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# Nanocrystals as performance-boosting materials for solar cells

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Nanocrystals (NCs) have been widely studied owing to their distinctive properties and promising application in new-generation photoelectric devices. In photovoltaic devices, semiconductor NCs can act as efficient light harvesters for high-performance solar cells. Besides light absorption, NCs have shown great significance as functional layers for charge (hole and electron) transport and interface modification to improve the power conversion efficiency and stability of solar cells. NC-based functional layers can boost hole/electron transport ability, adjust energy level alignment between a light absorbing layer and charge transport layer, broaden the absorption range of an active layer, enhance intrinsic stability, and reduce fabrication cost. In this review, recent advances in NCs as a hole transport layer, electron transport layer, and interfacial layer are discussed. Additionally, NC additives to improve the performance of solar cells are demonstrated. Finally, a summary and future prospects of NC-based functional materials in solar cells are presented, addressing their limitations and suggesting potential solutions.

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## 1. Introduction

Nanocrystals (NCs), sometimes termed as quantum dots (QDs) or nanoparticles (NPs), with a size less than 100 nm, are popular worldwide and have been paid extensive attention owing to their outstanding photoelectric properties. In the energy field, photovoltaic devices based on semiconductor NCs are among the most potential systems with high power conversion efficiency (PCE), good stability, low cost, facile fabrication, and other advantages.<sup>1–16</sup> In recent years, NCs have been widely used as light harvesting layers in high-performance solar cells. Semiconducting NCs such as PbX (X = S, Se, and Te), CdSe, and CuInS<sub>2</sub> have been suggested as excellent light harvesters in third-generation solar cells.<sup>11,14,15,17–22</sup> Additionally, perovskite NCs are also good alternatives for light harvesting in solar cells.<sup>12–14,16,23–28</sup> Besides active layers (light harvesting layers), functional layers based on NCs, mainly including hole transport layers (HTLs),<sup>29–99</sup> electron transport layers (ETLs)<sup>100–173</sup> and interfacial functional layers (IFLs),<sup>174–221</sup> are of great importance in solar cells. Notably, NC additives also boost the performance of solar cells through defect passivation, plasmonic effect, solar concentration, light up-conversion and down-conversion/shifting, light scattering and reflection, and heat sinks.<sup>222–258</sup>

To efficiently transport charge in solar cells, HTLs and ETLs must have suitable energy levels matching the active layers such

as dyes, Si, Pb-based light harvesting layers, and perovskite films. For example, to fabricate high-performance perovskite solar cells (PSCs), the work function of HTLs and ETLs should have hole and electron transport layers aligned with the valence band edge and conduction band edge of a perovskite. As is well known, the energy levels of NCs can be easily controlled and adjusted by changing their sizes, ligands, and dopants during their synthesis process, which is favourable to satisfy the energy alignment. Meanwhile, the easily-accomplished modifications in NCs mentioned above also favour high mobility to allow carrier transport and form a more effective current circulation path. Furthermore, the transmittance of HTL or ETL based on NCs can be improved during synthesis processes, which leads to less light loss and thus, higher performance of solar cells. Consequently, NCs are a good choice as HTLs and ETLs for efficient solar cells and have gained much attention.

Some researchers found that inserting different IFLs in solar cells could promote the power conversion efficiency (PCE) and stability of the devices. Good IFL can modulate the formation of adjacent layers (especially the perovskite layer in PSCs), optimize energy alignment, and impede charge recombination. As multi-functional IFL, NCs have been extensively investigated due to their compatible properties, such as appropriate morphology for compact, smooth films, gradual energy level to transfer carriers, and self-stability to protect the devices.

Besides acting as a separate functional layer in efficient solar cells, NCs have also been used as additives to improve active layer quality, accelerate carrier transfer, convert infrared or ultraviolet light to visible light, scatter and reflect light, sink heat, and other functions.<sup>222–258</sup> The addition of NCs could enlarge the grain size of perovskite film, reduce the

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recombination, enhance charge extraction, improve the charge mobility, broaden the spectral response range, and so on.

In this review, functional materials based on NCs for high-performance solar cells are summarized. NCs as HTL, ETL, IFL, and additives for NC-light-harvestor solar cells (NC-LHSCs), PSCs, organic solar cells (OSCs), Si solar cells, and dye-sensitized solar cells (DSSCs) are successively analyzed. In Section 2, NCs as charge transport layers are analyzed in detail. This can provide a deep understanding of the extensive application of NCs in solar cells. As an important functional layer, IFL based on NCs is summarized in the next section. Section 4 describes NCs as efficient additives in different functional layers due to their small sizes and excellent photoelectric properties. Finally, we discuss the existing challenges of NCs for boosting the performance of solar cells and provide some feasible suggestions on these issues, expecting to improve the performance of solar cells based on NCs.

## 2. Nanocrystals as charge transport layers

In this section, we focus on NCs-based charge transport layers for solar cells, mainly including top/bottom HTL and ETL in n-i-p and p-i-n solar cells.

### 2.1 Nanocrystals as HTL

As known to us, solar cells work as follows: absorption of sun light, generation and separation of hole–electron pairs, transport of holes through HTL and electrons through ETL, and current produced by the flow of electrons through external circuits. Solar cells using NCs as HTL are not exceptional, and the typical structures of solar cells based on NC HTL are shown in Fig. 1. According to the position of HTL, we call HTL between the ITO/FTO and active layer as bottom HTL while the HTL between metal electrode and active layer as top HTL.

**2.1.1 Recent NC HTL.** Semiconductor NCs have shown great potential in photoelectronic devices due to their excellent properties. The advances of NC HTLs for solar cells are listed in Table 1, including the size of NCs, device structure, PCE, and stability of solar cells.



Fig. 1 Typical structure of solar cells based on top (left) and bottom (right) NC HTLs.

Lead chalcogenide NCs, especially PbS, have been massively used as efficient top HTL in NC-LHSCs.<sup>29–56</sup> Additionally, other metal chalcogenide NCs are also excellent choices as top HTL for high-performance perovskite solar cells (PSCs), mainly containing CuInS<sub>2</sub>/ZnS (core/shell),<sup>57</sup> CdZnSe@ZnSe,<sup>58</sup> Cu<sub>2</sub>ZnSnS<sub>4</sub>/Se<sub>4</sub>,<sup>59</sup> SnS,<sup>60</sup> CuInSe<sub>2</sub>,<sup>61</sup> Ag–In–Ga–S,<sup>62</sup> Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>,<sup>63</sup> Cu<sub>2</sub>SnS<sub>3</sub>,<sup>64</sup> CuGaS,<sup>65</sup> and CuInS<sub>2</sub>.<sup>66</sup> Metal oxide NCs of NiO have shown potential for hole transport on top of the light harvesting layer in PSCs and Si solar cells.<sup>67–69</sup> Besides NiO, some other metal oxide NCs such as MoO<sub>2</sub>,<sup>70</sup> Co<sub>3</sub>O<sub>4</sub>,<sup>71</sup> Cu<sub>2</sub>O,<sup>72</sup> CuCrO<sub>2</sub>,<sup>73</sup> CuGaO<sub>2</sub>,<sup>74</sup> and CsPbI<sub>3</sub> (ref. 75) have been used as efficient top HTL for PSCs due to their excellent properties. It can be noticed that when PbS NCs are used as top HTL in solar cells, the light harvesting layers are mostly based on the PbS/Se family. There are not many perovskite used as light harvest materials when PbS/Se is used as top HTL. Only MAPbI<sub>3</sub> was applied in 2015, and 7.88% PCE was gained.<sup>29</sup> We suppose this is because the PbS NCs with long carbon chains or 1,2-ethanedithiol are not good at charge transport. If high-temperature annealing is adopted to enhance the conductivity of PbS, the perovskite underneath will be destroyed. This encourages us to regulate the synthesis or modification of NCs with less or even no charge transfer inhibition capture and improve their electronic properties.

Similar to top HTL, NCs can also be applied as bottom HTL for high-performance solar cells. NCs of PbS,<sup>76</sup> Cu<sub>2</sub>ZnSnS<sub>4</sub>,<sup>77,78</sup> NiO<sub>x</sub> and its doped derivatives,<sup>79–91</sup> CuO,<sup>92</sup> and ternary oxides of CuCrO<sub>2</sub>,<sup>93,94</sup> CuGaO<sub>2</sub>,<sup>95</sup> NiCo<sub>2</sub>O<sub>4</sub>,<sup>96,97</sup> ZnCoO<sub>4</sub>,<sup>98</sup> and doped ternary oxide In:CuCrO<sub>2</sub> (ref. 99) have offered excellent hole transport ability in PSCs and PTB7-Th-based organic solar cells (OSCs).

Ever since demonstrated as efficient HTL by Luther *et al.* in 2008,<sup>248</sup> PbS NCs with a 1,2-ethanedithiol (EDT) ligand (named as PbS-EDT or EDT-PbS) have been massively applied for hole transport in solar cells. From the established NC HTLs listed in Table 1, we can find some regular patterns: (i) as top HTL, EDT-linked sulphides were mainly used in NC-LHSCs but were not popular in PSCs. This is because EDT will strongly attack the perovskite materials in the n-i-p device and decrease the device performance.<sup>61</sup> (ii) As bottom HTL, oxides are widely used and sulphides are rare. We speculate that it is (iii) NiO<sub>x</sub> with high hole transport quality mostly used to transport holes in PSCs.

The previous light harvesting NC layers are mainly based on the Pb-based chalcogenide family or their mixture. NC-LHSCs using NCs as HTL have gained high PCE above 13%,<sup>45,50</sup> but this is significantly lower than that of the theoretical value.<sup>11</sup> Some strategies were also adopted to modify the light-harvesting NCs, which is not the keynote in this review. The current relatively low PCE of NC-LHSCs may be on account of non-radiative recombination resulting from the high density of surface traps due to some intrinsic properties of NCs, such as high surface-to-volume ratios. Using NC top HTL, the PCE value can be improved. Some oxides, for instance, NiO, Ti-doped MoO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Cu<sub>2</sub>O, CuCrO<sub>2</sub>, and CuGaO<sub>2</sub>, have acted as excellent top HTL in high-performance PSCs. As shown in Fig. 2a, SnS NCs prepared by the one-pot hot-injection method were utilized as top HTL in efficient and stable



Table 1 Recent advances in selected NC HTLs for solar cells (EDT = 1,2-ethanedithiol, relative humidity = RH)

	NC	Active layer	PCE (%)	Long-term stability	Ref.	
Top HTL	PbS-EDT	CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub>	7.88	8% decay after 2 days	29	
			PbS	11.6	Null	30
				10.4	100%, after 103 days in the dark under ambient conditions	32
				9.44	~100%, after 4 months in ambient air	33
				13.2	Null	37
				10.4	①96%, after baking on a hotplate in air for 120 min; ②97%, after 60 min oxygen plasma treatment	38
				13.3	Null	39
				10.5	Null	40
				13.0	Null	41
			PbS-PbI <sub>2</sub>	11.2 ± 0.22	Nearly no drop of PCE after 180 h under continuous heating at 85 °C in ambient air >90, after 600 h under ambient condition	44
				11.29		45
			PbS:F	12.7	Null	46
			PbX <sub>2</sub> -PbS	8.16	Null	47
				10.35	Null	48
				10.6	Null	49
		PbS-PbX <sub>2</sub> -KI <sub>3</sub>	12.1	94%, after 20 h continuous operation in air	50	
		PbSe-PbS	1.24 (infrared PCE)	~95%, after 25 days in air	51	
		PbSe-PbI <sub>2</sub>	10.4	90%, after 30 days in ambient condition	51	
		CsMAFA-PbS	11.3	96%, after 1200 h shelf storage	53	
		MAPbI <sub>3</sub> -PbS	9.5	95%, after 2 months in ambient environment	54	
		Sb <sub>2</sub> Se <sub>3</sub>	6.5 (certified)	Null	55	
		KPbS	12.6	83%, after 300 h under continuous operation at MPP in ambient air	56	
		CuInS <sub>2</sub> /ZnS core/shell	MAPbI <sub>3</sub>	8.38	Null	57
		CdZnSe@ZnSe	CdZnSe@ZnSe	8.65	Null	58
		Cu <sub>2</sub> ZnSnSe <sub>4</sub>	MAPbI <sub>3</sub>	9.72	Null	59
		Cu <sub>2</sub> ZnSnS <sub>4</sub>		10.72		
		SnS	(CsPbI <sub>3</sub> ) <sub>0.05</sub> (FAPbI <sub>3</sub> ) <sub>0.79</sub> (MAPbI <sub>3</sub> ) <sub>0.16</sub> (PbI <sub>3</sub> ) <sub>0.03</sub>	13.7	①99%, after 1000 h storage in air; ②75%, after 500 h under continuous 1 sun illumination in a N <sub>2</sub> atmosphere at 25 °C	60
	CuInSe <sub>2</sub>	MAFAPbClBrI	12.8	78%, after 96 h in air	61	
	Ag-In-Ga-S	CsPbBr <sub>3</sub>	8.46	96.1%, after 240 h in air	62	
	Cu <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>	CsPbI <sub>3</sub>	10.02	94%, after storage in ambient air for 360 h	63	
	Cu <sub>2</sub> SnS <sub>3</sub>	Cs <sub>0.05</sub> (MA <sub>0.17</sub> -FA <sub>0.83</sub> ) <sub>0.95</sub> Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub>	13.01	90%, after 1200 h in an ambient atmosphere	64	
	CuGaS	(FAPbI <sub>3</sub> ) <sub>1-x</sub> (MAPbBr <sub>3</sub> ) <sub>x</sub>	17.56	81%, aging for 30 days	65	
	CuInS <sub>2</sub>	(FAPbI <sub>3</sub> ) <sub>1-x</sub> (MAPbBr <sub>3</sub> ) <sub>x</sub>	18.81	91%, aging for 30 days	66	
	NiO	MAPbI <sub>3</sub>	6.2	Null	67	
		MAPbI <sub>3</sub> NCs	10.89	Null	68	
	Ti-doped MoO <sub>2</sub>	MAPbI <sub>3</sub>	15.8	~95%, after 15 days with 50–70% RH	70	
	Co <sub>3</sub> O <sub>4</sub>	MAPbI <sub>3</sub>	13.27	Up to 2500 hours under ambient conditions	71	
	Cu <sub>2</sub> O	Cs <sub>0.05</sub> FA <sub>0.81</sub> MA <sub>0.14</sub> PbI <sub>2.55</sub> Br <sub>0.45</sub>	18.9	80%, after 30 days in air with ~30% RH	72	
	CuCrO <sub>2</sub>	Cs <sub>0.05</sub> (MA <sub>0.15</sub> FA <sub>0.85</sub> ) <sub>0.95</sub> Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub>	16.68	88%, after 500 h at the MPP under one sun and a N <sub>2</sub> atmosphere	73	
	CuGaO <sub>2</sub>	MAPbI <sub>3</sub>	18.51	>85%, after 30 days at 25 °C with 30–55% humidity without encapsulation	74	
	CsPbI <sub>3</sub>	MAPbI <sub>3</sub>	17.0	Null	75	



