties favors the formation of smooth, continuous films as ETL, and a PCE of 5% was achieved in PBDTT-DPP:PC₆₀BM-based inverted OSCs^[27] (Figure 15a,b). Recently, Bai et al. synthesized the high crystalline Sb-doped SnO₂ NCs by the same solvothermal method and applied it as ETL for efficient n-i-p planar PVSCs through a facile low-temperature solution process.^[79]

Improved PCE of PVSCs from 15.7% to 17.7% (steady state efficiency) was obtained due to the increased conductivity and reduced charge recombination. Jen and co-workers exploited the solution-processed SnO₂ nanocrystals via the hydrothermal method as ETL in the inverted PVSCs. The obtained NCs can be dispersed in isopropyl solution, which makes it feasible to be used in the inverted structure by spin coating the SnO₂ nanoparticles on C₆₀ as a bilayer electron transport layer. A high PCE of 18.8% was demonstrated with a remarkable ambient stability, which can retain over 90% of its initial PCE after being stored in the ambient with >70% relative humidity for 30 d^[41] (Figure 15c,d). Yang et al. demonstrated low-temperature in situ hydrothermal-synthesized yttrium-doped SnO₂ nanosheets for significantly reducing the hysteresis and enhancing the performance of PVSCs.^[42]

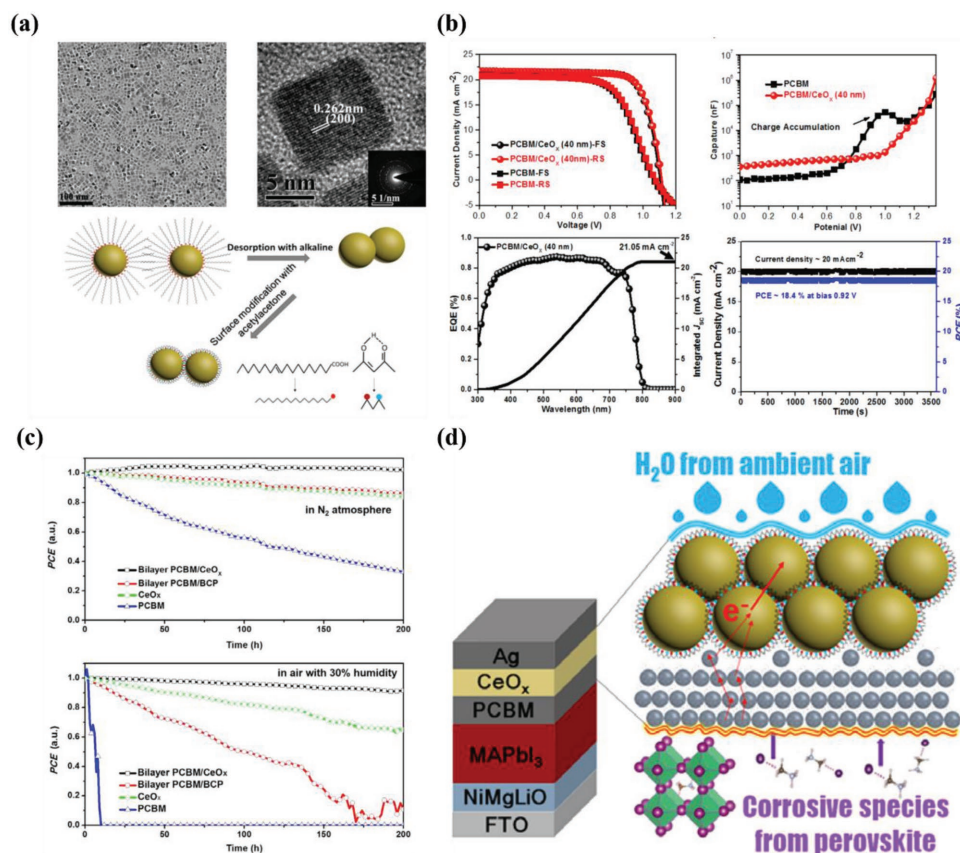


Figure 16. a) TEM image, high-resolution transmission electron microscope (HRTEM) image, selected-area electron diffraction pattern (inset) of a CeO_x NC, and schematic illustrating the ligand exchange procedures. b) J - V curves, dependences of capacitance of the best devices based on PCBM/ CeO_x (40 nm) bilayer ETL and sole PCBM ETL, IPCE spectrum (the corresponding integrated photocurrent density) and stabilized photocurrent density (black) and PCE (blue) of the best device based on the PCBM/ CeO_x (40 nm) bilayer ETL. c) The unencapsulated devices were aged for 200 h in an N_2 -filled glovebox and an air-filled environment-testing chamber with controlled humidity of $\approx 30\%$, held at room temperature under continuous light soaking and maximum power point tracking. d) Schematic illustrating for the improved device stability. All panels reproduced with permission.^[44] Copyright 2018, the American Chemical Society.