Table 1 (Contd.)

	NC	Active layer	PCE (%)	Long-term stability	Ref.
Bottom	PbS	MAPbI <sub>3</sub>	7.5	Null	76
HTL	Cu <sub>2</sub> ZnSnS <sub>4</sub>	MAPbI <sub>3</sub>	15.4	Null	77
			6.02	87%, after 43 days in N <sub>2</sub> atmosphere	78
	Ni–NiO core–shell	P3HT	0.86	Null	79
	NiO <sub>x</sub>	Cs <sub>0.08</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>0.92</sub>	12.8	Null	81
		Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub>			
		MAPbI <sub>3</sub>	16.1	90%, after 60 days in air at RT	84
		Cs <sub>0.05</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>0.95</sub>	18.6	>80%, after 1000 h	85
		Pb(I <sub>0.9</sub> Br <sub>0.1</sub> ) <sub>3</sub>			
		MAPbI <sub>3</sub>	17.60	93%, after 30 days	86
			1.02 cm <sup>2</sup> :	90%, after 500 h in the thermal aging test	87
			18.49 (rigid)	(85 °C, 85% RH)	
			and 15.89		
			(flexible)		
	Cu:NiO <sub>x</sub>		15.01	86%, after 1 month in an ambient environment at 25 °C with about 40% humidity	88
			(flexible, >1 cm <sup>2</sup> )		
			18.3	Null	89
	(Li,Cu):NiO <sub>x</sub>	MAPbI <sub>3-x</sub> Cl <sub>x</sub>	20.80	95%, after 60 days of storage	90
	NiO <sub>x</sub>	CsPbI <sub>x</sub> Br <sub>3-x</sub>	16.1	85%, after 350 h light soaking	91
	CuO	MAPbI <sub>3</sub>	15.3	Null	92
	CuCrO <sub>2</sub>		19.0	~90, after 30 days in an Ar-filled dry glove box and continuously irradiated by a UV optical fiber with 5 mW cm <sup>-2</sup>	94
	CuGaO <sub>2</sub>		15.6	Null	95
	NiCo <sub>2</sub> O <sub>4</sub>	MAPbI <sub>3-x</sub> Cl <sub>x</sub>	18.23	~90%, after 500 h illumination at AM 1.5G	96
	ZnCo <sub>2</sub> O <sub>4</sub>	PTB7-Th:PC <sub>71</sub> BM	9.37	>60%, after 60 h in ambient environment with 50% RH without capsulation	98
		MAPbI <sub>3-x</sub> Cl <sub>x</sub>	18.14	>60%, after 110 h in ambient environment with capsulation and under continuous 1 sun illumination soaking	
	In:CuCrO <sub>2</sub>	Cs <sub>0.05</sub> (MA <sub>0.15</sub> FA <sub>0.85</sub> ) <sub>0.95</sub>	20.54	~90%, after 800 h of continuous radiation in glovebox	99
		Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub>			

(CsPbI<sub>3</sub>)<sub>0.05</sub>(FAPbI<sub>3</sub>)<sub>0.79</sub>(MAPbI<sub>3</sub>)<sub>0.16</sub> PSCs. The high PCE mainly resulted from good surface coverage and an excellent hole extraction ability demonstrated by Nyquist plots. Additionally, SnS-based PSC presented better air stability than the 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD)-based device. Surface-modified Cu<sub>2</sub>O NCs boosted the efficiency of PSC to 18.9% with distinctly better stability than the reference device based on spiro-OMeTAD.<sup>61</sup> One important reason is the difference in hydrophobicities illustrated by water contact angles in Fig. 2b. Ternary oxide CuGaO<sub>2</sub>NCs with promising photoelectronic properties boosted the n-i-p PSCs with higher PCE and stability than spiro-OMeTAD (Fig. 2c).<sup>75</sup>

In n-i-p type solar cells, NiO<sub>x</sub> and its doped family oxide NCs are the most popular NC HTLs because of their facile synthesis and outstanding photoelectronic properties.<sup>86,101</sup> Meanwhile, sulphides of PbS and Cu<sub>2</sub>ZnSnS<sub>4</sub> together with multi basic oxides of CuCrO<sub>2</sub>, CuGaO<sub>2</sub>, NiCo<sub>2</sub>O<sub>4</sub>, ZnCo<sub>2</sub>O<sub>4</sub>, and In:CuCrO<sub>2</sub> are valuable substitutes for NiO<sub>x</sub> family. Ligand-free NiO<sub>x</sub> NCs in ethanol (E-NiO<sub>x</sub>) are spin-coated onto a substrate to form a smooth and compact NiO<sub>x</sub> film that has good hole extraction capability. As seen in Fig. 3a, this E-NiO<sub>x</sub> bottom HTL can be

used both in rigid and flexible PSC, producing high PCE and stability. Similar to top HTL, ternary oxide NCs like CuCrO<sub>2</sub> were also utilized as bottom HTL for high-performance solar cells. The low-temperature solution-processed CuCrO<sub>2</sub> NCs provide suitable electronic structure, charge carrier transport properties, and greater UV light-harvesting, demonstrating its potential as an efficient HTL for highly efficient and photostable n-i-p PSCs (Fig. 3b).

**2.1.2 Advantages of NC HTL.** One important inherent advantage of semiconductor NCs is their bandgap variation along with modification. The conduction band, valence band, and Fermi level of PbS NCs can be modified by changing surface ligands (Fig. 4), thus enhancing the performance of solar cells.<sup>252</sup> Fig. 4 shows that the energy level of PbS NCs is easily changed in a large range by different ligands, facilitating energy matching with the light-harvesting layer and other functional layers. Compared with mostly used organic HTLs of spiro-OMeTAD, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), inorganic NCs show higher stability with good hole transport ability, suggesting great potential for boosting solar cell performance. Equally



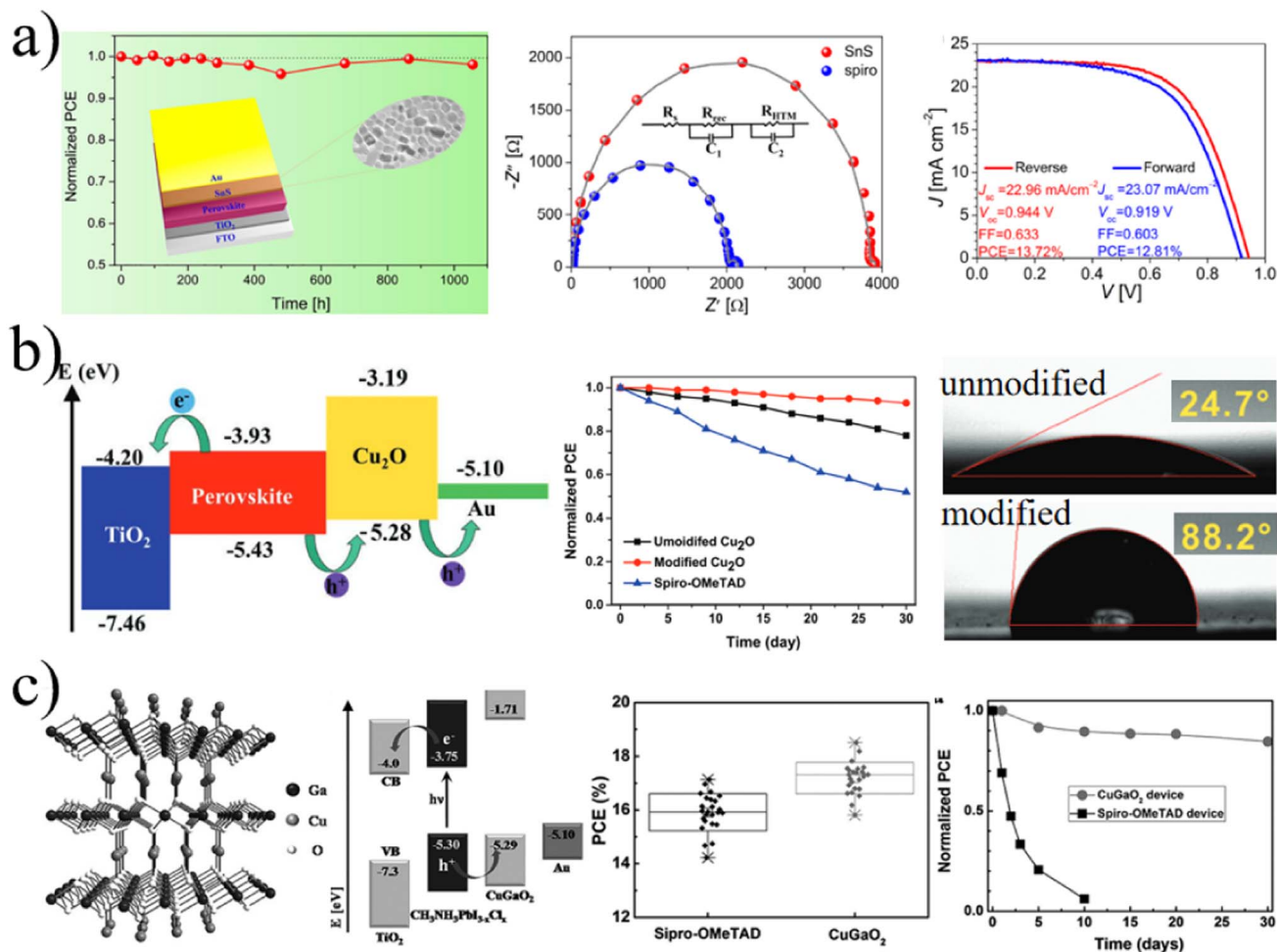


Fig. 2 (a) Evolution of PCE over time of the unencapsulated SnS-based PSCs in the ambient air of ~30–50% humidity, Nyquist plots at 0.9 V forward bias measured in the dark, forward, and reverse  $J-V$  curves of champion PSCs based on SnS. (b) Schematic view of PSC configuration, device performance durability of PSCs based on different HTLs in ambient air for 30 days, and water contact angles of unmodified and modified  $\text{Cu}_2\text{O}$ . (c) Schematic illustration of the crystal structure of  $\text{CuGaO}_2$ , device architecture of a regular PSC based on  $\text{CuGaO}_2$ , standard deviations of PCEs to evaluate reproducibility by statistics of 50 devices based on  $\text{CuGaO}_2$  and Spiro-OMeTAD.<sup>61</sup> Copyright 2019, American Chemical Society. (b) Adapted with permission.<sup>75</sup> Copyright 2019, Wiley-VCH. (c) Adapted with permission.<sup>75</sup> Copyright 2017, Wiley-VCH.

important, facile synthesis and low cost would be helpful for the commercialization of new-generation solar cells.

**2.1.3 Potential NC HTL.** To further develop more strategies for fabricating high-performance solar cells and boost the device PCE and stability, we should find more potential NCs for efficient hole transport in solar cells. According to the previous reports and our understanding, excellent NC HTLs should satisfy the following requirements: (i) matched energy level alignments with other functional layers; (ii) high hole mobility and conductivity; (iii) enhancing the quality of adjacent layers; (iv) intrinsic resistance to heat, light and water; (v) convenient fabrication with low cost; and (vi) high transmittance for bottom HTL and reflectivity for top HTL. NCs have many good properties such as easily-controlled energy level, excellent spreading and filling ability due to their small sizes, stable intrinsic structure, skilled synthesis process, and variant surface ligand. Considering the above rules and the advantages

of NCs, besides the existing NC HTLs, some other p-type sulphide and oxide NCs have huge potential for efficient and stable solar cells. Additionally, semiconductor NCs with enhanced hole-transporting ability by p-type doping are also good alternatives.

## 2.2 Nanocrystals as ETL

**2.2.1 Recent advances of NC ETL.** As important as HTL, ETL is also of great significance for high-performance solar cells to transport electrons and block holes, and it acts as well as a trap passivating layer and water/oxygen preventing layer. The typical structure of solar cells based on NC ETL is shown in Fig. 5.

ZnO is good at electron transport in photoelectrical devices due to excellent properties such as bandgap (3.3 eV), low cost, high electron mobility ( $\sim 10^{-5}$ – $10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), and matching energy levels.<sup>100,101</sup> ZnO NCs with different sizes have been used



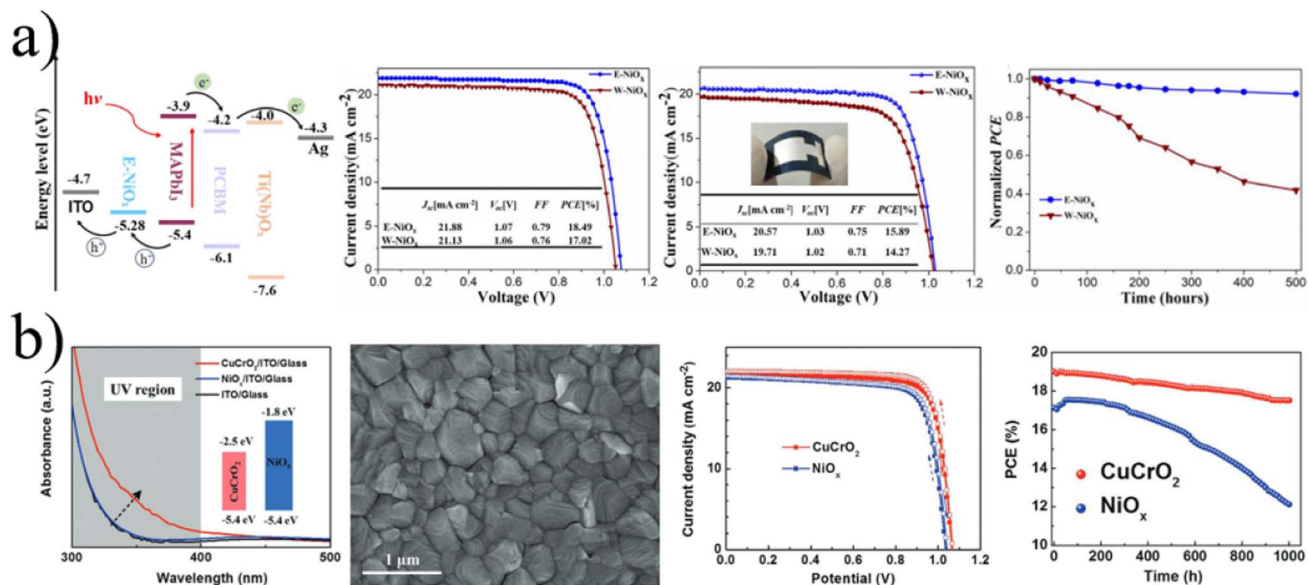


Fig. 3 (a) Energy level diagram of the materials used in the device,  $J$ - $V$  curves of rigid and flexible PSCs, normalized PCE. (b) UV-vis spectra of the CuCrO<sub>2</sub> and NiO<sub>x</sub> layer with optimum thickness with energy level in the inset. Adapted with permission.<sup>87,94</sup> Copyright 2018, Wiley-VCH.

as efficient top ETL in NC-LHSCs, OSCs, and PSCs.<sup>43,84,85,91,101-108</sup> TiO<sub>2</sub> and SnO<sub>2</sub>NCs are as popular as ZnO for electron transport due to their outstanding photoelectronic properties of high mobility and conductivity.<sup>250</sup> Certainly, these oxide NCs can be modified by doping, ligand changing, and other strategies. Tetrabutylammonium hydroxide (TBAOH)-capped metal oxide NCs for SnO<sub>2</sub> also extend to TiO<sub>2</sub>, ITO and CeO<sub>2</sub>NCs as top ETL for PSCs.<sup>108</sup> TiO<sub>2</sub>NCs have always been as the top ETL for PSCs.<sup>109-111</sup> CeO<sub>x</sub>,<sup>112</sup> In<sub>2</sub>O<sub>3</sub> and its Sn doped derivative formed bilayer ETL,<sup>113</sup> and CdSe<sup>114</sup> were also used for high-performance n-i-p PSCs. As efficient bottom ETL, modified TiO<sub>2</sub> by Sn, Al, Co, Cu, and N doping and N, F and S co-doped graphene NCs were widely used in dye-sensitized solar cells (DSSCs) based on N719 and N3 (*cis*-Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(NCS)<sub>2</sub>, H<sub>2</sub>dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl).<sup>115-120</sup> Additionally, TiO<sub>2</sub>, CdS NCs-modified TiO<sub>2</sub>, and Nb-doped TiO<sub>2</sub>NCs were applied for electron transport in PSCs with high PCE and stability.<sup>121-123</sup> Meanwhile,

TiO<sub>2</sub>NCs have been widely applied in n-i-p solar cells using chalcogenide NC as light harvesters, such as CdSe, CdS, and PbS.<sup>124-130</sup> Similarly, ZnO NCs were used as ETL for n-i-p PbS-

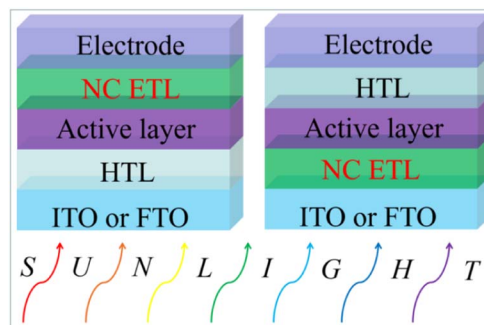


Fig. 5 Structure of solar cells based on top (left) and bottom (right) NC ETLs.

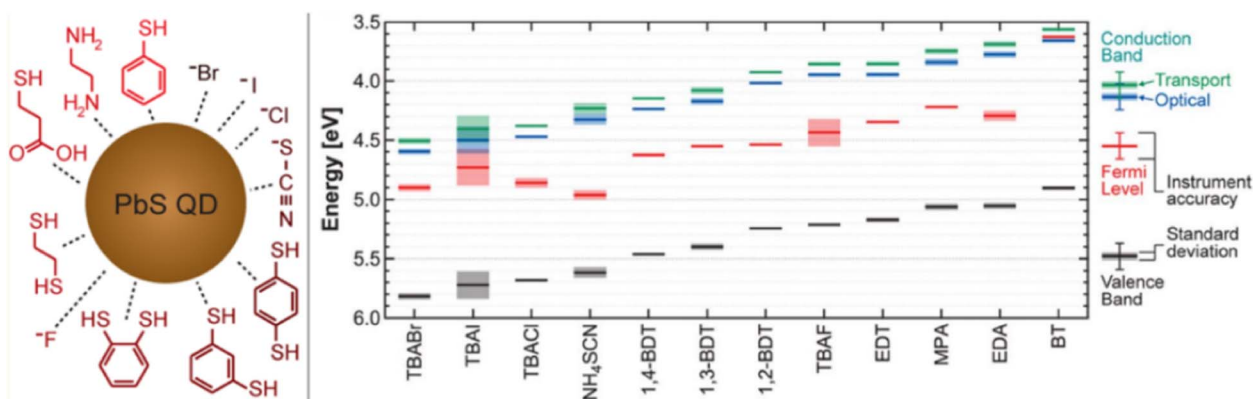


Fig. 4 Energy band position of PbS NC films for different surface ligands. Adapted with permission.<sup>249</sup> Copyright 2014, American Chemical Society.



Table 2 Recent advances in NC ETLs (bathocuproine = BCP)

	NC	Active layer	PCE (%)	Long-term stability	Ref.	
Top ETL	ZnO	PbS–PbX <sub>2</sub>	10.35	Null	43	
		PCDTBT:PC <sub>61</sub> BM	2.66	Null	100	
		CsPbI <sub>3</sub> NCS	13.1	80%, after 40 h under 25 °C with 30–40% RH	103	
		MAPbI <sub>3</sub>	17.2	66%, after 120 days stored in air	105	
		MAPbI <sub>3</sub>	16.1	90% after 60 days in air at RT	84	
		Cs <sub>0.05</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>0.95</sub> Pb(I <sub>0.9</sub> Br <sub>0.1</sub> ) <sub>3</sub>	18.6	>80% after 1000 h	85	
		CsPbI <sub>x</sub> Br <sub>3-x</sub>	16.1	85%, after 350 h light soaking	91	
		MAPbI <sub>3</sub>	15.5	Null	106	
		In:ZnO	MAPbI <sub>3</sub>	16.2	85% after 460 h of light soaking	107
		TBAOH-SnO <sub>2</sub>	MAPbI <sub>3</sub>	18.77	90% after aging at 45 °C for 240 h, followed by 65 °C for 240 h and 85 °C for 240 h	108
	TiO <sub>2</sub>	Cs <sub>0.05</sub> (MA <sub>0.15</sub> FA <sub>0.85</sub> ) <sub>0.95</sub> Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub>	20.5	~90% after 350 h MPP tracking test	109	
	Carbide-TiO <sub>2</sub>	CsPbI <sub>2</sub> Br	14.8	①>94%, after 1000 h at 85 °C in dark under N <sub>2</sub> ; ②>90%, after 1000 h at 60 °C under continuous illumination	110	
	CeO <sub>x</sub>	MAPbI <sub>3</sub>	16.7	100%, after 200 h in air with 30% RH	112	
	Sn:In <sub>2</sub> O <sub>3</sub> /In <sub>2</sub> O <sub>3</sub> (bilayer)	Cs <sub>0.05</sub> (MA <sub>0.15</sub> FA <sub>0.85</sub> ) <sub>0.95</sub> Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub>	20.65	①91.9% after 69 days under 85 °C; ②91.8% after 2000 h, 12 h continuous 1 sun illumination and then 12 h interval in the dark	113	
	Bottom ETL	CdSe	MAPbI <sub>3</sub>	15.1	Null	114
		Sn:TiO <sub>2</sub>	N719	6.24	Null	115
		Al:TiO <sub>2</sub>		4.27	Null	116
		Co:TiO <sub>2</sub>		4.85	Null	117
		Ti <sub>0.94</sub> Cu <sub>0.06</sub> O <sub>2</sub>	N3/electrolyte	6.51	Null	118
TiO <sub>2</sub> modified by N, F and S, co-doped graphene NCS		N719	11.7	~85.5, after one month	120	
TiO <sub>2</sub>		Cs–FA–MA mixed cation perovskite	19.03	84%, after 30 days	121	
CdS NCS-modified TiO <sub>2</sub>		MAPbI <sub>3</sub>	8.16	Null	122	
Nb-doped TiO <sub>2</sub>		Cs <sub>0.05</sub> (MA <sub>0.15</sub> FA <sub>0.85</sub> ) <sub>0.95</sub> Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub>	18.97	Null	123	
TiO <sub>2</sub>		CdS	4.59	Null	125	
Cu <sub>2</sub> O doped TiO <sub>2</sub>		CdSe/CdS/ZnS/electrolyte	3.01	Null	126	
TiO <sub>2</sub>		Mn–CdSe	3.55	Null	128	
TiO <sub>2</sub>		CdSe/ZnS/SiO <sub>2</sub> /Cu <sub>2</sub> S	4.00	Null	129	
Cl@ZnO		PbS	11.6	Null	30	
ZnO		PbX <sub>2</sub> –PbS	9.5	95%, after 2 months in ambient environment	33	
MgZnO		PbS	10.4	100%, after 103 days in the dark under ambient conditions	32	
ZnO		Lead halide-PbS	12.7	Null	46	
ZnO		PbS	13.1 ± 0.1	Null	37	
ZnO		PbS NC	12.44	Null	140	
Cs-ZnO		PbS	10.43	97%, after 3 months under 20 °C and 30% RH without any encapsulation	144	
ZnO	CsPbBr <sub>3</sub> –CsPb <sub>2</sub> Br <sub>5</sub>	6.81	No detectable decay after 100 days under 25 °C and 45% RH	146		
ZnO	PTB7-Th:PC <sub>71</sub> BM	12.02	Null	147		
Na–ZnO	p-DTS(FBTTh <sub>2</sub> ) <sub>2</sub> :PC <sub>70</sub> BM	9.2	90%, after 28 h	149		
SnO <sub>2</sub>	N719	3.2	Null	151		
Ni:SnO <sub>2</sub>		3.6				
Zn:SnO <sub>2</sub>		4.2				
SnO <sub>2</sub>	Eosin-Y	3.89	Null	155		
Sn <sub>0.92</sub> O <sub>2</sub> :Sb <sub>0.08</sub>		4.15	Null	156		



Table 2 (Contd.)