After suitable surface modification, Chen's group demonstrated low-cost CeO_x nanocrystals dispersed in both polar and nonpolar solvents as high-quality ETLs in inverted PVSCs. The devices displayed a promising PCE of 18.7% for the configuration of $\text{NiMgLiO}/\text{MAPbI}_3/\text{PCBM}/\text{CeO}_x$ and dramatically enhanced long-term stability, which not only retained the initial PCE in the dark after 30 d (30% humidity) but also kept the initial PCE after continuous light soaking for 200 h (N_2 atmosphere)^[44] (Figure 16).

Recently, Seok and co-workers reported low-temperature high-dispersed Zn_2SnO_4 (ZSO) nanocrystal at a reduced temperature of below 100°C as ETL in perovskite solar cells. Based on the high-quality ZSO ETLs, flexible perovskite solar cells with a PCE of 14.85% were achieved.^[48] More recently, they have further synthesized ZSO NCs and quantum dots to tailor the energy level and the electron transporting ability and fabricated flexible PVSCs with a steady state PCE of 16%.^[80] Zhu et al. demonstrated highly crystalline and discrete La-doped BaSnO_3 (LBSO) NCs synthesized by a low-temperature solution processed method and applied these as a mesoporous ETL in PVSCs. The LBSO-based devices exhibited a good charge transfer efficiency and low recombination rate, resulting in the best PCE of 15.1%.^[23]

4. Conclusion and Outlook

In this article, we have reviewed the synthesis methods for solution-processed metal oxide nanocrystals and their performance as CTLs in OSCs and PVSCs. However, it needs more efforts to promote their application in photovoltaic devices.

- 1) The preparation of metal oxide nanomaterials with well-defined size and morphology is an important challenge for various applications, especially in photovoltaic application. When the material dimension is reduced to the nanoscale, they demonstrate unique properties, which are different from those of their bulk counterpart. Such features make nanomaterial attractive for unique applications and at the same time cause complication in their synthesis. Even though varieties of techniques have been applied for the synthesis of metal oxide nanocrystals, it still needs to exploit new synthesis methods according to its application. Furthermore, to control the size and morphology of MONCs, better understanding of the formation mechanism of new synthesis methods and manipulation of the reaction conditions are needed.

- 2) Surface ligands used to stable metal oxide nanocrystals need to fulfill demands from the aspects of both solution processability and charge transport. Ligands with long hydrocarbon chains are insulated, e.g., ethylene glycol, which limited their application as CTLs. Therefore, a number of ligand-exchange strategies have been proposed, including ligand exchange with smaller molecules, thermal-degradable ligands, or metal-chalcogenide complexes, to address this issue. More efforts on ligand-exchange strategies can help the approaches for achieving oxide nanocrystal in CTL applications. Consequently, there is still an urgent need to exploit efficient ways to simultaneously improve the processability of metal oxide nanocrystals in solution and charge transport of their corresponding films.
- 3) Good CTLs require good film-forming properties ensuring uniform coverage as possible. Moreover, CTLs lie on top of the active layer are limited reported. Since it is the layer to come into contact with humidity and oxygen as well as interfacing with the active layer, its resistance to chemical degradation as well as guaranteeing a stable electronic interface is necessary. Composite materials/layers may be considered effective strategies to deal with it, and further studies along these lines will contribute to enhancing the efficiency and stability.

Overall, we envisage that oxide-based CTLs is very favorable for both OSCs and PVSCs, mainly because of their supreme stability, good electrical properties, and potential transparency. The continuous exploration of a larger number of new oxide-based CTLs, which can guarantee high efficiency, high stability, low-cost, and good film-forming properties over large areas, is important for their practical applications in emerging optoelectronic devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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