NC	Active layer	PCE (%)	Long-term stability	Ref.
SnO <sub>2</sub>	PBDR-T & ITIC-4	12.023	①>90%, up to 75 h after exposure to an ambient atmosphere with continuous illumination; ②>95%, after storage in N <sub>2</sub> for 200 h with continuous illumination	157
	PM6:Y6	14.9	81%, after 15 days stored in the air at RM without encapsulation	158
	PTB7-Th:PC <sub>71</sub> BM PM7:ITC6-4F PM6:Y6	10.30 13.93 15.38	Null Null 94.3%, after 100 h light aging	159
Cl@SnO <sub>2</sub>	CsPbI <sub>3</sub> NCs	14.5	80%, without encapsulation under 1-sun light soaking and 50% relative humidity for 8 h	27
	Ga:SnO <sub>2</sub> SnO <sub>2</sub>	Cs <sub>0.05</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>0.95</sub> Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub> CsPbI <sub>3</sub> /FAPbI <sub>3</sub>	18.18 16.07	Null 96%, after 1000 h in ambient storage
SnO <sub>2</sub> /TiO <sub>2</sub> (bilayer)	Cs <sub>x</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>(100-x)</sub> Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub>	17.92	89%, after 2500 h stored under 20 ± 5% RH	163
	MAPbI <sub>3</sub>	13.90 (flexible device)	Null	164
	(CsPbI <sub>3</sub> ) <sub>0.04</sub> (FAPbI <sub>3</sub> ) <sub>0.82</sub> (MAPbBr <sub>3</sub> ) <sub>0.14</sub>	20.34 ± 0.5	90%, after 720 h storage	165
	Cs <sub>0.05</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> ) <sub>0.95</sub> Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub> FAPbI <sub>3</sub>	20.79 25.39 (0.0803 cm <sup>2</sup> )	Null ①80% after 1000 h in ambient air at 25% RH and 25 °C without sealing; ②70.5% after 700 h light soaking; ③95% (encapsulated cell) after 100 h MPP tracking and 2 h dark recovery under ambient conditions	167 168
		23.3 (1 cm <sup>2</sup> )	Null	
		21.7 (20 cm <sup>2</sup> )	Null	
		20.6 (64 cm <sup>2</sup> )	Null	
		15.86	①~95%, after 1 month storage in N <sub>2</sub> glovebox without encapsulation; ②>80%, after 1 month stored under RT and 20–30% RH without encapsulation	169
		15.22	>80%, after 500 h in N <sub>2</sub> without encapsulation	170
		6.01	Null	171
SnO <sub>2</sub> /InP–ZnS (bilayer)	Ni:Co <sub>3</sub> S <sub>4</sub>	6.82		
	Ni:Co <sub>4</sub> S <sub>3</sub>	7.43		
	NiCo <sub>2</sub> S <sub>4</sub>	4.9 ± 0.2		172
	Zn <sub>2</sub> SnO <sub>4</sub>	19.0	91%, after 1000 h stored in N <sub>2</sub>	173
	Y:SrSnO <sub>3</sub>	FA <sub>0.85</sub> MA <sub>0.15</sub> Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub>		

based NC-LHSCs,<sup>30,32,35,39,40,44,45,58,131–145</sup> PSCs,<sup>146</sup> and OSCs.<sup>147–149</sup> SnO NCs as ETL for DSSCs,<sup>150–156</sup> for OSCs,<sup>157–159</sup> and for PSCs,<sup>27,160–168</sup> have been demonstrated. Additionally, a bilayer of SnO<sub>2</sub>/TiO<sub>2</sub> (ref. 169) and SnO<sub>2</sub>/InP–ZnS<sup>170</sup> were used for PSCs and DSSCs. Ni-doped Co<sub>3</sub>S<sub>4</sub> and Co<sub>4</sub>S<sub>3</sub> and ternary sulphide NCs of NiCo<sub>2</sub>S<sub>4</sub> and Zn<sub>2</sub>SnO<sub>4</sub> have been used for DSSCs,<sup>171,172</sup> while

doped SrSnO<sub>3</sub> NCs for PSCs.<sup>173</sup> NCs have been used as IFL for NC-LHSCs,<sup>49,141,174–179</sup> OSCs,<sup>180–185</sup> DSSCs,<sup>186–195</sup> PSCs,<sup>196–212</sup> and Si solar cells.<sup>213–220</sup> FAPbBr<sub>3</sub> perovskite NCs have been used as a multifunctional luminescent-downshifting passivation layer for GaAs solar cells.<sup>221</sup>





Explored dopants (orange)  
Potential dopants (turquoise)

\* Lanthanide series  
 \*\* Actinide series

Fig. 6 Summary of the explored and potential elements as dopants in  $\text{TiO}_2$ -based electron transporters for PSCs in the periodic table, as in 2017.<sup>253</sup> Copyright 2017, Wiley-VCH.

From the reported literature listed in Table 2, selenide NCs of CdSe, and doped sulfide NCs of  $\text{Ni}:\text{Co}_2\text{S}_4$ ,  $\text{Ni}:\text{Co}_4\text{S}_3$ , and  $\text{Ni}:\text{Co}_2\text{S}_4$  have shown their potential, suggesting more substitutes for traditional NC ETL. The advantages of NC ETL and some potential NCs suitable as ETLs are discussed in the following sections.

**2.2.2 Advantages of NC ETL.** Compared with common organic ETLs such as fullerenes ( $\text{C}_{60}/\text{C}_{70}$ ) and phenyl-C61-butyric acid methyl ester (PCBM), semiconductor NCs can easily overcome the shortcomings of poor stability, high cost, and unsuitable energy levels. In detail, PCBM film degrades at  $85^\circ\text{C}$ , indicating its thermal instability.<sup>110</sup> The cost of synthesis and purification for organic electron transport materials is higher than most semiconductor NCs.<sup>252</sup> Moreover, the semiconductor NCs can offer adjustable energy levels by easily

controlling the size. The above advantages strongly demonstrate that semiconductor NCs are a very good choice as efficient ETL in high-performance solar cells.

**2.2.3 Potential NC ETL.** Thanks to their unique application advantages in solar cells, NC ETLs have been widely used, boosting the devices to higher PCE and stability. More oxide and chalcogenide NCs as well as their doped congeners are anticipated alternatives. As we know,  $\text{TiO}_2$ NCs always act as splendid ETL in solar cells. The properties of  $\text{TiO}_2$ NCs can also be improved by doping, enhancing the device performance. As shown in Fig. 6, many elements were successfully doped in  $\text{TiO}_2$  as ETL for PSCs. Meanwhile, more elements are potential dopants for high-quality  $\text{TiO}_2$  and this suggests that there is much room for doped- $\text{TiO}_2$ NC ETL. Additionally, we reasonably



Fig. 7 Typical position sketch of interfacial layers in solar cells.



Table 3 Recent advances in selected NCIFLs

	IFL and its adjacent layers	PCE (%)	Functions	Ref.
PbCdS	TiO <sub>2</sub> /PbCdS/CdS	3.35	Enhance light absorption; suppress interfacial recombination	174
CdS + amine/ZnS	TiO <sub>2</sub> :Al <sup>3+</sup> /CdS + amine/ZnS/ electrolyte/CuS	2.4	Decrease electron–hole recombination	175
Cu <sub>x</sub> S	CIZS + mp-TiO <sub>2</sub> /electrolyte/Cu <sub>x</sub> S/ electrode	1.13	Null	176
CdSe	ZnO/CdSe/PbS	7.9	Suppress interface recombination; contribute additional photogenerated carriers	141
NiO	PbS-EDT/NiO/Au	10.4	Improve hole extraction efficiency; suppress the penetration of moisture and oxygen; good band alignment	49
PbS-EDT	PbS-TBAI/PbS-EDT/P3HT	8.7	Adjust the valence band; improve charge transfer	177
CsPbBr <sub>3</sub>	PbSe-MPA/CsPbBr <sub>3</sub> /Au	7.22	Suppress carrier recombination	178
ZnO	Mg-doped ZnO/ZnO/PbS	7.06	Decrease the interface recombination	179
CdSe	ZnO/CdSe/P3HT:PCBM	2.25	Increase conductivity; electron transport and hole block	180
CuInS <sub>2</sub> -ZnS	TiO <sub>2</sub> /CuInS <sub>2</sub> -ZnS/PCDTBT:PC <sub>71</sub> BM	7.01	Increase the electron extraction; reduce impedance	181
CdSe	P3HT:PCBM/CdSe/Al	3.08	Down-conversion, reduce charge recombination	182
ZnCdS	TiO <sub>2</sub> /ZnCdS/PTB7:PC <sub>71</sub> BM	7.75	Suppress the recombination; reduce the series resistance	183
SnO <sub>2</sub>	ITO/SnO <sub>2</sub> /ZnO	7.16	Enhance optical transmission; reduce energy barrier; suppress carrier recombination	184
Ag <sub>2</sub> Se	TiO <sub>2</sub> /Ag <sub>2</sub> Se/N719	5.89	Null	186
CdS	TiO <sub>2</sub> /CdS/N719	7.54	Suppress the charge recombination; increase the optical absorption	187
CeO <sub>2</sub> :Eu <sup>3+</sup>	N719/CeO <sub>2</sub> :Eu <sup>3+</sup> /electrolyte	8.36	Down-convert UV light to visible light, light scattering	190
NaGdF <sub>4</sub> :Eu <sup>3+</sup>	FTO/TiO <sub>2</sub> /N719/electrolyte/Pt/FTO/ NaGdF <sub>4</sub> :Eu <sup>3+</sup>	9.34	Act as luminescent down-conversion centers and light scatterers in the ultraviolet and visible domains	191
CaCe <sub>2</sub> (MoO <sub>4</sub> ) <sub>4</sub> :Er <sup>3+</sup> /Yb <sup>3+</sup>	Electrolyte/CaCe <sub>2</sub> (MoO <sub>4</sub> ) <sub>4</sub> :Er <sup>3+</sup> /Yb <sup>3+</sup> / Pt	7.78	Convert the NIR and UV radiation to visible emissions	192
NaYF <sub>4</sub> :20%Yb, 2% Er@NaYF <sub>4</sub> :7%Eu	N719/NaYF <sub>4</sub> :20%Yb,2% Er@NaYF <sub>4</sub> :7%Eu/Pt	7.664	Convert NIR and UV lights to visible lights	193
SrF <sub>2</sub> :Pr <sup>3+</sup> -Yb <sup>3+</sup>	FTO/SrF <sub>2</sub> :Pr <sup>3+</sup> -Yb <sup>3+</sup> /TiO <sub>2</sub> -N719	9.07	Absorb blue light and emit green and red light	194
BaWO <sub>4</sub> :Pr <sup>3+</sup>	TiO <sub>2</sub> /BaWO <sub>4</sub> :Pr <sup>3+</sup> /N719	8.08	Absorb UV light and emit blue, green, and red light	195
MAPbBr <sub>0.9</sub> I <sub>2.1</sub>	TiO <sub>2</sub> /MAPbI <sub>3</sub> /MAPbBr <sub>0.9</sub> I <sub>2.1</sub>	13.32	Facilitate hole transfer from MAPbI <sub>3</sub> to HTL	196
CuInS	MAPbI <sub>3</sub> /CuInS/spiro-MeOTAD	13.8	Enhance charge transfer; suppress charge recombination pathways	198
MgO	FTO/MgO/SnO <sub>2</sub>	18.23	Smoother surface; less FTO surface defects; suppressed electron–hole recombination	199
CdS	TiO <sub>2</sub> /CdS/MAPbI <sub>3</sub>	10.52	Longer electron lifetime; lower charge carrier recombination rate	200
SnO <sub>2</sub>	PC <sub>61</sub> BM/SnO <sub>2</sub> /Al	19.7	Block holes; enhance the conductivity; reduce the recombination	201
Cl-SnO <sub>2</sub>	FTO/Cl-SnO <sub>2</sub> /CsMAFAPbI <sub>3</sub> Br <sub>3-x</sub>	17.3	Fill the pinholes; passivate the trapping defects	202
FAPbX <sub>3</sub>	MAPbI <sub>3</sub> /FAPbX <sub>3</sub> /C60	7.59	Enhance absorption	203
PbS	MAPbI <sub>3</sub> /PbS/spiro-OMeTAD	19.24	Enhance hole extraction; retard interfacial recombination; improve perovskite film morphology	204
CuO <sub>x</sub>	NiO <sub>x</sub> /CuO <sub>x</sub> /MAPbI <sub>3</sub>	19.91	Lead higher transfer efficiency and lower carrier recombination	205
MAPbBr <sub>0.9</sub> I <sub>2.1</sub>	SnO <sub>2</sub> /MAPbBr <sub>3</sub> /MAPbBr <sub>0.9</sub> I <sub>2.1</sub>	20.21	Optimize the energy level; improve hole extraction	206
Co-CuGaO <sub>2</sub>	Cs <sub>0.05</sub> (MA <sub>0.15</sub> FA <sub>0.85</sub> ) <sub>0.95</sub> Pb(I <sub>0.85</sub> Br <sub>0.15</sub> ) <sub>3</sub> / Co-CuGaO <sub>2</sub> /spiro-OMeTAD	20.39	Reduce the energy gap; prevent direct contact between PVK and oxygen and moisture	207
MoS <sub>2</sub> :RGO	MAPbI <sub>3</sub> /MoS <sub>2</sub> :RGO/spiro-OMeTAD	20.12	Extract holes and block electrons	208
CsCu <sub>5</sub> S <sub>3</sub>	MAFAPbI <sub>3</sub> /CsCu <sub>5</sub> S <sub>3</sub> /spiro-OMeTAD	22.29	Favor for energy levels; reduce carrier recombination	209
Cu <sub>2-x</sub> S@SiO <sub>2</sub> @Er <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub> /Cu <sub>2-x</sub> S@SiO <sub>2</sub> @Er <sub>2</sub> O <sub>3</sub> /MAPbI <sub>3</sub>	17.8	Upconvert infrared light to visible light	210
NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Er <sup>3+</sup> / @NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Nd <sup>3+</sup>	IR-783 + NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Er <sup>3+</sup> / @NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Nd <sup>3+</sup> + Au/ CsMAFAPbBrI	20.5	Convert IR to visible light, scatter light	212
MoS <sub>2</sub>	SiO <sub>x</sub> /MoS <sub>2</sub> /MoO <sub>x</sub>	22.8	Provide electron-blocking and hole-extraction properties	213
PbS	PbS/c-Si solar cell	12.6	Luminescent solar concentrator	214
CdS	Si solar cell/CdS	9.37	Reduce the reflectance spectral ranging from 250 to 1100 nm, passivation, and down-conversion	216



Table 3 (Contd.)

	IFL and its adjacent layers	PCE (%)	Functions	Ref.
$Zn_xCd_{1-x}S-ZnS:Mn$	Si solar cell/ $Zn_xCd_{1-x}S-ZnS:Mn$	$14.271 \pm 0.268$	Down-conversion	217
$Cd_{0.5}Zn_{0.5}S-ZnS:Mn$	Si solar cell/ $Cd_{0.5}Zn_{0.5}S-ZnS:Mn$	17.90	Down-convert UV light of 250–450 nm to yellow-orange light at 583 nm	218
$NaGdF_4:Ce@NaGdF_4:Nd/Yb@NaYF_4$	c-Si solar cell/ $NaGdF_4:Ce@NaGdF_4:Nd/Yb@NaYF_4$	0.8 (under 254 nm illumination)	Expand the spectrum of quantum cutting in the NIR	219
$CsPbCl_{1.5}Br_{1.5}:Yb^{3+},Ce^{3+}$	c-Si solar cell/ $CsPbCl_{1.5}Br_{1.5}:Yb^{3+},Ce^{3+}$	21.5	Larger absorption cross-section, weaker electron-phonon coupling and higher inner luminescent quantum yield	220



Fig. 8 (a) Schematic illustration of the possible electron transfer process in bare CdS and PbCdS/CdS based solar cells and  $J-V$  curves of CdS and PbCdS/CdS based solar cells. (b) The perovskite can directly contact the FTO surface along a shunt pathway in the absence of SnO<sub>2</sub> ETLs; the MgO<sub>2</sub> layer can inhibit the penetration of perovskite reaching the FTO surface, and the best performance of the PSCs with and without MgO. (c) Corresponding energy level diagram of PSCs, steady-state PL spectra of the perovskite film deposited on the PC<sub>61</sub>BM layer and PC<sub>61</sub>BM:SnO<sub>2</sub> bilayer,  $J-V$  characteristics in the illumination for the devices based on the PC<sub>61</sub>BM layer and PC<sub>61</sub>BM:SnO<sub>2</sub> bilayer. (a) Adapted with permission.<sup>174</sup> Copyright 2017, Elsevier. (b) Adapted with permission.<sup>199</sup> Copyright 2017, Wiley-VCH. (c) Adapted with permission.<sup>201</sup> Copyright 2018, American Chemical Society.



think this strategy is also applicable to other oxide NCs like  $\text{SnO}_2$  due to its comparable nature with  $\text{TiO}_2$ .

### 3. Nanocrystals as IFL

Besides HTL and ETL, another essential layer is the interfacial functional layer (IFL). Interfaces play a non-ignorable role in improving both PCE and stability through many paths. The position of a typical IFL is shown in Fig. 7. The IFL can be located at different positions in the solar cells to make different contributions. NCs IFL can enhance light absorption, decrease carrier recombination, improve charge transport ability, reduce impedance, convert ultraviolet (UV) or near-infrared (NIR) light to visible light, enhance optical transmission, decrease trap states of the active layer, and so on. Table 3 shows the recent advances of NC IFLs, and the detailed discussion is as follows.

#### 3.1 Suppressing recombination

As shown in Fig. 7, IFL is a separate layer between the charge transport layer/active layer or charge transport layer/electrode. So, it can convincingly act as a functional layer to prevent hole–electron recombination. Ternary semiconductor NCs of  $\text{PbCdS}$  were deposited on  $\text{TiO}_2$  as an IFL to impede the direct contact between ETL and the active layer of  $\text{CdS}$ , thus suppressing recombination efficiently and boosting the device PCE significantly (Fig. 8a). As the same, oxide NCs of  $\text{MgO}$  and  $\text{SnO}_2$

film inserted between ETLs and electrodes blocked holes and reduced recombination (Fig. 8b and c).<sup>199,201</sup>

#### 3.2 Charge transport improvement

As we know, charge transport ability inevitably affects the performance of solar cells. As shown in Fig. 9a,  $\text{MAPbBr}_{0.9}\text{I}_{0.1}$  NCs with good energy alignment enhance the hole transport ability and the PCE of the PSCs.  $\text{Co-CuGaO}_2$  NCs with  $\sim 20$  nm size were synthesized by hydrothermal method and used for surface passivation at the interface of perovskite and spiro-OMeTAD. Furthermore, the larger bandgap and lower valence band energy of  $\text{Co-CuGaO}_2$  reduced the energy gap between  $\text{Co-CuGaO}_2$  and perovskite. Considering that the reduced energy gap improved hole conduction and electron blocking, the PCE of PSCs was enhanced from 18.60% to 20.39%.<sup>207</sup>  $\text{MoS}_2$  NCs were also used to improve hole transport and the device PCE and stability (Fig. 9b).

#### 3.3 Light conversion and harvest enhancement

It is known that the active layer of recent solar cells cannot respond to the whole solar spectrum, resulting in energy loss and relatively low efficiency. Broadening the absorption of the active layer is an efficacious strategy to reduce energy loss and enhance the performance of solar cells.  $\text{CdS}$  NCs with general Stocks shifts were used in Si solar cells for spectral range

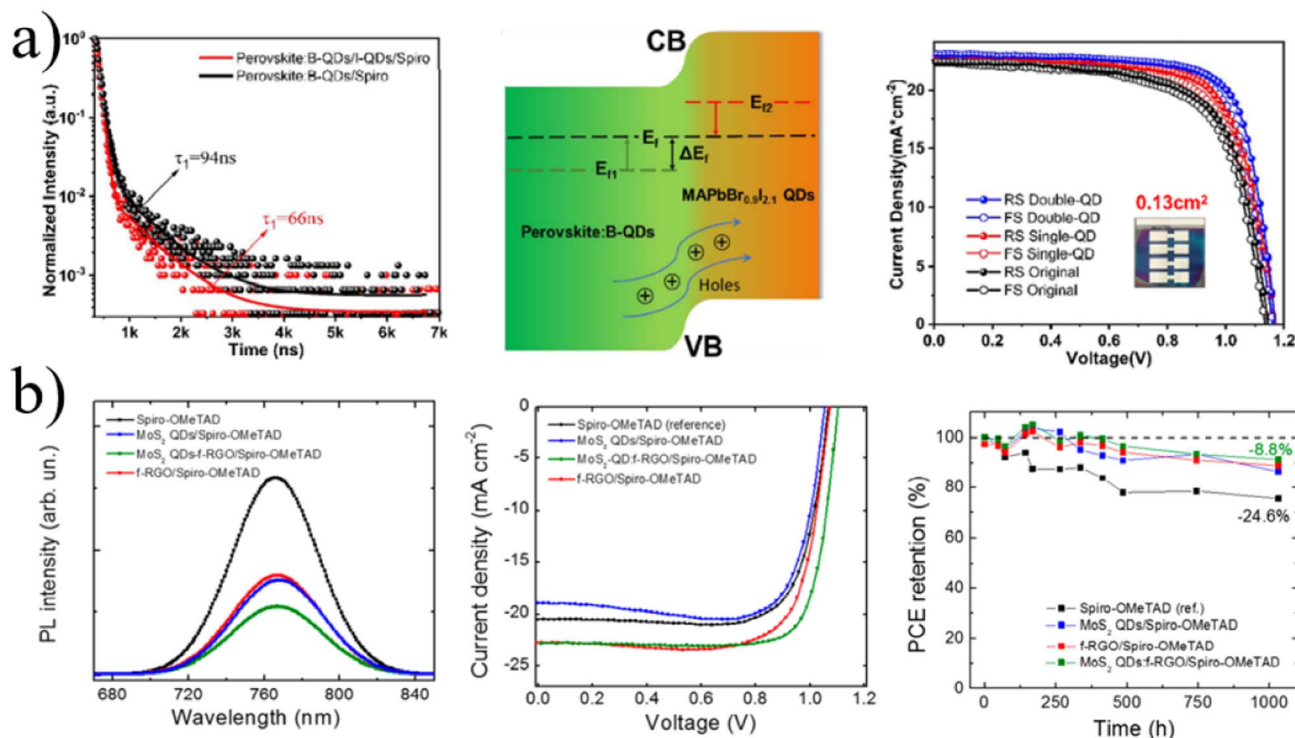
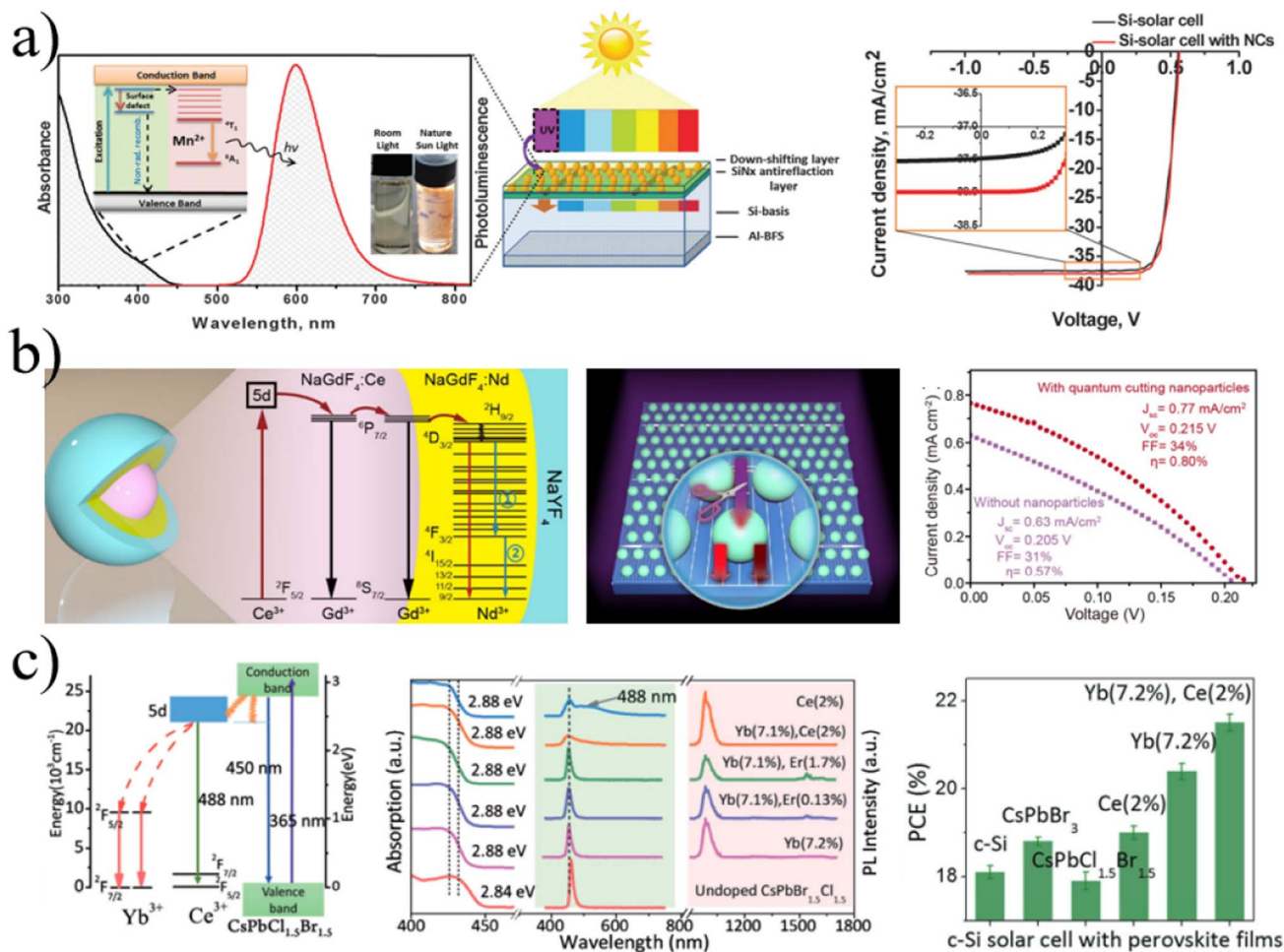


Fig. 9 (a) TRPL spectra of the perovskite film with and without  $\text{MAPbBr}_{0.9}\text{I}_{0.1}$  NCs, schematic diagram of band bending in the heterojunction structure formed by the perovskite and  $\text{MAPbBr}_{0.9}\text{I}_{0.1}$  NCs. (b) Steady-state PL measurements of  $\text{MAPbI}_3$  after the deposition of spiro-OMeTAD and different IFL/spiro-OMeTAD,  $I$ - $V$  characteristics of tested PSCs using different IFLs, normalized PCE trends vs. time extracted by  $I$ - $V$  characteristics under 1 sun illumination, periodically acquired during the shelf life test for the PSCs. (a) Adapted with permission.<sup>206</sup> Copyright 2020, American Chemical Society. (b) Adapted with permission.<sup>208</sup> Copyright 2018, American Chemical Society.





**Fig. 10** (a) Scheme of the down-shifting mechanism of the Zn<sub>0.5</sub>Cd<sub>0.5</sub>S:Mn (5%)/ZnS NC converter material and the design of proof-of-concept solar cell; *J*-*V* curves of the corresponding solar cells. (b) Schematic and proposed energy transfer for Ce<sup>3+</sup>-sensitized quantum cutting in Nd<sup>3+</sup> ions; schematic design for boosting the energy-harvesting efficiency of c-Si solar cells with quantum cutting nanocrystals; comparison of current density-voltage characteristic for c-Si solar cells with and without a nanocrystal coating layer (the solar cells were illuminated with a 254 nm UV lamp at a power density of 7 mW cm<sup>-2</sup>). (c) Schematic diagram of energy transfer mechanism in the Yb<sup>3+</sup>, Ce<sup>3+</sup> codoped CsPbCl<sub>1.5</sub>Br<sub>1.5</sub>NCs, absorption; visible and near-infrared emission spectra of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> perovskite NCs codoping with different rare earth ions; PCE of Si solar cells with different perovskite NCs. (a) Adapted with permission.<sup>217</sup> Copyright 2016, the Royal Society of Chemistry. (b) Adapted with permission.<sup>219</sup> Copyright 2017, American Chemical Society. (c) Adapted with permission.<sup>220</sup> Copyright 2017, Wiley-VCH.

enhancement.<sup>216</sup> In Fig. 10a, we can see that Mn-doped NCs expand the spectral range response of solar cells by absorbing short-wave lights and emitting the characteristic light around 580 nm, suggesting a larger range of light harvesting by active layer and PCE improvement. Zn<sub>x</sub>Cd<sub>1-x</sub>S/ZnS:Mn<sup>2+</sup> NCs were also used to broaden the light response range of Si solar cells.<sup>217</sup> Furthermore, Mn-doped semiconductor NCs have a large Stokes shift, avoiding self-absorption and thus reducing energy loss. Sr<sub>2</sub>CeO<sub>4</sub> NCs with down-shifting properties could improve the stability of organic P3HT:PCBM solar cells without significant loss of short-circuit current.<sup>185</sup> Certainly, by using NCs with a Stokes shift for expanded light harvesting, the photoluminescence yield and other photoelectronic properties should keep the rules of high-performance solar cells.

Besides the above NCs, rare elements are good at light conversion due to their special energy levels. Undoped and doped NCs based on rare elements were massively applied to

broaden the light response in solar cells and efficiently boost the device performance. As seen in Fig. 10b and c, Yb<sup>3+</sup>, Ce<sup>3+</sup>, and Nd<sup>3+</sup> based NC layers efficiently convert light and enhance the device performance. Additionally, Eu<sup>3+</sup>, Er<sup>3+</sup>, and Pr<sup>3+</sup> were also used for efficient solar cells.

### 3.4 Energy level optimization

To ensure propitious charge transfer among the functional layers in solar cells, un-matched energy levels are a tricky issue that we need to address. One origin of the open-circuit voltage (*V*<sub>oc</sub>) loss of NC-LHSC, Si solar cells, PSCs, and OSCs is mainly analyzed quantitatively *via* the energy difference between bandgap and the Schokley-Queisser limit voltage.<sup>15</sup> For n-i-p solar cells, band alignment between the active layer and ETL directly limits the splitting of the quasi-Fermi level. For p-i-n solar cells, the band alignment between HTL and active layer has a great impact on the *V*<sub>oc</sub>. The conduct band of recent HTL



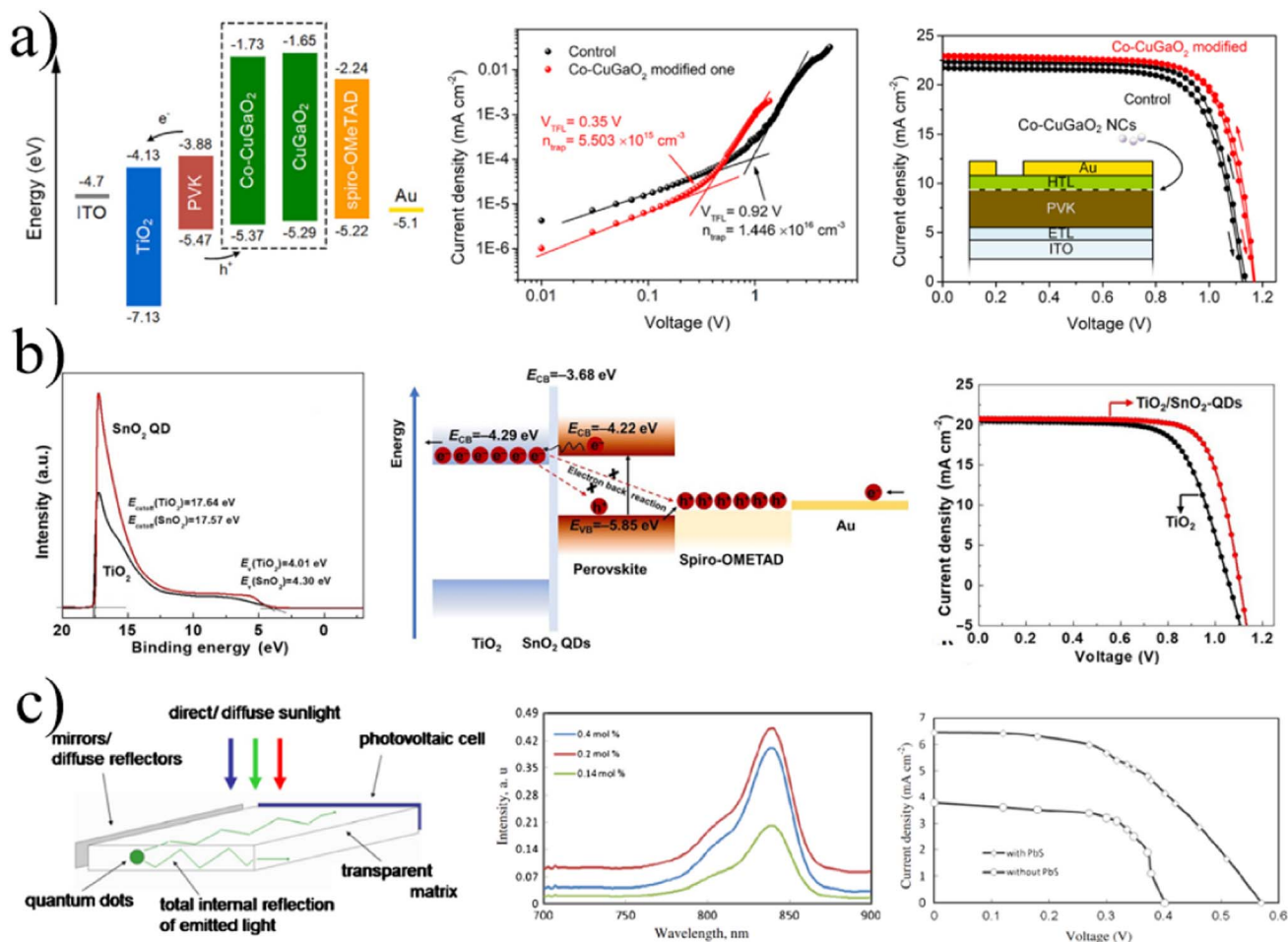


Fig. 11 (a) Energy level diagram of PSCs with the ITO/TiO<sub>2</sub>/PVK/Co-CuGaO<sub>2</sub>/Spiro-OMeTAD/Au structure, dark  $I$ - $V$  curves of devices based on Spiro-OMeTAD and Co-CuGaO<sub>2</sub>/Spiro-OMeTAD, forward and reverse scan  $J$ - $V$  curves based on Spiro-OMeTAD and Co-CuGaO<sub>2</sub>/Spiro-OMeTAD. (b) Band edge alignment and photocarrier dynamics in the resultant device. (c) Schematic illustration of an NC-luminescent solar concentrator, PL spectra of PbS NC-luminescent solar concentrator with different concentrations of PbS, and  $J$ - $V$  curves for solar cells with and without PbS NC-luminescent solar concentrator. (a) Adapted with permission.<sup>207</sup> Copyright 2022, Elsevier. (b) Adapted with permission.<sup>202</sup> Copyright 2019, Elsevier. (c) Adapted with permission.<sup>215</sup> Copyright 2015, Springer.

is relatively deep, and the barrier for electron transport is not sufficient, resulting in electron leakage and reducing the device performance. Therefore, energy level is of great importance to improve the performance of solar cells. Shown in Fig. 11a and b, Co-doped CuGaO<sub>2</sub> and SnO<sub>2</sub>NCs film were used for energy level optimization for high-performance solar cells, illuminating the large potential of NCs as ITL for reducing  $V_{oc}$  loss of solar cells.

### 3.5 Concentrating luminescent solar radiation

Solar radiation is geographically extensive, but the energy density is not high. So, concentrating solar light for higher density is a feasible strategy to improve solar cell performance. PbS NC luminescent solar concentrator (LSC) was found to show potential advantages over silicon solar cell panels (Fig. 11c). They can reduce the size of solar cells and offer great flexibility in design, which results in cost reduction with any desired shape. One of the attractive LSCs is based on NCS.

### 3.6 Prevention

The main reason for unstable solar cells is the invasion of oxygen and water. IFL between the active layer and HTL, ETL, or electrode can arrest this invasion to a great degree and increase the stability of solar cells. The above-mentioned IFL of Co-CuGaO<sub>2</sub> NCs in Fig. 11a not only acts as a hole transport accelerator but also prevents the direct contact of perovskite with oxygen and moisture, boosting the stability of the PSCs.<sup>207</sup>

## 4. Nanocrystals as efficient additives

Besides an independent layer to improve the performance of solar cells, NCs have also been used as additives for boosting active layer quality, carrier transfer acceleration, spectral response broadening due to plasmonic effect, light conversion, light scattering/reflection, heat sinking, and some other functions. Table 4 lists the recent progress of NCs as efficient additives for high-performance solar cells.



Table 4 Recent advances in NC additives for high-performance solar cells

NC	Added layer	NC additives and the mixture	PCE (%)	Functions	Ref.
SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>3</sub>	Bottom ETL	SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub>	7.7	①Improve the electron mobility and light harvesting; ②avoid the recombination	222
PbS		PbS + m-TiO <sub>2</sub>	5.04	①Enlarge the grain size of CsPbBr <sub>3</sub> perovskite film;	223
		PbS + TiO <sub>2</sub>	14.95	②suppress the activation of intrinsic trap sites of m-TiO <sub>2</sub> Downshift the conduction band of TiO <sub>2</sub> , promote the driving force of an electron injection	227
Cu-Zn-In-S-Se (CZISSe)		CZISSe + mp-TiO <sub>2</sub> + CsPbBr <sub>3</sub>	5.37	①Enhance charge extraction;	225
Ho <sup>3+</sup> -Yb <sup>3+</sup> -F <sup>-</sup> tri-doped TiO <sub>2</sub>		Ho <sup>3+</sup> -Yb <sup>3+</sup> -F <sup>-</sup> tri-doped TiO <sub>2</sub> + TiO <sub>2</sub>	9.91 ± 0.3	②reduce charge recombination Convert NIR light to green light	232
Gd <sub>1.54</sub> Er <sub>0.46</sub> (MoO <sub>4</sub> ) <sub>3</sub> (GMO:Er)		GMO:Er + TiO <sub>2</sub>	3.41	Convert NIR light to the visible region (near 550 nm)	233
β-NaYF <sub>4</sub> :Yb <sup>3+</sup> /Er <sup>3+</sup> / Sc <sup>3+</sup> @NaYF <sub>4</sub>		β-NaYF <sub>4</sub> :Yb <sup>3+</sup> /Er <sup>3+</sup> /Sc <sup>3+</sup> @NaYF <sub>4</sub> + TiO <sub>2</sub>	20.19	Convert NIR to red and green light	243
SrAl <sub>2</sub> O <sub>4</sub> :Eu <sup>3+</sup>		SrAl <sub>2</sub> O <sub>4</sub> :Eu <sup>3+</sup> + TiO <sub>2</sub>	4.64	Elevation of the Fermi energy level of TiO <sub>2</sub> , improves light harvesting	245
ZnS/Te	Bottom HTL	ZnS/Te + PEDOT:PSS	2.31	Reduce series resistance, increase shunt resistance, improve mobility	230
NaCsWO <sub>3</sub> @NaYF <sub>4</sub> @ NaYF <sub>4</sub> :Yb,Er	Top HTL	NaCsWO <sub>3</sub> @NaYF <sub>4</sub> @NaYF <sub>4</sub> :Yb,Er + spiro	18.28 ± 0.34	①Widen the perovskite spectral response range; ②increase the light reflection; ③ prolong the light path, and light absorption	231
NaLuF <sub>4</sub> :Yb,Er@NaLuF <sub>4</sub>		NaLuF <sub>4</sub> :Yb,Er@NaLuF <sub>4</sub> + PTAA	15.86	Convert NIR light to visible light, scatter light	237
Li(Gd,Y)F <sub>4</sub> :Yb,Er	Active layer	Li(Gd,Y)F <sub>4</sub> :Yb,Er + spiro-MeOTAD	18.34	Convert NIR to visible light	242
SnO <sub>2</sub>		SnO <sub>2</sub> + P3HT-PCBM	3.39	Reduce the recombination	224
Fe-doped SnO <sub>2</sub>		Fe-doped SnO <sub>2</sub> + P3HT	3.04	Extension of photogenerated exciton lifetime, overcome the burn-in regime faster	247
NaYF <sub>4</sub> :Yb,Er/NaYF <sub>4</sub>		NaYF <sub>4</sub> :Yb,Er/NaYF <sub>4</sub> + N719	9.15	Convert NIR light to visible light (450–700 nm)	235
TiO <sub>2</sub> :Sm <sup>3+</sup>		TiO <sub>2</sub> :Sm <sup>3+</sup> + P25 + N719	5.31	Convert UV to visible light	244
SnS		SnS + MAPbI <sub>3</sub>	14.26	①Provide more nucleation sites for the growth of perovskite grains; ② accelerate carrier transfer and reduce the recombination	226
NaYF <sub>4</sub> :Yb/Er		NaYF <sub>4</sub> :Yb,Er + MAPbI <sub>3</sub>	17.8	Broaden the solar spectral use to NIR light, minimize the non-absorption energy loss	236
IR-806-β-NaYF <sub>4</sub> :Yb,Er		IR-806-β-NaYF <sub>4</sub> :Yb,Er + MAPbI <sub>3</sub> Er <sup>3+</sup> -Yb <sup>3+</sup> doped Zn	17.49	Convert NIR light (800–1000 nm) to visible emissions	238
Ho <sup>3+</sup> -Yb <sup>3+</sup> -Li <sup>+</sup> -doped TiO <sub>2</sub>		Ho <sup>3+</sup> -Yb <sup>3+</sup> -Li <sup>+</sup> -doped TiO <sub>2</sub> + FAMAPbBrI <sub>3</sub>	16.88 ± 0.5	Convert NIR to visible light, improve electron injection efficiency, and decrease recombination	240
β-NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Tm <sup>3+</sup> @TiO <sub>2</sub>		β-NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Tm <sup>3+</sup> @TiO <sub>2</sub> + MAPbI <sub>3</sub>	16.27	Convert NIR to visible light, serve as the light scatter centers	241

#### 4.1 Active layer quality improvement and carrier transfer accelerator

The performance of solar cells largely depends on the quality of the active layer, such as the purity of Si for Si solar cells and the composition of perovskite for PSCs. For example, defects unavoidably exist at the surface of perovskite thin film during

the low-temperature fabrication process, and reducing defects is a very useful way to improve the performance of PSC.<sup>254</sup> This subsection discusses NCs as outstanding additives in the active layer for boosting its quality and carrier transfer acceleration.

SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> NCs were used to modify TiO<sub>2</sub> nanorod arrays for electron mobility improvement and electron transport



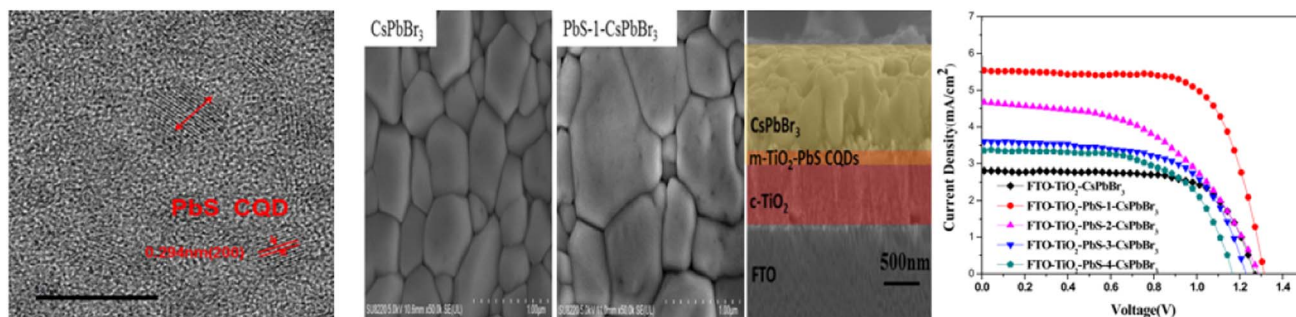


Fig. 12 Top-view and cross-section images of CsPbBr<sub>3</sub> film decorated with PbS NCs, and J–V curves of all-inorganic PSCs based on different TiO/PbS photoanodes. Adapted with permission.<sup>243</sup> Copyright 2019, American Chemical Society.

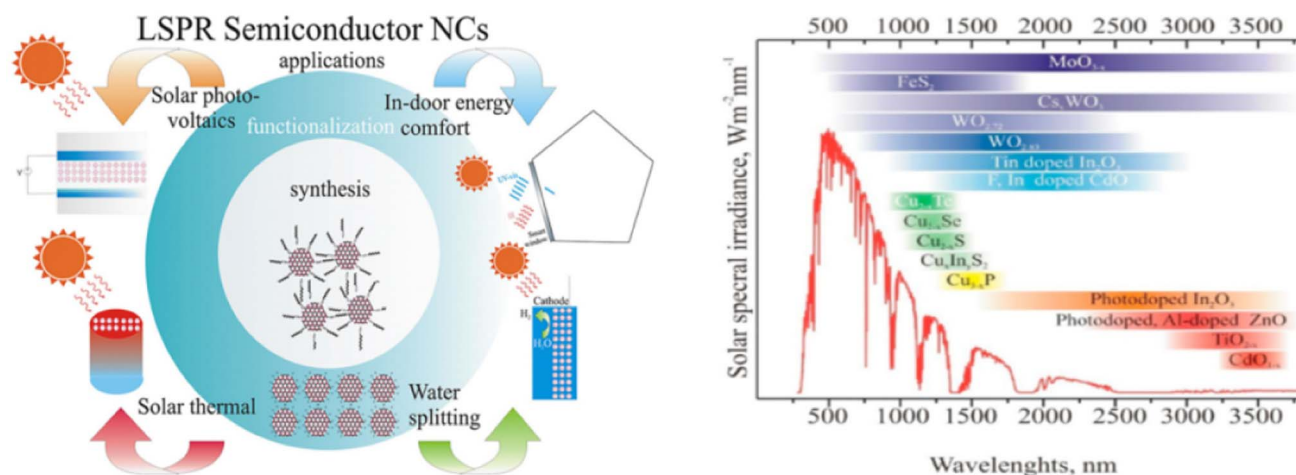


Fig. 13 Schematic of the applications of LSPR semiconductor NCs; the solar spectrum and its relevancy for energy-targeted applications of LSPR semiconductor NCs via their tunable plasmon absorbance. Adapted with permission.<sup>255</sup> Copyright 2021, Elsevier.

resistance reduction. This NCs modified ETL enhanced the PCE of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> PSC from 6.5% to 7.7%.<sup>222</sup> PbS NCs suppress the activation of the intrinsic trap sites, provide nucleation sites to enlarge the grain size, and suppress the charge combination in CsPbBr<sub>3</sub> PSCs (Fig. 12).<sup>223</sup> Adding SnO<sub>2</sub> NCs of size around 5 nm into the active layer of P3HT:PC<sub>61</sub>BM made electrons more easily pass through the active layer and accelerate the electron transfer, improving the PCE of OSC from 2.67% to 3.39%.<sup>224</sup> S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-capped Cu–Zn–In–S–Se NCs with ~5 nm size was introduced in the perovskite precursor of PbBr<sub>2</sub> solution to boost 22.6% enhancement of the PCE of inorganic Cs-based PSCs, which was due to promoted crystallization of CsPbBr<sub>3</sub> and hole extraction.<sup>225</sup> SnS NCs with an average size of 6.9 nm were implanted into the active layer of carbon-based HTL-free mesoporous PSCs, and the device gained a high PCE of 14.26% with a 12.42% improvement. This improvement was demonstrated by more nucleation sites for the growth of perovskite grains and the accelerated carrier transfer.<sup>226</sup> PbS NCs doped TiO<sub>2</sub> nanotubes (TNTs) modified the electronic and optical properties by downshifting the conduction band of TiO<sub>2</sub> ETL from –4.22 to –4.58 eV and promoting the driving force of an electron injection to the conductive electrode.<sup>227</sup>

## 4.2 Plasmonic Effect

Semiconductor NCs have exhibited localized surface plasmon resonances (LSPR), and this plasmonic effect has been used in many fields, such as solar photovoltaics, in-door energy comfort, water splitting, and so on (Fig. 13). Compared with traditional LSPR materials (noble metals), the semiconductor LSPR NCs allow a wide range of wavelength tunability from visible towards near-infrared (NIR) and further to mid-IR, leading to larger absorption of solar light. Higher absorption of the active layer in solar cells increases the current intensity and thus, the device performance. DSSCs based on plasmonic effect by ZnO or SnO<sub>2</sub> and TiO<sub>2</sub>/SnO<sub>2</sub> have been investigated.<sup>254</sup> From Fig. 13, it can be seen that different oxides, sulfides, and selenides such as MoO<sub>3-x</sub>, Cs<sub>x</sub>WO<sub>3</sub>, TiO<sub>2-x</sub>, CdO<sub>1-x</sub>, doped In<sub>2</sub>O<sub>3</sub>, doped ZnO, Cu<sub>2-x</sub>S, Cu<sub>x</sub>In<sub>y</sub>S<sub>2</sub>, Cu<sub>2-x</sub>Se, *etc.* broaden the response spectra from 500 nm to nearly 3800 nm. Effective light harvesting due to the plasmonic effect shows great potential in solar cell application. Given the limited self-absorption bands of solar cells, the above oxide and sulfide NCs can be applied as additives to widen the light harvesting range. Clearly, this will reduce energy loss and raise the device performance in a considerable way.





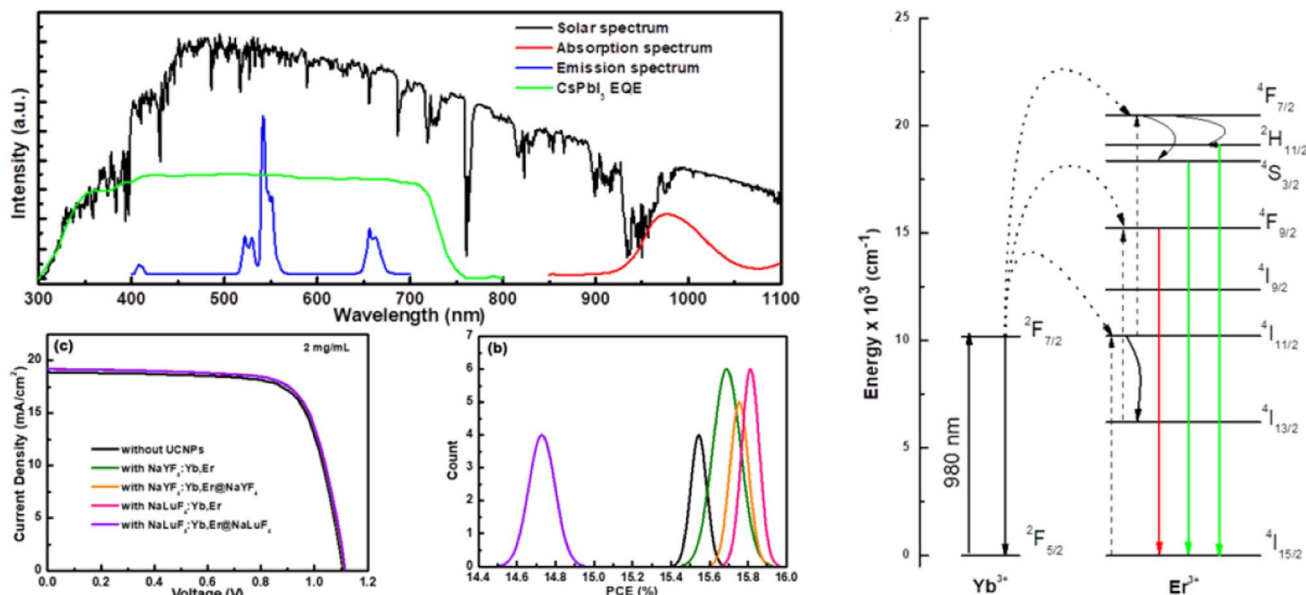


Fig. 14 Solar spectrum, absorption and emission spectrum of up-conversion nanocrystals and EQE curve of  $\gamma$ -CsPbI<sub>3</sub> PSC, *J*-*V* curves of PSCs based on different nanocrystals, and statistical PCE distribution histograms of 30 devices, schematic energy diagram for Yb<sup>3+</sup> and Er<sup>3+</sup>. Adapted with permission.<sup>237</sup> Copyright 2019, American Chemical Society.

### 4.3 Light conversion

As discussed in Section 3, light conversion is an efficient way to boost the PCE and stability of solar cells. Based on this point, NC light-converting layers were investigated in the previous part. It is also true that light conversion can be realized by NC additives, which will be summarized in this part.

**4.3.1 Up-conversion.** Rare-earth (RE) elements are famous for light up-conversion and further application in solar cells. RE element-doped semiconductor NCs have been added as additives in active layers and charge transport layers for high-performance DSSCs and PSCs. NIR lights were up-converted to visible lights and thus elevated the device PCE due to wider solar radiation absorption (Fig. 14). The RE element-based NCs, which can be used in up-converting materials as additives in solar cells, mainly contain Yb, Er, Ho, and Sc doped materials like Ho–Yb–F doped TiO<sub>2</sub>, Er–Yb doped ZnO<sub>2</sub>, Ho–Yb doped Gd<sub>2</sub>O<sub>3</sub>, Yb–Er doped NaYF<sub>4</sub> and Yb–Er doped Li(Gd,Y)F<sub>4</sub>. As shown in Fig. 14, the schematic energy diagram for Yb<sup>3+</sup> and Er<sup>3+</sup> are suitable for up-conversion and the related solar cells gain high efficiency. The up-conversion NCs can be added in the active layer, ETL, and HTL in different solar cells like OSC, DSSC, and PSC. The original active layers cannot absorb the whole range of sunlight and thus result in energy loss. After assembling NCs with up-conversion ability, the non-responsive long-wavelength range of sunlight will be converted to shorter wavelengths and absorbed by active layers to re-generate hole-electron pairs. This strategy can enhance the utilization of the infrared range of sunlight and the performance of solar cells.

**4.3.2 Down-conversion and down-shifting.** Down-conversion and down-shifting NCs are advantageous for high-performance solar cells due to the efficient utilization of UV lights. Typical Sm<sup>3+</sup>-based TiO<sub>2</sub>NCs were used in DSSCs and obvious improvement of PCE was gained (Fig. 15) through

converting ultraviolet to visible light. Better performance of solar cells was obtained by means of down-converting NCs such as ZnS:Er in Si-based devices and CeO<sub>2</sub>:Gd in OSC.<sup>249,250</sup> The shortest wavelength response by perovskite is about 400 nm.<sup>256</sup> The energy of sunlight with wavelengths shorter than 400 nm will be wasted. Furthermore, the UV lights can damage the perovskite or organic active layer and reduce the device stability. So, the PCE and light stability of solar cells can be increased by using down-conversion or down-shifting NCs.

### 4.4 Light scattering and reflection

Light scattering and reflection are well-known for boosting the optical absorption of different solar cells. TiO<sub>2</sub>:Zn NCs can scatter light and promote the performance of conventional DSSCs.<sup>257</sup> Due to the ultralow (<1%) photoluminescence quantum yield, NaLuF<sub>4</sub>:Yb,Er@NaLuF<sub>4</sub>NCs acted as scattering centers and extended the sunlight optical path by combining scattering and reflecting sunlight.<sup>237</sup> NaYF<sub>4</sub>:Yb<sup>3+</sup>,Tm<sup>3+</sup> NCs serve as scatter centers to enhance light harvesting for PSCs.<sup>241</sup> We can conclude that NCs are good at light absorption enhancement due to light scattering and reflecting, and this is an available approach for improving the device performance.

### 4.5 Heat sinks

Except for optical management, heat control is also important for solar cell operation because elevated temperatures may increase energy loss and destroy the devices. In the traditional photovoltaic/thermal (PV/T) system, the temperature of thermal energy is always limited by the operation temperature of PV cells. The oleylamine solution of Cu<sub>9</sub>S<sub>5</sub>NCs was adopted in the spectral splitting filter to harvest the moderate-temperature heat. After successful thermal energy collection, the maximum



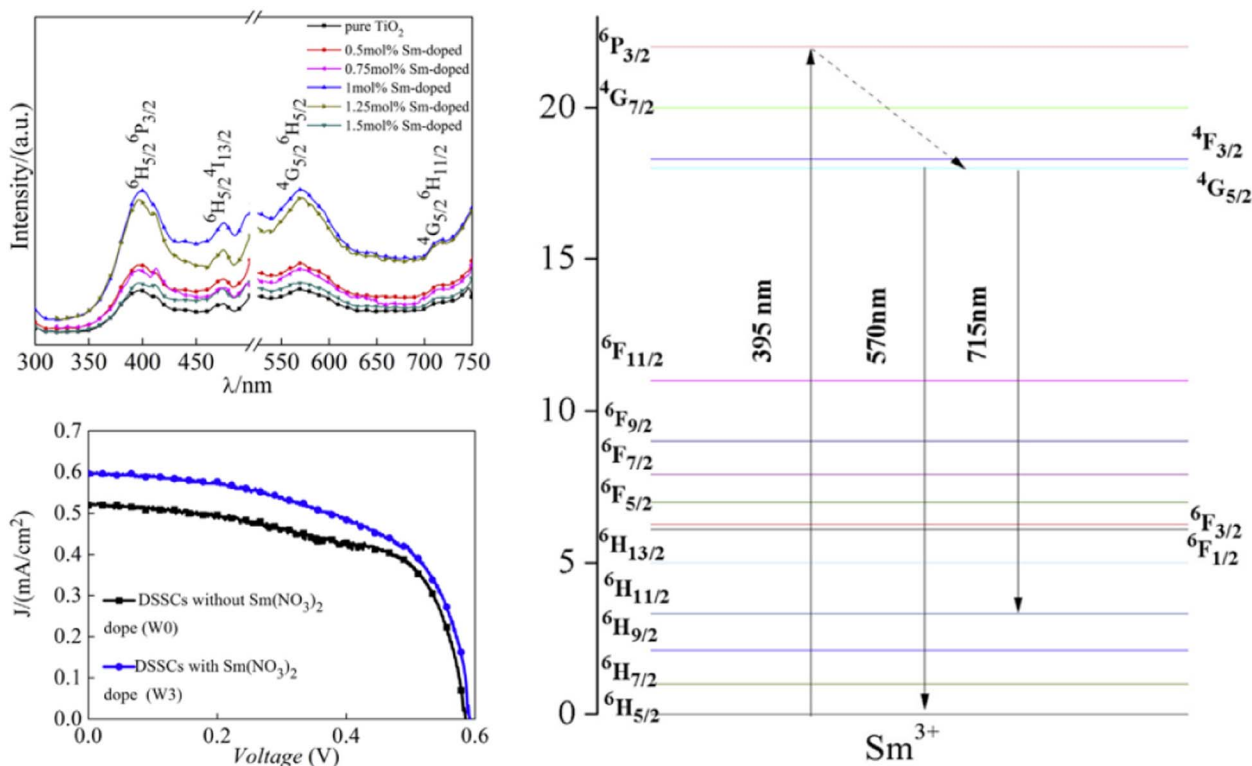


Fig. 15 Excitation spectrum ( $\lambda_{em} = 567$  nm) and emission spectrum ( $\lambda_{ex} = 395$  nm) of  $\text{TiO}_2:\text{Sm}^{3+}$  NCs with different  $\text{Sm}^{3+}$  doping concentrations, and schematic energy-level diagrams to show the details of down-conversion mechanisms *via* excitation using 395 nm radiation for  $\text{TiO}_2:\text{Sm}^{3+}$  NCs. Adapted with permission.<sup>244</sup> Copyright 2016, Elsevier.

overall efficiency of the present PV/T collector is 34.2%, with a 17.9% improvement.<sup>258</sup> In a concentrator photovoltaic nanocrystal-phase change material (PCM) hybrid system,  $\text{Al}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{SiO}_2$  were used to save energy and offer safe operating conditions. Compared with pure PCM (0 wt%),  $\text{Al}_2\text{O}_3$ -PCM at 5 wt% increased the thermal conductivity, and the melting rate reduced the solar cell temperature. The electrical efficiency was improved from 6.36% to 8% and gained temperature uniformity from 20 °C to 12 °C. This strategy would be recommended for residential and industrial applications in solar cells.<sup>259</sup>

#### 4.6 Other functions

ZnTe NCs with an average of 2.96 nm in the active layer demonstrated increased photo-generation and improved efficiency by reduced series resistance and improved mobility.<sup>230</sup> Fe-doped  $\text{SnO}_2$  NCs incorporated into the active layer of P3HT:PCBM improved the  $J_{sc}$  of OSC due to the extension of photogenerated exciton lifetime as a result of the magnetic field. Meanwhile, these NC-reinforced devices showed the tendency to overcome the burn-in regime faster and indicated the diluted magnetic semiconductor NCs had the potential to increase the stability of the devices.<sup>247</sup>

## 5. Summary and outlook

In recent years, NCs as functional layers and additives have been widely used in solar cells, significantly enhancing their

performance. Here, we summarize NCs-based HTL, ETL, IFL, and additives for solar cells. NCs can boost the device performance in many ways, such as increasing the charge transport ability, suppressing charge recombination, broadening light harvest, and so on.

Based on previous investigations, we propose some promising strategies to enhance the performance of solar cells by using NCs.

(I) Optical management. Full spectrum absorption under low-cost conditions: both up-converting and down-shifting materials. For down-shifting, doped NCs with large Stokes shift, such as Mn or Cu doped NCs, have great potential due to no self-absorption, facile synthesis, and low cost.  $\text{Cu}^+$ ,  $\text{Ag}^+$  doped n-type metal oxide NCs,<sup>260</sup>  $\text{Fe}_{1-x}\text{S}_2$  NCs,<sup>261</sup> and In doped  $\text{Cu}_x\text{S}$  NCs,<sup>262</sup> with great potential for spectra broadening are also suggested for high-performance solar cells.  $\text{CaMoO}_4:\text{Er}^{3+}, \text{Yb}^{3+}$  NCs would offer great potential for conserving energy in Si solar cells.<sup>263</sup> Certainly, the photoluminescence efficiency of NCs is very important when they are used to convert light in solar cells. Excellent optical management of solar cells can utilize more sunlight and improve the device performance.

(II) Electronic optimization. The charge transfer ability is mainly determined by the electronic properties of charge transport materials. The performance of solar cells can be improved by electronic optimization. One approach is a component change of materials such as n doping for n-type NCs and p doping for p-type NCs. Finding more suitable dopants for NCs will further boost the PCE and stability of solar



cells. Meanwhile, the size and ligand control of NCs are also considered to optimize their electronic properties and fabricate better-performance solar cells.

(III) Interface engineering. Interfacial layers between different functional layers show different functions in solar cells. In further developments, more NCs IFL will be used to improve device performance by preventing direct contact between the active layer and charge transport layer, impeding the entry of water and oxygen, and protecting and destroying the active layer with UV lights.<sup>264</sup> So, NC IFL, with good photo-electronic properties, can adjust energy alignment, accelerate charge transport, enhance light harvest, and protect the active layer.

(IV) Cross utilization. The metal-organic framework (MOF) materials can improve the efficiency and stability of solar cells due to their unique properties.<sup>265</sup> NCs with small sizes can be considered to mix with MOF and enhance the performance of devices. In addition, NCs can be utilized as light harvesters, HTL, ETL, and IFL, so we suggest their application in all-NC solar cells.

## Conflicts of interest

The authors declare no conflict of interest.

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